STUDIES ON CARBONIUM IONS

by

Virgile BERTOLI, Chimiste Diplômé (Paris)

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January, 1967
PAGES BETWEEN 121-122 NOT DIGITISED BY REQUEST OF THE UNIVERSITY
I wish to thank Professor H. D. Springall, for providing the necessary facilities for this work.

Dr. P. H. Plesch, who suggested this work, for his most adequate supervision, helpful discussions and vast store of experience which proved to be invaluable.

All members of Dr. Plesch's polymer and physical chemistry group, for stimulating criticism and discussions.

Dr. D. Cohen and Dr. G. Jones for helpful discussions concerning the n.m.r. spectra.

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And finally the British Council, for the scholarship starting from 1st October 1965, which made this work possible.
ABSTRACT

The interaction of styrene and its unsaturated and saturated dimers ($10^{-5}$ to 1 M) with conc. sulphuric, or chlorosulphonic acids, and with anhydrous perchloric acid ($10^{-4}$ to 1 M) in methylene dichloride, has been studied and related to the behaviour of other similar systems, such as $\alpha$-methylstyrene and its dimers.

The origin of the u.v. and visible absorption spectrum which had been wrongly attributed to the 1-phenylethyl cation and its higher homologues was established:

a) the 3-methyl-1-phenylindanyl cation, and its higher homologues constitute most of the ionic species formed when styrene and its dimers interact with $\text{HClO}_4$ in $\text{CH}_2\text{Cl}_2$;

b) the 1,3-diphenyl-n-butyl cation and its higher homologues are formed when styrene and its unsaturated dimer interact with conc. $\text{H}_2\text{SO}_4$ and $\text{HSO}_3\text{Cl}$ at low temperature and concentration, and this ion has been characterised.

The u.v. - visible and n.m.r. spectra of carbonium ions derivable from the cyclic dimer of styrene were investigated, and spectroscopic correlations were established in the following series of diphenylalkyl cations: diphenylmethyl and ethyl, phenyl-(2'-methyl-phenyl)methyl and ethyl, phenyl-(2'-ethylphenyl)methyl and ethyl (all 1,1-ethyl), 1,1-diphenyl-n-butyl, 1-phenylindanyl and 3-methyl-1-phenylindanyl.
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A la recherche de l'ion perdu
The work to be described in this Thesis is concerned with the study of a series of mono and diphenylalkylcarbonium ions by u.v. and visible spectroscopy, n.m.r. spectroscopy, and conductimetry. It forms an extension of the investigation on the interaction of styrene with strong acids carried out in this laboratory by Dr. A. Gandini and, it is hoped, comes as a contribution to the rapidly growing interest towards the study of stable carbonium ions.

This interest is best illustrated by the fact that in the past two years not less than six reviews directly related to the subject have been published, and that the last review, covering the 1965 literature, quotes 170 references. Carbonium ions, long proposed as ubiquitous and somehow fleeting intermediates, are now readily investigated in solution, with the development of direct spectroscopic (n.m.r. and i.r.) observation methods. Thus, a number of alkyl and monophenylalkylcarbonium ions, previously suggested as transient entities, or tentatively identified on circumstantial evidence, have now been directly observed by n.m.r. spectroscopy. For instance, the most controversial (Ref. 2, p. 134) t-butyl cation, previously identified erroneously by the 300 m·
region absorption formed on addition of t-butyl alcohol
(or isobutene)\textsuperscript{11} to 96\% H\textsubscript{2}SO\textsubscript{4}, has recently been observed\textsuperscript{10} by
its n.m.r. spectrum in Sb\textsubscript{5}F\textsubscript{5}-FSO\textsubscript{3}H at -60\°, even in the presence
of the very reactive ethyl cation. It is now well established\textsuperscript{10,12}
that the t-butyl cation does not exhibit any absorption above 220 m\textmu,
and that the absorption near 300 m\textmu is due to cycloalkenyl cations
resulting from a surprising maze of alkylation-dealkylation,
rearrangement, and hydride transfer reactions.\textsuperscript{12} I shall show in this
work that the behaviour of isobutene is not an exception, and that
most ionic species resulting from styrene, far from being the product
of simple protonation, actually represent the last step of a sequence
of dimerisation, cyclisation, ring opening and hydride abstraction
reactions. Eventually, it appears that four molecules of styrene are
required to form one ion.

The interaction of styrene with strong acids, such as HClO\textsubscript{4}
and H\textsubscript{2}SO\textsubscript{4}, in so-called protonation conditions (excess of acid) leads
to the formation of ions which exhibit a u.v. and visible spectrum
with two main peaks, at around 310 and 430 m\textmu. This spectrum was
attributed to the 1-phenylethyl cation and its polymeric homologues
(Ref. 1-8, Chapter 3 of this work), mainly on the grounds of
circumstantial evidence. Thus, in similar conditions 1,1-diphenylethylene
yields the 1,1-diphenylethyl cation, as shown by dilution experiments,\textsuperscript{13} in which the precursor was recovered from the carbonium
ion solution, or by n.m.r. spectroscopy.\textsuperscript{14,15} It was certainly
tempting to extrapolate to styrene the finding unambiguously established for 1,1-diphenylethylene. Unfortunately, no direct proof of the existence of the 1-phenylethyl cation was available (such as supplied by the n.m.r. spectrum or recovery experiments) and its assignment was challenged. The main criticism was aimed at Gandini and Plesch's pseudocationic polymerisation mechanism, partly based on the assumption that the styryl cation shows its major absorption at around 427 m\(\mu\). The fact that this absorption formed only at the end of the polymerisation of styrene (together with a large increase of electrical conductivity) was interpreted by these authors as evidence for the absence of carbonium ions during the polymerisation.

The original aim of my work was to attempt the identification of the ionic species responsible for the alleged 1-phenylethyl cation spectrum, and to investigate the mechanism leading to their formation. Recovery experiments showed that the 1-phenylethyl cation was not formed in any measurable amount, neither in HClO\(_4/\)CH\(_2\)Cl\(_2\), nor in 98-100% H\(_2\)SO\(_4\) (in agreement with the recent finding that this cation cannot be formed even in SO\(_2\)-SbF\(_5\)-FSO\(_3\)H at \(-60^\circ\)). Thus, the assignment of the 310 and 430 m\(\mu\) absorption spectrum to the 1-phenylethyl cation was definitely invalidated. Moreover, further investigation showed that the interaction of styrene with concentrated and dilute strong acids gave reactions of unsuspected complexity and
variety, leading to the most unexpected cations, such as the 3-methyl-1-phenylindanyl cation, formed in nearly 50% yield in HClO₄/CH₂Cl₂ (Section 3.6.7.2 of this work). I demonstrated that the latter cation is mainly responsible for the u.v. and visible spectrum (308 and 420 mμ peaks) observed when styrene interacts with dilute acids. At the best, and when great care is taken (Sections 3.1.2), the interaction of styrene with 98-100% H₂SO₄ can lead to the formation in low yield of the 1,3-diphenyl-n-butyl cation, which exhibits only one prominent peak, at 315 mμ.

It appeared during the preliminary stages of this work that no straightforward experiment would give the answer to the problem investigated, and that many different lines of approach were required, such as:

a) Study of the interaction of styrene and its dimers with various acids, by u.v. and visible spectroscopy and by conductimetry; analysis of the kinetic data; recovery experiments.

b) Same study with related olefins, such as α-methylstyrene and its dimers, β-methylstyrene, 2,6-dimethylstyrene, pentafluorostyrene etc.

c) Synthesis of compounds which could be direct precursors to the ions formed via complex reactions from styrene; protonation of these compounds and comparison of the u.v. and visible spectra of the carbonium ions with those of
ionic species derivable from styrene; comparison of the products recovered after dilution. 24 compounds were synthesised, 3 of which are apparently new (no reference found in Chem. Abs. and Beilstein).

As an indirect consequence of this study interesting u.v. and n.m.r. spectroscopic correlations were found in a series of diphenylcarbonium ions, as is fully described in Sections 3.7. These correlations give direct evidence of the unequal charge delocalisation when diphenylmethyl and diphenylethyl cations are compared.

Note: The nomenclature rules recommended by the I.U.P.A.C. were followed throughout this work.

In naming cations, the carbon with the positive charge is numbered as 1.

Example: \( \text{CH}_3\cdot \text{CH}\cdot \text{CH}_2\cdot \text{CH}^+\cdot \text{Ph} \)

\[ \text{1,3-diphenyl-}n\text{-butyl.} \]
References to Chapter One.


### Numbering of compounds and cations for reference.

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<th>Compound</th>
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<td>I</td>
<td>1,3-diphenylbut-2-ene</td>
</tr>
<tr>
<td>II</td>
<td>1,3-diphenylbut-3-ene</td>
</tr>
<tr>
<td>III</td>
<td>1-methyl-3-phenylindene</td>
</tr>
<tr>
<td>IV</td>
<td>1-phenyl-3-methylindene</td>
</tr>
<tr>
<td>V</td>
<td>4-methyl-2,4-diphenylpent-1-ene</td>
</tr>
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<td>VI</td>
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<tr>
<td>VII</td>
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</tr>
<tr>
<td>VIII</td>
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*Note: Refer to tables A and B (page 128) for numbering used in sections 3.7.3 and following.*
CHAPTER TWO

EXPERIMENTAL

2.1 MATERIALS

2.1.1 Solvents

2.1.1.1 Methylene dichloride. This solvent (I.C.I. Ltd.) was purified as described by Weissberger. It was then dried for 12 hr. over freshly ground CaCl₂ and finally distilled through a 160 cm. column filled with nickel-gauze rings at a reflux ratio of 15:1. Head and tail fractions each consisting of 20% of the total volume were rejected and the boiling point of the middle fraction was found not to vary by more than 0.1 °; b.p. 39.0/745 mm. (lit. 1 40.1 °/760 mm.).

The middle fraction was collected in dark bottles, mixed with Fisher "Certified Reagent" phosphorus pentoxide (50 g. per litre CH₂Cl₂), and finally the suspension of P₂O₅ in CH₂Cl₂ was poured into a 5 l. reservoir which was attached to the vacuum line. The reservoir was then closed with a mercury seal and the solvent degassed and refluxed for several days.

Vapour phase chromatography showed that the only impurities detectable were chloroform (about 1:10,000 vol/vol) and isopropyl chloride (about 1:50,000 vol/vol). Both impurities are known not to interfere with protonations and polymerisations carried out in the solvent. The solvent distilled from the vacuum line was periodically
tested by standard methods\textsuperscript{1,3} for acidity (HCl, P\textsubscript{2}O\textsubscript{5}, H\textsubscript{3}PO\textsubscript{4}) and for residual or accidentally admitted moisture, and was always found acid free within the limits of detection\textsuperscript{3} (about 10\textsuperscript{-6}M) and dry (no bubbles of hydrogen evolved when mixed with fresh CaH\textsubscript{2}). During the course of this work three batches of solvent were prepared and in each case perfectly reproducible results were obtained. The reservoir and line containing the solvent were protected from direct sunlight.

Other properties of methylene dichloride, such as electrical conductivity, optical transparency, volatility, etc., and the procedure used in its dosing will be discussed in the appropriate sections of this thesis.

2.1.1.2 Acetic acid. AnalaR B.D.H. glacial acetic acid was used without further purification.

2.1.1.3 Thionyl chloride. The B.D.H. product, purity not less than 97\%, was distilled under dry nitrogen and the middle fraction collected in a flask protected from moisture. B.p. 78.5\textdegree/745 mm. (lit.\textsuperscript{4} 78.8/746 mm.). The n.m.r. spectrum of this fraction did not show any peak.

2.1.1.4 Hexane. The B.D.H. "Special for spectroscopy" product was used without further purification.
2.1.1.5 Pentane. The B.D.H. Standard pentane was used after a distillation through a 50 cm. Vigreux column at a reflux ratio of 5:1. Collected fraction b.p. 34-35°/750 mm. (lit. 36°/760 mm.).

2.1.1.6 Other solvents. Solvents for common laboratory routine work (extraction, recrystallisation, synthesis, thermometer calibration, i.r. and n.m.r. spectroscopy, g.l.c. etc.) were purified and, when required, dried by standard techniques. 1
2.1.2 Carbinols

2.1.2.1 l-Phenylethanol (DL). This compound, supplied by B.D.H., was fractionated under reduced pressure; b.p. 101-102°/20 mm., $n^D_{25} = 1.5252$ (lit. $^4$ b.p. 102°/20 mm.; lit. Ref. 4, 46th Ed. 1965, $n^D_{25} = 1.5244$).

2.1.2.2 2-Phenylpropan-2-ol. The commercial product (Light) showing a clean n.m.r. spectrum and a single peak g.l. chromatogram, was used without further purification; m.p. 35-36° (lit. $^4$ 35-37°).

2.1.2.3 1,2-Diphenylpropan-2-ol. This compound was synthesised following Hell's procedure $^5$, in which acetophenone is treated with benzylmagnesium bromide or chloride. The raw product was fractionated under high vacuum, and the carbinol fraction collected at 99°/0.02 mm. (lit. $^5$ b.p. 175/15 mm.), as a viscous colourless oil which, after slow cooling to $-10^\circ$ from a 20% solution in hexane, yielded the crystalline carbinol. This was twice recrystallised from hexane, and after prolonged vacuum drying melted at 50° (lit. $^5$ 50-51°).

2.1.2.4 1,1-Diphenylbutan-1-ol. From the many conventional Grignard routes described for the synthesis of this carbinol $^6$-8 I decided to start with Klages and Heilmann's $^6$ (for the simple reason that the required reagents were available on the shelf),
in which benzophenone is caused to react with n-propylmagnesium bromide. Unfortunately, the main product of this reaction was diphenylmethanol (60%) and only about 20% of the expected carbinol was obtained, accompanied by 10% of residual benzophenone and 10% of unidentified side products. Although diphenylmethanol was easily isolated in purity higher than 99% by crystallisation from hexane, no conventional purification method (fractional distillation under vacuum, crystallisation from hexane or pentane, chromatography on grade III alumina with hexane as solvent and methanol or methylene dichloride as eluent) did yield a sufficiently pure sample of the required compound.

The second procedure, in which ethyl-n-butyrate is treated with phenylmagnesium bromide, yielded 80% of carbinol, easily isolated by crystallisation from hexane as large colourless crystals. Twice recrystallised from pentane, they melted at 35-36° (lit. 33-34°, and 36°).

It is worth mentioning that although the reduction of benzophenone by Grignard reagents with reactive beta hydrogens is now well known, understood and reviewed, it was apparently unsuspected in 1904, when Klages and Heilmann published their work. The melting point these authors attribute to 1,1-diphenylbutan-1-ol: 65°, is indeed the one of diphenylmethanol (m.p.: this work: 67-68°; lit. 68-69°).
2.1.2.5 1,1-Diphenylbut-3-ene-1-ol. In a slight variation of Jaworski's method, 0.6 mole allyl bromide and 0.3 mole benzophenone in 250 ml. ether were added over 2 hr. to a very vigorously stirred suspension of 0.6 mole magnesium in 250 ml. ice-cold ether, and the resulting compound hydrolysed with 30 g. ammonium chloride in 200 g. crushed ice. The extracted carbinol (98% yield) was vacuum distilled at 106-107°/0.01 mm. (lit. 11 b.p. 182-183°/32 mm.), to a colourless oil; \( n_D^{25} = 1.5824 \).

2.1.2.6 1,3-Diphenylbutan-3-ol. Synthesised by a conventional Grignard reaction between benzylacetone and phenylmagnesium bromide. White wooly crystals from pentane (yield 75%); m.p. 44-45° (lit. 12 47-48°).

2.1.2.7 Diphenylmethanol. The B.D.H. and my synthesis (Section 2.1.2.4) products were recrystallised three times from pentane and melted both at 67-68° (lit. 4 68-69°).

2.1.2.8 Phenyl-(2'-methylphenyl)methanol. As published by Chichibabin, benzaldehyde was treated with 2-methylphenylmagnesium bromide to yield after conventional hydrolysis about 80% of oily yellowish carbinol, which was decolorised by boiling its 15% solution in hexane with activated charcoal. Cooling the filtered solution at -10° gave crystals of carbinol (white needles) which after two recrystallisations from hexane melted at 92.5° (lit. 13 95°).
2.1.2.9 Phenyl-(2'-ethylphenyl)methanol. This carbinol was prepared according to Lamneck and Wises' indications,\textsuperscript{14} by treating benzaldehyde with 2-ethylphenylmagnesium bromide and hydrolysing it with 3% aqueous sulphuric acid. The carbinol was purified as in Section 2.1.2.8. White silky crystals, m.p. 62° (lit.\textsuperscript{14} 60.8°).

2.1.2.10 1-Phenyl-l-(2'-methylphenyl)ethanol. No reference found in Beilstein and Chem.Abs. Acetophenone (11.7 g.) was treated with 2-methylphenylmagnesium bromide (16.7 g. of 2-bromotoluene plus 2.4 g. of magnesium) at room temperature over one hr., followed by 2 hr. refluxing, to give after hydrolysis the carbinol in 20% yield, which was purified by two molecular distillations at 85° and 10\textsuperscript{-3} mm.; \(n_\text{D}^25 = 1.5826\).

2.1.2.11 1-Phenyl-l-(2'-ethylphenyl)ethanol. Conventional Grignard route\textsuperscript{15} by reaction of acetophenone (7.15 g.) with 2-ethylphenylmagnesium bromide (11 g. of 1-ethyl-2-bromobenzene plus 1.45 g. of magnesium) to yield 25% of carbinol. Purified by molecular distillation at 85° and 10\textsuperscript{-3} mm. White crystals from pentane, m.p. 44-45°.

2.1.2.12 1-Phenylindan-l-ol. Von Braun's method\textsuperscript{16} (indan-l-one plus phenylmagnesium iodide) yielded only a mixture of the carbinol and of 3-phenylindene (n.m.r. spectrum). No separation of the carbinol was attempted, as it was needed only as an intermediate to 3-phenylindene.
2.1.2.13 3-Methyl-1-phenylindan-1-ol. 3-Methylindan-1-one (20 g.) was treated with phenylmagnesium iodide (27.9 g. of iodobenzene plus 3.33 g. magnesium) at room temperature over 1 hr., followed by 2 hr. refluxing (appearance of thick slush), and hydrolysis (6 g. ammonium chloride in 50 g. crushed ice) to give the carbinol in 75% yield. The solvent (ether) was evaporated at 0° and under vacuum, and left the carbinol, a colourless viscous liquid, turning slowly yellowish and green when exposed to air and light; \( n^25_D = 1.5881 \). (New compound).

The clean n.m.r. and i.r. spectra correspond to the expected structure. Attempts to fractionate the carbinol under high vacuum yielded the corresponding olefin: 1-methyl-3-phenylindene.

3-Methylindan-1-one was prepared according to Koelsch et al.\(^{29}\): 34 g. crotonic acid in benzene (250 ml.) plus 159 g. (3 eq.) \( \text{AlCl}_3 \) were refluxed for 3 hr. to give about 47 g. of 3-methylindan-1-one; b.p. 131-133\(^o\) /17 mm., \( n^25_D = 1.5538 \) (lit.\(^{29}\) b.p. 132-137/15 mm.).

2.1.2.14 Triphenylmethanol. Two different batches of this compound were used (E.D.H. and Koch-Light Ltd), after two recrystallisations from carbon tetrachloride, and gave identical results; m.p. 163\(^o\) (lit.\(^{17}\) 163\(^o\)).

2.1.2.15 Tribenzylmethanol. Prepared in 75% yield by a conventional Grignard reaction\(^{6}\) between phenylmagnesium chloride and ethyl phenylacetate. White small crystals from hexane; m.p. 115.5\(^o\) (lit.\(^{6}\) 114-115\(^o\)).
2.1.3 Esters.

2.1.3.1 Benzyl acetate. The commercial product (B.D.H.) was purified by distillation under reduced pressure; b.p. 100°/18 mm. (lit. 18 100°/18 mm.).

2.1.3.2 1-Phenylethyl acetate. A mixture of glacial acid (60 ml.), 1-phenylethanol (60 ml.), and acetic anhydride (200 ml.) was refluxed for 15 hr., cooled down to room temperature, treated with cold water, then with saturated aqueous NaHCO₃. The decanted oil was left overnight over CaCl₂, in order to remove any residual carbinol. After a final drying with CaSO₄, the ester was vacuum distilled in a dry nitrogen stream. B.p. 98°/23 mm., n_D²⁵ = 1.4924 (lit. 19 b.p. 213-216°/760 mm.). Purity higher than 99.8% (g.l.c.); final yield 95%.

2.1.3.3 2-Phenyl-2-propyl acetate. Prepared by a conventional route by treating in ether 2-phenylpropan-2-ol with acetyl chloride in presence of N-dimethylaniline. Yield about 50%. B.p. 96-97°/12 mm., n_D²⁵ = 1.4959 (lit. 20 58-61°/3 mm.).

2.1.3.4 Ethyl benzoate. The commercial product (B.D.H.) was left 24 hr. over CaCl₂ and distilled under reduced pressure; b.p. 101-102°/20 mm. (lit. 4 101.5°/20 mm., interpolated).

2.1.3.5 Benzyl benzoate. The B.D.H. product was used without further purification; n_D²⁵ = 1.5039 (lit. 4 n_D¹⁷.³ = 1.5068).
2.1.4 Olefins

2.1.4.1 Styrene. The commercial product (Koch-Light Ltd, Puriss.) was purified as published, transferred to the vacuum line, dried over CaH₂ and thoroughly degassed by repeated thawing and freezing. About 20% of the styrene was then distilled into a flask and discarded by sealing-off. Finally, about 80% of the remaining olefin was distilled to a reservoir containing BaO (which had been previously activated by prolonged heating at 360⁰ under high vacuum), stirred with the drying agent, and stored in the dark at liquid nitrogen temperature. Two batches of this olefin were used throughout this work and gave identical results.

2.1.4.2 α-Methylstyrene. The commercial product (B.D.H.) was fractionated under high vacuum, generous head and tail fractions being discarded. It was then kept at -10⁰ under its own vapor pressure in a flask fitted with a lightly greased tap; n_D^{25} = 1.5358 (lit. n_D^{25} = 1.53586).

2.1.4.3 β-Methylstyrene. The commercial product (Aldrich) was used without further purification; n_D^{25} = 1.5471 (lit. n_D^{25} = 1.5480).

2.1.4.4 2,6-Dimethylstyrene. The commercial product (Koch-Light "Pure") was fractionated under high vacuum and stored at -10⁰. No impurity detected by g.l.c.; n_D^{25} = 1.5294.
2.1.4.5  **Pentafluorostyrene.** The product supplied by Imperial Smelting Co. was fractionated under high vacuum and the middle fraction stored at $-10^\circ$. No impurity detected by g.l.c.; $n_D^{25} = 1.4439$ (lit. $n_D^{20} = 1.4414$).

2.1.4.6  **1,1-Diphenylethylene.** The commercial product (Eastman-Kodak) was fractionated under high vacuum and stored at $-10^\circ$; $n_D^{25} = 1.6063$ (lit. $n_D^{14} = 1.610$).

2.1.4.7  **1,3-Diphenylbut-1-ene.** This compound was prepared following a slight modification of Risi and Gauvin's method.\[^{23}\] Styrene (500 g.) and 56% weight aqueous $\text{H}_2\text{SO}_4$ (125 g.) were refluxed for 6 hr. at $130^\circ$, with very vigorous stirring, to yield 98% of unsaturated dimer, which was distilled under reduced pressure, and determined by g.l.c. as 99.5% pure. B.p. $178^\circ/18$ mm., $n_D^{25} = 1.5912$ (lit.\[^{15}\] b.p. $183/20$ mm., $n_D^{20} = 1.5932$).

A strong i.r. band at 965 cm.$^{-1}$ (out-of-plane bending vibration of trans ethylenic hydrogens\[^{24}\]) with a molar absorptivity of about 200, shows that the major component of this compound is the trans isomer.

2.1.4.8  **1,3-Diphenylbut-2-ene.** Treating for 3 hr. at room temperature 1,3-diphenylbutan-3-ol (10 g. in 40 ml. $\text{CCl}_4$) with 65% weight aqueous sulphuric acid (100 ml.) and vigorous stirring, yielded a mixture of about 78% of 1,3-diphenylbut-2-ene (I) and 22% of 1,3-diphenylbut-3-ene (II) as determined by n.m.r. spectroscopy.
and g.l.c. By fractional distillation under high vacuum I was obtained as a tail fraction in about 95% purity (g.l.c.);
b.p. 89-90°/0.02 mm., \( n_D^{25} = 1.5867 \) (lit. \( 12 \) b.p. 169-170°/12 mm.
\( n_D^? = 1.577 \)).

The purification of II was not attempted. The only information available is that II boils at a lower temperature than I, the head fractions being richer in II.

2.1.4.9 1,1-Diphenylbut-1-ene. Prepared as published by Sabatier and Murat\textsuperscript{25} by distilling 1,1-diphenylbutan-1-ol at pressures above 35 mm. The dehydration is complete at about 180°. B.p. 175°/20 mm.,
\( n_D^{25} = 1.5853 \) (lit. \( 25 \) b.p. 296/760 mm., \( n_D^{16} = 1.595 \)).

2.1.4.10 1,1-Diphenylbuta-1,3-diene. The dehydration of 1,1-diphenylbut-3-ene-1-ol by 65% weight aqueous H\textsubscript{2}SO\textsubscript{4} is complete in about 2 hr. at room temperature. Great care must be taken in preparing the sulphuric acid, because below 60% the dehydration is too slow, and above 70% the diolefin cyclises to 1-methyl-3-phenylindene.

The carbinol (5ml.) dissolved in 20 ml. of CCl\textsubscript{4} is treated for two hours under vigorous stirring (to form an emulsion) with
65% weight H\textsubscript{2}SO\textsubscript{4} (100 ml.) at room temperature. Washed with saturated aqueous NaHCO\textsubscript{3} and dried over CaSO\textsubscript{4}, the CCl\textsubscript{4} phase yielded 4 ml. of diolefin, which was fractionated under vacuum. The colourless oil crystallised (white waxy crystals) after standing overnight.
at -10°. B.p. 102°/0.1 mm., m.p. 33-35°, n_25^D = 1.6393 (supercooled liquid) (lit. 26 b.p. 109°/0.3 mm., n_17.5^D = 1.6412; lit. 27 b.p. 108-110°/0.4 mm., m.p. 35-37°).

2.1.4.11 Indene. The commercial product (B.D.H.) was fractionated under high vacuum and the middle fraction was stored at -10°; n_25^D = 1.5712 (lit. 28 n_20^D = 1.5766).

2.1.4.12 3-Phenylindene. Distilling 1-phenylindan-1-ol at about 30 mm. yielded, by dehydration, 3-phenylindene. This was purified by fractionation under high vacuum to give a colourless oil, which crystallised after standing for one week at -10°. M.p. 25-26°, b.p. 100°/about 0.03 mm., n_25^D = 1.6299 (lit. 16 b.p. 200-201°/29 mm.).

2.1.4.13 1-Methyl-3-phenylindene. No reference was found in the literature (Beilstein, Chem.Abs.), but one publication 15, in which the name 1-methyl-3-phenylindene (III) is erroneously attributed to the structure 1-phenyl-3-methylindene (IV). In IV the methyl group is adjacent to the double bond, while in III it is the phenyl which is adjacent to it.

Two routes were followed to prepare this olefin:

a) Dehydration of the corresponding carbinol 3-methyl-1-phenylindan-1-ol (prepared as described in Section 2.1.2.13) by direct distillation under vacuum (104°/0.02 mm.). The olefin is obtained in quantitative yield. This
route involves three steps: 1) preparation of 3-methylindan-1-one; 2) Grignard reaction to the corresponding carbinol; 3) dehydration. The overall yield is about 50%.

b) A one step route starting with a non conventional Grignard synthesis of 1,1-diphenylbut-3-ene-1-ol (simultaneous addition of all reagents, as described in Section 2.1.2.5), and then simultaneously hydrolysing, dehydrating and cyclising at room temperature the intermediate organomagnesium compound with 75% weight H$_2$SO$_4$, with a yield of about 65% of raw 1-methyl-3-phenylindene. The H$_2$SO$_4$ treatment requires about 48 hr. of very vigorous stirring. But this is a rather drastic method, and the indene may be obtained in higher yield and purity by starting from 1,1-diphenylbuta-1,3-diene (Section 2.1.4.10) and proceeding as follows:

5 ml. of the diene in 20 ml. of CCl$_4$ are treated at room temperature with 75% by weight aqueous H$_2$SO$_4$ (100 ml.) for 48 hr., a vigorous stirring assuring the formation of an emulsion. The organic phase is then decanted, washed with saturated aqueous NaHCO$_3$, dried over K$_2$CO$_3$ and fractionated under high vacuum to yield 4 ml. of pure 1-methyl-3-phenylindene, which crystallises at -10°. Recrystallised from absolute methanol, the colourless crystals
melt at 36-37°; b.p. 87°/0.01 mm., \( n_D^{25} = 1.6143 \) (super-cooled liquid).

Anal.: Calc. for \( C_{16}H_{14} \): C: 93.16; H: 6.84; Mol. wt.: 206.29.

Found here......: C: 93.05; H: 6.92; Mol. wt.: 204

The perfectly clean and simple n.m.r. spectra (VB 238, 258 and 261) confirm the assigned structure.

2.1.4.14 4-Methyl-2,4-diphenylpent-1-ene (V) and 4-methyl-2,4-diphenylpent-2-ene (VI). The currently accepted structure for the \( \alpha \)-methylstyrene unsaturated dimer is VI.\(^{22,30,31}\) In this work three batches of unsaturated dimer were prepared by Hersbergers' method.\(^{22,32}\) In every case the major component (85-90%) of the product was V, the remaining 10-15% being a mixture of VI and of the saturated dimer (Section 2.1.5.2). Although compounds V and VI appeared to have very nearly the same boiling point, a very slow fractionation under reduced pressure, with a reflux ratio of about 20/1 through a 50 cm. Fenske column yielded a head fraction containing 95% of V and a small tail fraction (1% of the total distillate) containing more than 50% of VI (mixed with V). The availability of almost pure V and of a very enriched phase of VI made possible the spectroscopic determination of their structure. The n.m.r. spectra are unambiguously clear and show in V the proton resonance doublet of the vinylidene hydrogens (expected shift and splitting) and the methyl and methylene peaks of appropriate intensity. In VI, apart from the phenyl protons,
a large peak shows the presence of 9 methyl hydrogens and a small peak, 1 hydrogen attached to the trisubstituted double bond. The i.r. spectra confirm this assignment by the presence in V of a strong band at 895 cm.\(^{-1}\) (hydrogen out-of-plane deformation of asymmetric di-substituted ethylenes\(^{24}\)).

Thus, the structure of the major component of the unsaturated \(\alpha\)-methylstyrene dimers is not VI, as accepted,\(^{22,30,31}\) but V. The physical properties of a 95% pure sample of V are:

b.p. 118/0.06 mm., 171º/15 mm.; \(n^D_{25} = 1.5679\).

To prepare the unsaturated dimers, 1 part of pure \(\alpha\)-methylstyrene is treated for 8 hr. at room temperature with 4 parts of 60% by weight aqueous \(H_2SO_4\). A very vigorous stirring is required to assure the formation of an emulsion.
2.1.5 Aryl alkanes.

2.1.5.1 1-Methyl-3-phenylindane. To prepare the cyclic dimer of styrene, 70 ml. of unsaturated dimer (Section 2.1.4.7) and 250 ml. of 70% weight aqueous sulphuric acid were refluxed with vigorous stirring for 6 hr. at 150-160°. The organic phase, still containing about 2% of olefin was then stirred for 30 min. at 0° with 20 ml. of 100% H$_2$SO$_4$, to give, after conventional washing and drying a perfectly pure, colourless cyclic dimer, as determined by g.l.c., n.m.r., u.v., and i.r. spectroscopy and by bromine treatment. As with any conventional method of preparation,$^{15,23}$ this product was a mixture of cis and trans isomers. B.p. 156-157°/15 mm., n$_D^{25}$ = 1.5794 (lit.$^{15}$ b.p. 170-172°/20 mm., n$_D^{20}$ = 1.5808).

2.1.5.2 1,1,3-Trimethyl-3-phenylindane. In a variation of Hersbergers' method,$^{22,32}$ a mixture of α-methylstyrene unsaturated dimers (20 ml.) were treated for 15 hr. with 80% weight aqueous sulphuric acid (100 ml.) at 40° and good stirring (emulsion). After conventional extraction, washing and drying, fractional distillation under high vacuum gave 15 ml. of saturated dimer which crystallised by slow cooling to 0° of its 20% solution in hexane. Recrystallised from hexane or methanol, this compound gives by slow cooling of its saturated solution in hexane clear and colourless crystals, whose size seems to be limited only by the vessel's dimensions (a single
crystal $4 \times 2 \times 0.3$ cm. was obtained in this laboratory).

M.p. 52.5°, b.p. 118°/0.07 mm. and 170°/15 mm.
(lit. 31 m.p. 52°, b.p. 170°/17 mm.).

2.1.5.3 Triphenylmethane. The commercial product (B.D.H.) was used without further purification; m.p. 93° (lit. 4 92.5).

2.1.5.4 1-Methyl-1,3,3-triphenylindane. This compound, kindly supplied by Professor A.G. Evans, University College, Cardiff, was twice recrystallised from absolute ethanol; m.p. 143-144° (lit. 33 143°).

In all, sixty concentrated acid phials (about 1 ml. each) were made up in the dark at 0°. Two litres of acid were divided into phials were prepared containing sufficient acid to lower the pH to 10.72. Several checks were made on the extent of acid of the more concentrated phials by titration, and in the diluted phials by spectrophotometry, after reaction with an excess of trimethylsilyl chloride. The error involved was usually less than 2° for the concentrated phials, and less than 3° for diluted phials.

2.1.6 Sulphuric acid. This acid: 95% Analab and 100% (A.R., B.) was used satisfactorily without further purification. Three different batches gave identical results.

2.1.7 Phosphoric acid, $P_2O_5$, was supplied by Sigma (A.R., L.) Ltd., Dorset, Cambridge, with the following specifications:

- **Purity:** 98%
- **Water Content:** < 0.5%
- **Dissolvability:** Soluble in water
- **Other Components:** < 0.1%
2.1.6 **Acids.**

2.1.6.1 **Anhydrous perchloric acid.** This acid was prepared by the dehydration of 72% perchloric acid (Hopkin and Williams) with 20% oleum. The method used was derived from Eastham and Tauber's; a full description is given by Gandini. A serious explosion hazard is the breaking of the dosing burette containing HClO₄, during the thawing of the latter. This is best avoided by starting the thawing from the top of the burette, avoiding thus any possible pressure build up caused by the expansion of melting HClO₄.

In all, sixty concentrated acid phials (about 1 M, in methylene dichloride) were made and stored in the dark at 0°. From this stock of acid one hundred more phials were prepared containing solutions down to 10⁻³ M. Several checks were made on the contents of some of the more concentrated phials by titration, and on the dilute phials by spectroscopy, after reaction with an excess of triphenylmethyl carbinol. The error involved was usually less than 1% for the concentrated phials, and less than 5% for dilute phials.

2.1.6.2 **Sulphuric acid.** This acid, 98% AnalalR and 100% (B.D.H.) was used satisfactorily without further purification. Three different batches gave identical results.

2.1.6.3 **Deutero sulphuric acid.** D₂SO₄ was supplied by CIBA (A.R.L.) Ltd., Duxford, Cambridge, with the following specifications:
Sulphuric acid-d$_2$, 96-98% solution in D$_2$O, isotopic purity better than 99 atom% D, density d$_{20}$=1.86.

2.1.6.4 Chlorosulphonic acid. Supplied by May and Baker Ltd., was used without further purification; d$_{20}$=1.755-1.765 (lit. $^4$ d$_{18}$=1.766).
Table 1 A

Data on u.v. spectra of pure compounds obtained at 25° from methylene dichloride solutions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ m$\mu$</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>291</td>
<td>620</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>282</td>
<td>885</td>
<td></td>
</tr>
<tr>
<td></td>
<td>249</td>
<td>15,400</td>
<td></td>
</tr>
<tr>
<td>1,3-diphenylbut-1-ene (trans)</td>
<td>293</td>
<td>1,180</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>284</td>
<td>1,820</td>
<td></td>
</tr>
<tr>
<td></td>
<td>251</td>
<td>21,300</td>
<td></td>
</tr>
<tr>
<td>1-methyl-3-phenylindane</td>
<td>273</td>
<td>1,250</td>
<td>this work</td>
</tr>
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<td></td>
<td>266</td>
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</tr>
<tr>
<td></td>
<td>260</td>
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<td>425</td>
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<td></td>
<td>236</td>
<td>7,450</td>
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at 25° from hexane: Table 1 B

<table>
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<th>$\varepsilon_{\text{max}}$</th>
<th>Ref.</th>
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<td>3-phenylindene</td>
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<td>700</td>
<td>this work</td>
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<td></td>
<td>282 shr.</td>
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<td></td>
<td>254 shr.</td>
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<td>227</td>
<td>20,100</td>
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<td>1,350</td>
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<td>259</td>
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<td>227</td>
<td>22,500</td>
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<td>1,1-diphenylbuta-1,3-diene</td>
<td>284</td>
<td>23,100</td>
<td>this work</td>
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<tr>
<td></td>
<td>234</td>
<td>16,000</td>
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<td>1,1-diphenylbut-1-ene</td>
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<td></td>
<td>248</td>
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Table 1 B
(continued)

(Spectra of pure compounds obtained at 25° from hexane solutions, contd.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{max}$ $\mu$m</th>
<th>$\xi_{max}$</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>2,6-dimethylstyrene</td>
<td>276</td>
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<td>this work</td>
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<td></td>
<td>236</td>
<td>6,700</td>
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</tr>
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<td></td>
<td>$\sim$ 209</td>
<td>$\sim$ 22,000</td>
<td></td>
</tr>
<tr>
<td>1,3-diphenylbut-1-ene</td>
<td>293</td>
<td>1,180</td>
<td>this work</td>
</tr>
<tr>
<td>(trans)</td>
<td>284</td>
<td>1,820</td>
<td></td>
</tr>
<tr>
<td></td>
<td>251</td>
<td>21,300</td>
<td></td>
</tr>
<tr>
<td>1-phenylethyl acetate</td>
<td>263</td>
<td>156</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>257</td>
<td>205</td>
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</tr>
<tr>
<td></td>
<td>251</td>
<td>178</td>
<td></td>
</tr>
</tbody>
</table>

25° from acetic acid sol. (glacial)  

Table 1 C

| Phenyl-(2'-methylphenyl)-methanol       | 264                     | 520         | this work |
|                                         | 258                     | 525         |         |
| Tribenzylmethanol                       | 268 shr.                | 170         | this work |
|                                         | 264                     | 260         |         |
|                                         | 258.5                   | 340         |         |
|                                         | 253                     | 270         |         |

shr. denotes a shoulder
2.2 APPARATUS AND PROCEDURES

2.2.1 Spectroscopy.

2.2.1.1 Ultraviolet and visible spectroscopy. The spectra reported in this work were taken with a Beckman DB recording spectrophotometer and occasionally, for calibration purposes, with UNICAM SP.700 and UNICAM SP.800 recording spectrophotometers.

The Beckman DB instrument was frequently checked for wavelength accuracy, with a Holmium reference glass, and for absorbance linearity and accuracy, using the $K_2CrO_4$ in 0.05N KOH method; it was always found to be within the manufacturers' specification.

**Repeatability:**

**Wavelength:** 220-334 μm: better than 0.5 μm
335-574 μm: better than 2.5 μm
574-700 μm: better than 5.0 μm

**Absorbance:** 0.2 to 0.6: better than 0.01 absorbance units.

The cell compartment was thermostatted for most measurements, either at 25° or at 2°. Condensation of atmospheric humidity on the cells at 2° was avoided by continuously flushing the cell compartment with a tiny stream of dry air. A special light-tight lid allowing a large amount of free space above the cell holder replaced the conventional lid when bulky cell devices were used.

Standard spectra of alcohols, olefins and other stable
compounds (hexane and methylene dichloride solutions) were taken in calibrated silica cells (fitted with ground glass lids) of 0.1, 0.2, 0.5, 1 and 2 cm. path length. Successive changes in concentration or path length were overlapped, to make sure that any apparent deviation from Beer's law are detected. The molar extinction coefficients \( \varepsilon \) (molar absorptivities) were computed by measuring the slope of a Lambert-Beer plot of at least three experimental points. For the purposes relevant to the carbonium ions part of this work, it was never necessary to scan at wavelengths lower than 240 m\( \mu \). Methylene dichloride, acetic acid and sulphuric acid have transparency limits below this wavelength and could therefore be suitably used; chlorosulphonic acid was only used in the visible part of the spectrum. 1 cm. cells (silica) fitted with B7 ground-in joints were used in the "open" experiments with acids.

Most experiments in closed systems were carried out with the all-glass device illustrated in Fig. 1. The phial to be crushed was placed in the side tube A together with a glass-enclosed magnetic breaker and, whenever required, the desired amount of non-volatile reactant. The tube was then sealed off at B and the device was attached to the vacuum line at C. After the necessary pumping out, the solvent and the other required reactants were distilled into A, cooled to a temperature close to the melting point of the solvent, and the device sealed off at D. The solution was allowed to reach the temperature of
the cell holder, and a spectrum of the relevant species taken after some of the liquid had been tipped into the cell E.

The phial was then crushed into the whole of the solution, good mixing being ensured by vigorous shaking. I found it useful to attach the device during the phial-crushing step to a vibro-mixer, so that an efficient mixing is instantaneously assured. The liquid was then quickly transferred into the cell, the device placed into the cell holder, and the scanning started.

Between the moment of mixing of the reactants and the beginning of the scanning 15-20 sec. elapsed.

The minimum volume of liquid required for taking a spectrum with 1 cm. cells was about 3 ml; the maximum, compatible with the dimensions of the device and the cell compartment, was about 30 ml. A tenfold dilution of the reactants could therefore be performed, and a hundredfold decrease of the absorbance, when using the combination 1 cm. cell - dilution - 0.1 cm. cell. Dilutions, addition of further quantities of reactants and introduction of other reactants were easily carried out in vacuo through the break seal F.

The device illustrated in Fig. 2 was used when two phials for consecutive crushing were needed. Some care is required to avoid breaking the phial in tube G during the first step.

The device illustrated in Fig. 5 was used when simultaneous spectroscopic and conductimetric experiments were carried out and it
is described in the conductivity section (2.2.2).

Exploratory runs in open systems were carried out by mixing the reactants in a small, dry, stoppered test tube and quickly transferring some of its contents into a cell with a ground-in stopper. Scanning could be started within 20 sec. from the mixing. In a few cases, where a very early spectrum was required, the reactants had to be mixed directly in the cell, placed in the cell compartment; the interval between mixing and scanning was reduced to about 3 sec.

In order to obtain accurate reading, the absorbance was kept whenever possible within the limits 0.1-1.0. Before every experiment, blank spectra of the solvents and acids used were recorded.

During the course of this work, all together 1,050 u.v. and visible spectra were recorded and examined.

2.2.1.2 Infrared spectroscopy. Two instruments were used for the recording of infrared absorption spectra, depending upon the resolution needed: Perkin Elmer Spectrophotometer 221, fitted with a NaCl prism, and Perkin Elmer 257 Grating Infrared Spectrophotometer. Frequent tests for wavelength accuracy and for resolution were made using a polystyrene solid film or an indene liquid film, as recommended by the International Union of Pure and Applied Chemistry. 38

Conventional techniques 39 were adopted for the preparation of the compounds to be analysed.
Infrared spectra of all organic compounds used in this work were scanned both with 0.1M solutions and with undiluted samples (when liquids), so that a more appropriate estimation of the intensity and position of bands could be obtained. Carbon tetrachloride and carbon disulphide having very few interfering absorption bands, were used as a solvent pair for scanning the full spectrum between 4,000 and 650 cm\(^{-1}\); the upper half being run in CCl\(_4\), the lower in CS\(_2\). 1 cm. and 0.025 mm. NaCl window cells were used. 105 infrared spectra were scanned in experiments relevant to this work.

2.2.1.3 Nuclear Magnetic Resonance spectroscopy. A Perkin Elmer M-R10 NMR Spectrometer, provided with an integrated circuit and a CAT (computer of average transients) device was used throughout this work. This instrument has a 14,092 gauss permanent magnet (\(^1\)H resonance at 60 Mc sec\(^{-1}\)) thermostatted, probe included, at 35\(^\circ\). Soda-glass sample tubes with 0.4 mm. inner diameter required at least 0.2 ml. of solution. In a few experiments made under high vacuum, the sample tube was provided with a soda-to-Pyrex graded seal allowing joining to the vacuum line.

Resolution adjustment, calibration, and preparation of solutions to be examined were performed according to conventional techniques.\(^{40,41}\) The position of the n.m.r. bands in CCl\(_4\), CS\(_2\), CDCl\(_3\), CH\(_2\)Cl\(_2\) and SOCl\(_2\) solution were determined by reference to TMS (tetramethylsilane) at 10 \(\tau\) (Tau) in p.p.m. (parts per million) as an
internal standard. In \( \text{H}_2\text{SO}_4 \), \( \text{D}_2\text{SO}_4 \) and \( \text{HSO}_3\text{Cl} \), the internal standard was TMAS (tetramethylammonium sulphate), with its peak at 6.90 p.p.m. downfield from TMS), according to Deno et al.\textsuperscript{42} The use of TMAS as internal standard has been thoroughly investigated,\textsuperscript{42,43} and it appears to be perfectly suitable when used in standardised conditions. 

In all diagrams of actual spectra included in this thesis, the direction of increasing magnetic field is from left to right.

N.m.r. spectroscopy was extensively used during this work (more than 300 spectra were scanned) and proved to be of the greatest help. Many syntheses (where i.r. spectroscopy supplied ambiguous information) which would have required weeks of cumbersome conventional analytical work were carried out in one day, with the help of a few consecutive n.m.r. spectra. For this reason, I attempted to use where possible \( \text{CCl}_4 \) as reaction medium, in order to be able to have quick spectra at different stages of a reaction, without further treatment of the collected sample.

At this point, I feel compelled to express my deep respect to chemists who, not that long ago, were working using only patient skill and genius.
2.2.2 Electrical conductivity.

2.2.2.1 Electrical conductivity cells. Three all-glass electrical conductivity cells were built and used throughout this work.

Cell No I (Fig. 3) was meant to be used in exploratory runs and in experiments where a very quick reading after the mixing of the reagents was not essential. The smallest volume of liquid required to cover the Pt electrodes was 1 ml. and the largest, compatible with the dimensions of the device, was about 30 ml.

This cell consisted basically of a Pyrex cylinder G of inner diameter 20 mm., constricted in its lower part to 8 mm. and closed. The upper part was sealed to the cell holder Pyrex tube H; this plunged into G and was prolonged via a graded seal by a soda-glass tube into which the platinum leads Pt (0.5 mm. thick) were fused through a carefully annealed soda-to-Pyrex seal. The leads were attached to the platinum electrodes (1 mm. thick wire twisted three times to increase the conducting surface). Inside H, the leads were insulated with glass sleeves (melting point tubes). Through a side arm, G was connected to the tube A, provided with an appendix I.

The procedure involved in a normal run was as follows: after placing in the side tube A the phial to be crushed, together with the magnetic breaker and a second phial in I, when required, the tube was sealed at B and the device attached to the vacuum line at C, and pumped out as required. The solvent and the other reactants were then
Fig. 3 (page 34)
Conductivity cell n° I for small volumes of liquid.

Fig. 2 (page 30)
Device for vacuum u.v. and visible spectroscopy, allowing the use of two phials (for consecutive crushing).

Fig. 1 (page 29)
Device for vacuum u.v. and visible spectroscopy, with 0.1 and 1 cm. silica cells.
distilled into A, cooled to a temperature close to the melting point of the solvent, and the device sealed off at D and placed in the thermostat. After reaching thermal equilibrium, part of the liquid was tipped into the cell E, and the conductivity of the solution or of the pure solvent measured.

The phial was then crushed into the whole of the solvent or solution, and its contents mixed. The liquid was quickly transferred into the cell, with due care to avoid breaking the second phial (when present). The time lag between reagent mixing and first reading was about 20 sec. Further additions of reagent or of solvent could easily be carried out if required (second phial and break seal F).

A paraffin oil bath, thermostatted by conventional techniques to ± 0.1° was placed around the cell for the experiments carried at temperatures from 0 to 35°. For lower temperatures, carbon tetrachloride, chloroform or methylene dichloride slushes in large Dewars were used.

Cell no II (Fig. 4) was specially built to eliminate any time interval between mixing of the reagents and the beginning of the electrical conductivity recording. This cell consisted of an inverted pear shaped 100 ml. flask G, blown in its lower part in a convenient shape to allow room for the Pt electrodes and for an efficient propeller (assuring an upward circulation of the liquid), and sealed to the side tube A. The two platinum electrodes Pt (1 cm. × 1 cm.) were
Conductivity cell no II, especially built to eliminate any time interval between mixing of the reagents and the beginning of the electrical conductivity recording. The platinum electrodes are placed at about 3 mm. distance and held firm by four soda-glass beads, not shown on the figure for the sake of clarity.
placed at about 3 mm. distance and held firm by four soda-glass beads. The platinum leads attached to the electrodes were spot-welded onto 1 mm. tungsten rods W, which were fused through the upper part of the flask and were externally connected to copper leads Cu. The upper part of G was prolonged, via an internal seal, by the magnetic stirrer compartment K. The Pyrex shaft S connecting the propeller to the magnetic stirrer had to be perfectly balanced and straight in order to avoid any undue vibrations and shaking against the electrodes. Teflon rings Tf, which proved to be perfectly inert chemically, were used as shaft guides.

To assure an invariable cell constant, the platinum leads were protected by soda-glass sleeves Sd down below the liquid level. Corrosion of the tungsten connections was prevented by covering them entirely with Pyrex.

After a few shortcomings in its early stages, the final version of this device, as represented in Fig. 4, was successfully used at temperatures ranging from -65°C to +25°C, and under high vacuum conditions. The procedure for its use was as described for cell n° I, excepted than here the time lag between the crushing of the phial and the first reliable reading on the recorder was reduced to less than 1 sec.

Cell n° III (Fig. 5) was devised in order to allow simultaneous electrical conductivity and u.v. and visible spectroscopy measurement under high vacuum. 1 mm. thick platinum wire flattened by
hammering to increase its surface constituted the electrodes. These, fixed 1 mm. apart with soda-glass beads, plunged into a 1 cm. spectroscopy silica cell, about 2 mm. above the optical path. The silica cell was prolonged via a silica-to-Pyrex graded seal (SiP) by a Pyrex tube P, which was connected in turn through a Pyrex-to-soda graded seal (SoP) to a soda-glass tube, which was melted on the Pt leads, assuring a vacuum tight seal. P was connected to the sample tube A, and to the vacuum duct C. Inside P, the Pt leads (0.5 mm. thick) were isolated by melting point tube sleeves (fused-on at their ends).

The procedure involved in the use of this cell was as described above for cell no I. In all experiments this device was thermostatted via the spectrophotometer cell compartment (from 20 to 250). Devised in a most skeptical mood, this combined cell proved to be a useful tool and helped to solve a crucial problem in this work (Section 3.2.3).

In building these three cells, I used conventional techniques and precautions, as recommended by Robinson and Stokes.44

2.2.2.2 Cell constants of the conductivity devices. The cell constant was obtained by using the procedure suggested by Lind, Zwolenik, and Fuoss.45 Since in most cases the conductivity work was confined to a small range of temperatures, it was assumed that the value of the cell constant, determined at 250, could be applied in all measurements.
Considering that I was more interested in conductivity variations at constant temperature than in measurements of absolute accuracy, this approximation is justifiable.

Cell constants (cm$^{-1}$): cell n$^0$ I = 0.094  
                cell n$^0$ II = 0.134  
                cell n$^0$ III = 0.195.

2.2.2.3 **Conductivity bridges and recorders.** Conductivities for calibration purposes were measured with a Wayne-Kerr B221 Universal Bridge. This instrument which works on the transformer ratio-arm principle has a built-in source (1,592 cycles/sec.) and detector. Conductivities ($10^{-1}$ to $10^{-8}$ mho) and capacities (0 to 11 $\mu$F) are indicated separately, and the former can be measured within $\pm$ 0.1% over the complete range.

All routine conductivity measurements were made with a Chandos Linear Conductivity Meter. This instrument measured conductivities from $10^{-2}$ to $10^{-8}$ mho (within $\pm$ 1%). Its output was connected either to a Beckman Linear Potentiometric Recorder, for normal runs, or to a Rikadenki Kogyo fast response - low drift dual-pen recorder, when simultaneous conductivity and optical density variations had to be recorded (using cell n$^0$ III) or when fast variations of conductivity (using cell n$^0$ II) were measured.

2.2.2.4 **Conductivity of materials.** The specific conductivity of CH$_2$Cl$_2$ was at the lowest limit of detection, i.e., in the range of $10^{-8}$ to $2 \times 10^{-8}$ Mhos, at $0^\circ$. 
The concentrations of styrene used in the conductimetric runs (10^-5 to 10^-3 M) did not give any measurable increase of the specific conductivity of the solutions, as compared to the conductivity of the solvent (CH₂Cl₂).

The equivalent conductivity of anhydrous HClO₄ was in the range of 3.3x10^-3 Mho cm.² mole⁻¹ at 0°, and 4.8x10^-3 Mho cm.² mole⁻¹ at 18°, for 10^-4 to 10^-2 molar solutions in CH₂Cl₂.

As a comparison, the equivalent conductivity of the ionic species investigated in this work was in the range of 10 to 10² Mhos cm.² mole⁻¹. In most runs, the background specific conductivity, due to the solvent and to HClO₄, was less than 1% of the total specific conductivity.
2.2.3 Vapour phase chromatography.

Three different instruments were used to analyse the purity of materials or to identify (together with other techniques) recovery products.

Volatile compounds (solvents and some of the olefins) were passed through a Perkin-Elmer Model 452 fitted with a 6 metre P.E. Ref. 0 column. Calibration data for this column were kindly supplied by Dr. C. James of Keele University.

Medium range boiling point compounds (100° to 250°) were analysed with a Perkin-Elmer F-11, fitted with a 3 m. silicone-oil SE-30/Chromosorb P 100-120 mesh column.

For substances of high boiling point, an instrument working at high temperatures (constructed in the Department from conventional components) was used. I am grateful to Dr. G. Jones of Keele University for giving me the opportunity of using the latter chromatograph.

All three instruments had a flame ionisation detector.

Conventional procedures were adopted for sample preparation and instrument calibration (Perkin-Elmer manuals and lit. 46, 47).
2.2.4 Molecular weight determination.

Molecular weights were determined with a Mecrolab Vapour Pressure Osmometer Model 301 A, with a non aqueous probe and running at 37\(^\circ\)C. For my purpose this instrument was calibrated with triphenyl-methane in dioxane, the latter being the only solvent I used.

2.2.5 Elemental analysis.

Elemental analyses were performed with an F and M Automatic Carbon-Hydrogen-Nitrogen Analyser, in which the combustion products of the compound are determined by gas chromatography, by comparison with a standard.

2.2.6 Molecular distillation.

Compounds which decomposed by normal high vacuum distillation, or were available in a too small amount to be distilled, and could not be fractionated by crystallisation because too impure (no nucleation) were successfully purified by molecular distillation.

For this purpose I built the simple device (Fig. 6) based on a conventional design. 48

Up to 1 ml. of product from which any solvent had previously been removed by evacuation was placed in A, cooled externally with an ice bath, degassed by prolonged pumping, and then distilled at a rate of 2 drops per hr. under 10\(^{-3}\) to 10\(^{-4}\) mm., with gentle heating (40 to 90\(^\circ\)) assured by a small electrical heating ribbon, externally
wound. Due care was taken to avoid splashing of the liquid into B during the degassing (vigorous bubbling).

2.2.7 **Dosing of solvents and reagents under high vacuum.**

Methylene dichloride was dosed as published, volatile compounds were measured either by distillation into precision pipettes, or in the gas phase, via calibrated flasks. Non volatile and unstable compounds were dosed and diluted in phials to be crushed by a magnetic breaker, as described by Rutherford.
2.2.8 Protonations.

2.2.8.1 Introduction. Many works on carbonium ions published during the past years failed to give reliable results because insufficient attention was paid to the choice of appropriate experimental conditions, such as concentration of the reagents, temperature at which they are made to react, mode of mixing, purity of the protonating agent, etc.

In the experimental sections of this thesis I have shown that apparent extinction coefficients (computed on the assumption that all the precursor has been protonated) of a spectroscopically observed carbonium ion may vary by a factor of 10 or even of 100 according to the experimental conditions.

Deno et al. discuss reactivity problems associated with the preparation of carbonium ions and suggest techniques giving higher yields.

2.2.8.2 Protonations under high vacuum. All the work involving HClO was carried out in the spectroscopic and conductimetric devices described in sections 2.2.1.1 and 2.2.2. The n.m.r. runs were made with the device illustrated in Fig. 1, one of the silica cells being substituted (via a soda-to-Pyrex graded seal) by a n.m.r. sample tube, which was afterwards sealed off and placed in the n.m.r. instrument probe. Careful balancing of the graded seal was required to avoid irregular spinning.
Work involving HSO₃Cl and H₂SO₄ under high vacuum was carried out with the device illustrated in Fig. 7, based on a design suggested by Sorensen. The required amount of compound (1 to 500 mg.) being placed in A and the acid (5 to 20 ml.) in B, flasks A and B were cooled in liquid nitrogen, taps 1 and 2 were opened, and the system evacuated. Tap 2 was then closed and the acid degassed by repeated thawing and freezing. Finally, tap 1 was closed, tap 2 opened and the compound distilled slowly into B, the acid being rapidly stirred with the glass enclosed magnetic stirrer. The distillation took anywhere from 5 min. to 2 hr., depending upon the pressure and temperature differential between A and B. The acid was kept at any temperature between 20 and -30°C and the compound between 0 and 50°C.

This method allowed clean protonations to be carried out with compounds which gave mostly polymers when treated conventionally.

2.2.8.3 Open protonations. Even with compounds giving very stable carbonium ions, no perfectly clean reaction can be observed when the undiluted compound is directly mixed with the protonating agent. Grace and Symons have shown that any attempt to prepare stable solutions of reactive carbonium ions can succeed only if the concentrations of all compounds with which they can react is a minimum. When the reactants are polymerisable olefins or the corresponding carbinols, great care must be taken to minimise the contact between forming carbonium ions and reactants. This is best achieved by adding
**Fig. 5 (page 36)**

Cell n° III, for simultaneous electrical conductivity and u.v. and visible spectroscopy measurements under high vacuum.

**Fig. 6 (page 41)**

All Pyrex device for molecular distillation of small amounts of product (up to 1 ml.).

**Fig. 7 (page 44)**

Device for protonations by distillation under high vacuum.

The small bar in B is a glass-enclosed magnetic stirrer.
Fig. 5

Fig. 6

Fig. 7
a dilute solution of the compound to be protonated through a capillary to the periphery of the rapidly rotating acid. The fast shearing of the tip of the capillary facilitates thus the race through the dilute acid region with all possible speed. Experience shows that the lower the initial concentration of the reagent, the lower the temperature of the acid, and the higher the mixing speed are, the higher is the yield of pure carbonium ion.

An obvious difficulty is the choice of the right solvent, which has to be unreactive towards the reagent, the acid, and the carbonium ions formed, and sufficiently transparent for u.v. spectroscopy purposes. In most cases acetic acid is found perfectly suitable, but not in n.m.r. spectroscopy, where thionyl chloride may be used occasionally with advantage. Olah et al. have recently shown that ethanol can be used as a solvent for carbonium ion precursors in strong acids, for u.v. spectroscopy and, when no overlapping peaks appear, for n.m.r. spectroscopy.

In a few protonations of highly reactive compounds (polymerizable olefins), aiming at high concentrations for n.m.r. spectroscopy purposes (5-10%), I found CCl₄ a very convenient solvent when H₂SO₄ was used. Dilute solutions of the precursor in CCl₄ were added slowly to very rapidly stirred H₂SO₄; when the emulsion settled down, in a few minutes, the acid phase containing the carbonium ion was decanted and tipped directly into the n.m.r. sample tube. Analysis of the CCl₄ layer after this treatment showed that no traces of precursor remained
in solution. This method allowed clean protonations to be made with compounds with which all other techniques, including Sorensen's, had proved unsuccessful.

In order to check the possible effect of any dissolved gases (O₂, SO₂, SO₃, etc.) comparative protonations were made with acid taken directly from the bottle, or flushed by prolonged bubbling of pure dry nitrogen, in the open, or finally under high vacuum after prolonged degassing. Identical results being obtained in all three cases, the acid was used without any treatment in further protonations.

In all runs where the protonation was fast, no sulphonation by H₂SO₄ or by HSO₃Cl was found, as shown by the analysis of the recovery products.
2.2.9 Recovery of products from carbonium ions.

Essentially the same problems arise during the attempted recovery of precursors from carbonium ions as during the formation of the latter from the former. The ions must pass with all possible speed through regions of intermediate acidity, where both precursors and carbonium ions are unstable and hence destroyed by higher order reactions. Low concentration, low temperature and fast dispersal techniques minimize side reactions.

Exploratory recovery experiments showed that even with the most stable ions, such as the triphenylmethyl cation, the greatest care must be taken in devising the appropriate dilution technique for clean and quantitative recovery of the precursor.

Thus, a 5% solution of triphenylmethanol in 98% H₂SO₄ gave quantitatively the trityl cation, as determined by n.m.r. and u.v. spectroscopy (after due dilution in 98% H₂SO₄ in the latter case). Starting from this clean solution, different dilution techniques gave the following results, as determined by i.r. and n.m.r. spectroscopy after conventional extraction and drying:

a) Direct mixing with ice-cold water, fast stirring: 50% carbinol, plus substituted compounds.

b) Addition to 95% ethanol, fast stirring: 40% carbinol, ethoxy groups, para substituted compounds.

c) Addition to 10% aqueous ammonia solution, fast stirring:
50% carbinol, 25% amine, plus non identified products.

d) Addition to ice-cold excess alkali, slow stirring: 60% carbinol, para substituted compounds, insoluble materials.

e) Same as above, but very fast stirring: more than 90% carbinol, no impurities.

All recovery runs in this work were made by pouring the carbonium ion solution through a capillary into the periphery of very rapidly rotating excess of aqueous sodium hydroxide at -10°C. The extractions were made with hexane, carbon tetrachloride or carbon disulphide, according to the requirements (u.v., i.r., n.m.r. spectroscopy and g.l.c.). Where necessary, comparative extractions were from acetic acid solutions of pure precursors, and the yield of the extraction was always found to be nearly quantitative.
2.2.10 Identification procedures.

In the identification of pure compounds, reaction intermediates and recovery products I made a systematic use of u.v., i.r. and n.m.r. spectroscopy, and g.l.c., supported, when useful, by melting and boiling point, and refractive index determinations. Elemental analyses and molecular weight determinations were necessary only occasionally.

2.2.11 Polymerisation and isolation of polymers.

The polymerisation experiments with styrene were carried out in the spectroscopic devices described, together with the general procedure, in Section 2.2.1.1.

To isolate the polymer, the contents of the device were poured into vigorously stirred methanol; the fine precipitate was filtered off and dried at $50^\circ$ in a vacuum oven to constant weight. Slow evaporation of the methanol phase isolated the oily oligomers.

2.2.12 Other techniques.

Melting points, refractive indices, and other routine determinations were performed by standard techniques.54
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3.1 Interaction of styrene and related compounds with concentrated sulphuric acid.

3.1.1 Introduction.

When styrene, 1,3-diphenylbut-1-ene, or 1-phenylethanol are treated with excess of anhydrous perchloric or sulphuric acid in dilute solution, or when these compounds are introduced into concentrated sulphuric acid, or when the corresponding chlorides are treated with aluminium or stannic chloride, the resulting solutions have spectra with two main peaks at about 430 and 310 m\(\mu\). The \(\lambda_{\text{max}}\), the \(\varepsilon\), the ratio \(\varepsilon_{430}/\varepsilon_{310}\), and the shape of the peaks vary according to the experimental conditions.

It was long believed that this spectrum was due to the 1-phenylethyl and the corresponding oligostyryl cations. This assignment was challenged, and a very recent publication states that the 1-phenylethyl cation cannot be formed even in \(\text{SO}_2\text{-SbF}_5\text{-FSO}_3\text{H}\) at -60°, an acid with a protonating power at least \(10^4\) greater than 100\% \(\text{H}_2\text{SO}_4\).

The criticism was mainly aimed at Gandini and Plesch's pseudocationic polymerisation mechanism, based partly on the
assumption that the styryl cation always shows an absorption at about 310 and 430 mμ, the latter peak being the higher. Hanazaki and Nagakura⁹ suggest that the 1-phenylethyl cation probably does not exist at room temperature and state, from SCF molecular orbital calculations, that in any case its low wavelength peak should have the higher intensity. Higashimura et al.¹⁰ believe that the absorption at 430 mμ cannot be due, or directly related, to the styryl cation. Bywater and Worsfold¹¹ suggest that the polystyryl cation shows maximum absorption at 320 mμ and not at around 420 mμ, and show that the latter absorption is associated with the reaction products from cyclic end groups in the polymer. These latter findings are partly in agreement with my simultaneous and independant work.

As a starting point for this section of my work, two important questions had to be answered:

a) Do the 310 and 420 mμ peaks belong to the same species, and if so, attempt to identify the cation(s) responsible for this absorption.

b) Does the styryl cation exist as conventionally accepted, and if so, what is its ultraviolet and visible spectrum.

As only circumstantial (u.v. spectroscopy) evidence was available regarding the existence of the alleged 1-phenylethyl cation and its related polystyryl cation, I thought that an obvious (but surprisingly never attempted) step was to isolate the product(s)
deriving from the protonation of styrene, and analyse them.

A thorough look through the literature on stable carbonium ions showed that apart from n.m.r. spectroscopy (when possible) the only unambiguous identification of a carbonium ion was the recovery and identification of the precursor (olefin or carbinol) after due dilution.

Deno et al.\textsuperscript{14} have discussed the techniques to use in order to avoid side reactions during the neutralisation of the carbonium ion.
3.1.2 Interaction of styrene and 1-phenylethanol with 98% sulphuric acid.

3.1.2.1 Procedure. Styrene or 1-phenylethanol purified as described in sections 2.1.2.1 and 2.1.4.1 were introduced into rapidly stirred \( \text{H}_2\text{SO}_4 \) either by vacuum distillation,\(^{15}\) using the device illustrated in Section 2.2.8.2, or through a capillary.\(^{14}\) In the latter instance, \(10^{-4}\) to \(10^{-1}\) M solutions in \(\text{AcOH}\) (1 ml.) were diluted in 9 ml. \(\text{H}_2\text{SO}_4\). With both techniques, the final dilution was \(10^{-2}\) to \(10^{-5}\) M. All runs were performed at temperatures between \(-20\) and \(0^\circ\).

3.1.2.2 U.v. and visible spectroscopy. Styrene and 1-phenylethanol give the same spectra in conc. \(\text{H}_2\text{SO}_4\) (1-phenylethanol being first dehydrated to styrene, as shown by Gandini and Plesch\(^{16}\)), and will thus be considered as the same species.

Though some discrepancies are found in the published work on this system,\(^{4,6,8}\) and between the published results and my own findings, one essential point is clearly established: in the cleanest experimental conditions, styrene solutions in conc. \(\text{H}_2\text{SO}_4\) exhibit two main peaks, at around 315 and 430 \(\text{m}\mu\), with \(\varepsilon_{315} > \varepsilon_{430}\). The 315 \(\text{m}\mu\) peak being fairly reproducible in position, while the 430 \(\text{m}\mu\) peak varies considerably both in position and shape from one experiment to the next, suggesting that many different species, formed in variable proportions, absorb at this wavelength range.
In my runs, I found that after one to five days the 315 m\textmu{} peak is replaced by one at ca. 310 m\textmu{}; the peak at ca. 430 m\textmu{} decreases, and one at 415 m\textmu{} becomes prominent. A possible explanation of this shift is given in Section 3.6.2, (page 104).

In particularly "dirty" runs (room temperature, slow stirring, or high concentration of styrene) the 430 m\textmu{} region peak was prominent. Fig. 8 compares spectra from "clean" and "dirty" runs.

The low extinction coefficients of all peaks (between $10^3$ and $3\times10^3$) showed that even in the best conditions partial polymerisation occurred. In fact, theoretical and analogy considerations\textsuperscript{17} suggest that the extinction coefficient of a pure monoarylalkylcarbonium ion in the 315 m\textmu{} region should be at least $10^4$.

3.1.2.3 Recovery experiments. After measuring the u.v. spectrum of styrene or 1-phenylethanol solutions in $\text{H}_2\text{SO}_4$, at time intervals from 5 sec. to 1 hr. after mixing, and in consecutive experiments, the reaction products were recovered by adding the reaction mixture into an excess of ice-cold aqueous NaOH, using rapid dispersal techniques\textsuperscript{14} (Section 2.2.9) and extracting the aqueous solutions with $\text{CCl}_4$, $\text{CS}_2$, or hexane.

The u.v. and i.r. spectra of the extracts showed the presence of a mixture of unsaturated oligomers (293 m\textmu{} u.v. absorption) and of oligomers with indanyl end-groups (273 m\textmu{} u.v. and 6.8\textmu{} i.r. absorption), as shown in Fig. 9.
Two typical spectra of styrene in 98% H₂SO₄.

The "clean" spectrum (315 m\(\mu\) peak) was from styrene solutions prepared at 0° and by fast dispersal techniques, or by vacuum distillation. The "dirty" spectrum was given by styrene solutions prepared at 22°, with slow stirring.

A) Infrared spectrum showing the presence of indane end groups (1470 cm\(^{-1}\) peak) in the products recovered (after killing the ions) from protonated styrene.

B) U.v. spectrum showing the presence of unsaturated (293 m\(\mu\) ) and saturated (273 m\(\mu\) ) end groups in the recovered products.
Fig. 8

10^{-4} M Styrene
98% H_2SO_4

"clean" ---
"dirty" ---

Fig. 9

indane peak
6.8 \mu (1470 \text{ cm}^{-1})
Gas chromatography of the extracts showed that no detectable amounts of styrene or of 1-phenylethylene were recovered. This agrees with the recent finding that the 1-phenylethyl cation cannot be formed even in $\text{SO}_2 \cdot \text{SbF}_5 \cdot \text{FSO}_3 \cdot \text{H}$ at $-60^\circ$, but this point was not known when I started this work. In similar experiments with $\alpha$-methylstyrene (Section 3.4.2) up to 5% of the original olefin was recovered.

The g.l.c. of the extracts revealed only three components: 1,3-diphenylbut-1-ene(VIII), 1-methyl-3-phenylindane (IX), and unknown (U) in order of increasing retention time; VIII being the linear, unsaturated dimer, and IX the cyclic, saturated dimer of styrene. The first and second fractions were identified by the retention time of authentic specimens, and in the same way it was later ascertained that U could consist of one or more of the following: 1,3-diphenylbut-2-ene, 1-methyl-3-phenylindene, and 1,1-diphenylbut-1-ene.

A quantitative comparison of the gas chromatographic results (peak area) with the u.v. spectra (optical density D) of the extracts showed that these must have contained appreciable quantities of non-volatilisable oligomers.

But the most striking feature revealed by this comparison was that the ratio of VIII to IX in the recovered product was the larger, the higher the 315 m\(\mu\) peak had been in the sulphuric acid solution. In runs in which the 315 m\(\mu\) peak was hardly detectable and the 430 m\(\mu\) peak very large, no unsaturated dimer (VIII) was recovered at all. This finding suggests strongly that the 1,3-diphenyl-n-butyl cation
could well be the species responsible for the alleged styryl cation spectrum.

To substantiate this hypothesis, the linear and cyclic dimers of styrene were prepared (sections 2.1.4.7 and 2.1.5.1) and their interaction with conc. sulphuric acid investigated, as described in the following section.

Note: All reactions in concentrated $H_2SO_4$ were very fast (the peaks reached their maximum absorption by the time the first spectrum was scanned) and accordingly no kinetic information was obtained for the $H_2SO_4$ systems. Kinetic measurements were possible with the $HClO_4/CH_2Cl_2$ system, in which the reactions were much slower, and they will be discussed in the appropriate sections of this thesis.
3.1.3 Interaction of 1,3-diphenylbut-1-ene and 1-methyl-3-phenylindane with concentrated sulphuric acid.

3.1.3.1 1,3-Diphenylbut-1-ene and 98\% sulphuric acid. The experimental conditions were as described for styrene, in Sec. 3.1.2.1.

With this compound it was impossible to obtain perfectly clean reactions; even in the best conditions considerable oligomerisation and cyclisation occurred, with subsequent ionisation of the cyclic end groups (as further investigated in Section 3.1.3.2).

The u.v. spectrum (Fig. 10 A) is very similar to that obtained with styrene solutions (Fig. 8) and exhibits a peak at 314-315 m\(\mu\), and another one, broad and variable in shape, intensity and position, at around 420-440 m\(\mu\). In clean conditions (rather low extent of cyclisation) the first is larger than the second. As with styrene, the low extinction coefficient of the 315 m\(\mu\) peak (about 10\(^3\)) showed extensive polymerisation. The amount of unsaturated dimer recovered (g. l.o.) was the larger, the higher the 315 m\(\mu\) peak had been in H\(_2\)SO\(_4\).

Any attempt to protonate 1,3-diphenylbut-1-ene in high enough concentration (1 to 10\%) for n.m.r. spectroscopy purposes yielded only polymers (in H\(_2\)SO\(_4\) and in HSO\(_3\)Cl).

3.1.3.2 1-Methyl-3-phenylindane and 98\% H\(_2\)SO\(_4\). Solutions of the cyclic dimer of styrene in H\(_2\)SO\(_4\) (same procedure as for styrene) exhibit the clean and reproducible u.v. spectrum shown in Fig. 10 B, with two main peaks at 304 and 415 m\(\mu\), and two shoulders at 290 and
315 μ. The apparent extinction coefficient of these peaks increase with increasing dilution, to reach the approximate limiting values of $\varepsilon_{304} = 5.3 \times 10^3$ and $\varepsilon_{415} = 1.5 \times 10^4$, based on concentration of 1-methyl-3-phenylindane; (apparent extinction coefficient, i.e. obtained by dividing the optical density $D$ of the ionic species by the molar concentration of the precursor - styrene, cyclic dimer, etc.; "apparent", because nothing is known about the extent of conversion).

Again, as with styrene and 1,3-diphenylbut-1-ene, increasing concentration reduced the relative absorption of the 304 and 415 μ peaks, and raised the polymer absorption around 270 μ. Spectra after dilution of the $H_2SO_4$ solution in excess alkali showed that only the latter absorption persisted, unaltered, (the 304 and 415 μ peaks desappeared completely) and demonstrated that no stable poly-styryl cations were formed by rearrangement and polymerisation reactions.

Although superficially similar to the spectra of styrene and its unsaturated dimer in $H_2SO_4$ solution, the spectrum of 1-methyl-3-phenylindane in $H_2SO_4$ shows many specific characteristics which show that it must belong to different species:

a) The high wavelength peak always has the higher intensity, whatever the experimental conditions, with a ratio $\varepsilon_{415}/\varepsilon_{304}$ of the order of 2.5.

b) The two peaks are reproducible in position and shape; this excludes the possibility of variable side reactions, which
normally occur with styrene and its linear dimer.
c) The spectrum remains stable for weeks, while with styrene
and its linear (unsaturated) dimer it changes within a few
days (the 315 m\(\mu\) peak shifts to 310 m\(\mu\)).
d) It is identical to the spectrum which styrene exhibits in
\(\text{HClO}_4/\text{CH}_2\text{Cl}_2\) solutions (considering a bathochromic shift of
about 400 cm\(^{-1}\) of all peaks in the latter system), as shown
in Fig. 11.

Moreover, recovery experiments carried out as for styrene
(Section 3.1.2.3), yielded extracts in which u.v. spectroscopy did
not reveal any measurable amount of 1,3-diphenylbut-1-ene.

In all experiments with conc. \(\text{H}_2\text{SO}_4\), the ionisation was
complete in less than 15 sec.
Fig. 10 A (page 61)

Spectrum of a solution of unsaturated dimer of styrene in 98% H₂SO₄, prepared by vacuum distillation. Note the maximum at 315 μm, the same as exhibited by the "clean" styrene solutions, in Fig. 8.

Fig. 10 B (page 61)

Spectrum of the cyclic dimer of styrene in 98% H₂SO₄ solution.

Fig. 11 (page 63)

Comparison of the spectrum of styrene in HClO₄ (in high excess)/CH₂Cl₂ solution, λ_max 308 and 420 μm, and of its cyclic dimer, in 98% H₂SO₄ solution, λ_max 304 and 415 μm.)
Fig. 10A

1,3-diphenylbut-1-ene $10^{-4}$ M
98% H$_2$SO$_4$

Fig. 10B

1-methyl-3-phenylindane ($2 \times 10^{-5}$ M) in 98% H$_2$SO$_4$

Fig. 11

Styrene ($6 \times 10^{-5}$ M) in HClO$_4$/CH$_2$Cl$_2$

(2 $\times 10^{-5}$ M) 1-methyl-3-phenylindane in 98% H$_2$SO$_4$
3.1.4 Discussion.

The above results concerning the interaction of styrene and its dimers with concentrated sulphuric acid are of importance for the elucidation of the nature of the chain carriers in polymerisations of styrene catalysed by strong acids. They show that the 1-phenylethyl cation cannot be formed in any detectable amount even in these very favourable conditions, and invalidate any previous assignments of the spectra of styrene in \( \text{H}_2\text{SO}_4 \) to this cation.

The alleged 1-phenylethyl spectrum can only, and at the best, be attributed to the 1,3-diphenyl-n-butyl cation and its oligostyryl homologues, and only as far as the low wavelength absorption is considered. This is consistent with the recent demonstration\(^{12,18}\) (by n.m.r. and u.v. spectroscopy) that monophenylalkylcarbonium ions of very similar structure, such as the 2-phenylprop-2-yl and the 2-phenylbut-2-yl cations, exhibit the major absorption at around 320 m\(\mu\). The polystyryl anion absorbs\(^{19}\) at 340 m\(\mu\), and it is well established that wavelength positions and absorption intensities of arylalkyl anion and cation do not differ widely\(^{20}\).

The question remaining open at this point is which are the species responsible for the absorption in the 430 m\(\mu\) region? Experimental evidence shows that diphenylcarbonium ions absorb strongly in this region.\(^{12}\) Extensive rearrangement reactions
leading to such cations could plausibly account for the absorption around 430 m\(\mu\). This hypothesis is confirmed by my experimental investigations, which are fully described and discussed in further sections of this thesis (3.6.1 - 3.6.6).

Another important fact, as independently found by Bywater and Worsfold,\(^{11}\) is the interaction of the cyclic dimer 1-methyl-3-phenylindane with concentrated H\(_2\)SO\(_4\). We have seen (Section 3.1.3.2) that sulphuric acid solutions of this compound exhibit the u.v. spectrum of styrene in HClO\(_4\)/CH\(_2\)Cl\(_2\), which was believed\(^1\) to belong to the 1-phenylethyl cation. Unless improbable rearrangement reactions of 1-methyl-3-phenylindane to species very similar to the 1-phenylethyl cation (or rather its higher homologues, since it has been proven that the latter cation is not stable) can be demonstrated, it becomes fairly clear that what happens must be the other way round, i.e., in media of low dielectric constant and low acidity (HClO\(_4\)/CH\(_2\)Cl\(_2\) system) styrene may follow reactions paths which lead, directly or indirectly, to species identical or very similar to those obtained from the cyclic dimer.

Clearly, the above considerations are at this point only plausible speculations, and more experimental work is required to come to a conclusion. Further sections of this thesis will show that they were well founded (3.2.1 - 3.2.7).
3.2 Interaction of styrene and related compounds with anhydrous perchloric acid in methylene dichloride.

3.2.1 Introduction.

The system styrene (or related compounds) - anhydrous perchloric acid - methylene dichloride was considered for the following reasons:

a) Although this system has been extensively studied and reported, both under polymerisation and under protonation conditions, there was no agreement on the interpretation of the experimental results nor on their mechanistic implications (as discussed in Sec. 3.1.1 of this thesis), and apparently more experimental work was needed.

b) The reactions in this system are comparatively slow (minutes, as compared to seconds in the conc. H_2SO_4 systems) and useful kinetic information may be gained.

c) The system is clean, all work being performed under high vacuum conditions, and any practical range of acid concentration may be used.

d) Electrical conductivity measurements are possible, and thus more experimental data are made available.

e) The recovery experiments are simplified by the fact that no extraction is required after the killing of the carbonium ions.
My principal aim in the investigation of this system was the study of the interaction of styrene with a high excess of HClO₄, in so-called "protonation" conditions. We shall see farther that the term protonation cannot be properly used here, its conventional meaning implying the direct addition of a proton to a nucleophilic reagent. What occurs in our case being a long series oligomerisation, cyclisation, and rearrangement reactions, followed by ionisation yielding carbonium ions, possibly via a hydride ion abstraction mechanism, the expressions interaction and ionisation will be used in place of protonation.

All the headings "Interaction with HClO₄" in the following sections mean interaction with anhydrous acid in methylene dichloride, using high vacuum techniques.
3.2.2 Procedure.

U.v. spectroscopic runs were made under high vacuum conditions with the devices described in Section 2.2.1.1 of this thesis. Conductivity runs under high vacuum were performed with the conductivity cells I and II, and simultaneous spectroscopic and conductimetric experiments under high vacuum were made possible by using cell III.

The reactions were carried out either at $25^\circ$ or at $2^\circ$, as specified. Dosing of solvents and reagents under high vacuum was performed as described in Sec. 2.2.7, and the concentration of styrene was further controlled by measuring the intensity of its 291 m$\mu$ peak. The background absorption and conductivity due to HClO$_4$ were determined in preliminary runs and subsequently subtracted.

Killing of the carbonium ions was done by pouring the CH$_2$Cl$_2$ phase through a capillary into a rapidly stirred excess of aqueous sodium hydroxide, extracting by the same operation the undesired NaClO$_4$. The subsequently dried (over K$_2$CO$_3$) methylene dichloride phase was then analysed by u.v. spectroscopy and g.l.c. In order to make sure that no HClO$_4$ remained in the CH$_2$Cl$_2$ phase (which could result in a subsequent polymerisation of the extracts), styrene and 1-phenylethanol solutions were prepared in CH$_2$Cl$_2$ from which previously dissolved HClO$_4$ was extracted using this technique. G.l.c. revealed that both compounds remained unaltered.
3.2.3 Interaction of styrene with a large excess of HClO₄.

3.2.3.1 Spectroscopy. The best working conditions were attained with a 100 to 500 fold excess of acid with respect to the styrene concentration; less acid tended to decrease the yield of protonated species, more acid made the reactions too irreproducible.

The absorption maxima in the resulting spectrum were located in a few preliminary runs at 308 ± 1 mμ and 420 ± 2 mμ. A very variable absorption in the 270 mμ region was at first attributed to products from side reactions, of non-carbonium ion origin (they remained unaltered after addition of excess alkali or ethanol). I found later that this absorption was due to oligomers with indanyl end-groups, which take a most essential part in the ionisation reaction; actually, the carbonium ion studied cannot be formed without these alleged side-products. I have to say with some regret that most of my preliminary experiments were made trying hard to get "clean" reactions in which these "impurities" do not appear.

In an attempt to duplicate Gandinis' experiments,¹ I decided to measure the rate of reaction by scanning at 308 mμ against time. To my surprise, the analysis of the reaction traces, in two consecutive experiments at room temperature (PRV7-8St), gave second order plots (equal starting concentrations) up to 60-70% conversion. This was at variance with Gandinis' work,¹ who found first order plots scanning the increase of the 420 mμ peak.
I then performed two more reactions at room temperature (PRV10-11St) in which the increase of the 420 m\(\mu\) peak was scanned against time, and again found second order plots up to 60-70\% conversion (Table II). Fairly acceptable first order plots were obtained for the final 30-40\% portions of the 420 m\(\mu\) traces with first order rate constants of 2.65 \(\times\) 10\(^{-3}\) and 5.78 \(\times\) 10\(^{-3}\) sec\(^{-1}\) (computed from half-lives), as compared to 9.7 \(\times\) 10\(^{-3}\) and 8.7 \(\times\) 10\(^{-3}\) sec\(^{-1}\) in analogous runs performed by Gandini.\(^1\)

Fig. 12 A shows the first and second order plots of a typical spectroscopic run (PRV11St) in which the increase of the 420 m\(\mu\) peak was recorded. The experimental conditions were: temperature 25\(^{\circ}\); concentration of styrene 1.19 \(\times\) 10\(^{-4}\) M, concentration of HClO\(_4\) 8.35 \(\times\) 10\(^{-3}\) M. The second order plot gives a straight line; the first order plot gives a curve concave to the time axis; the third order plot (not shown here) gives a convex curve. Clearly, the second order plot is the most appropriate. More than 10 separate spectroscopic and conductimetric runs were plotted as above, and always only the second order plot gave a straight line, up to 50-70\% conversion.

The following integrated expressions\(^6\)\(^2\) were used for the characterisation of the reaction order of the spectroscopic and conductimetric experiments. The second and third order rate equations apply to the simplified case of equal starting concentrations, i.e., either two reagents of the same concentration, or one reagent
I. A typical reaction curve: \( D_{420} \) as a function of time, for styrene interacting with a high excess of HClO\(_4\).

II. First and second order (equal starting concentrations) plots.
PR V11 St

420 m\(\mu\) peak

\(D_f = 0.20\)

Fig. 12 A
reacting with itself:

First order: \( k_1 = \frac{2.303}{t} \log_{10} \frac{X_f}{X_f - X_t} \) sec. \(^{-1} \)

Second order: \( k_2 = \frac{1}{t} \left[ \frac{1}{X_f - X_t} - \frac{1}{X_f - X_0} \right] \)

Third order: \( k_3 = \frac{1}{2t} \left[ \frac{1}{(X_f - X_t)^2} - \frac{1}{(X_f - X_0)^2} \right] \)

\( X \) is alternatively the optical density \( D \), the specific conductivity \( \kappa \), or the ionic concentration \( x \).

\( X_0 \) = values at beginning of reaction,

\( X_t \) = values at time \( t \),

\( X_f \) = values at the end of reaction \((100\% \ conversion)\).

The concentration of ions, \( x \), can be expressed either in terms of their extinction coefficients \( \varepsilon_{308} \) and \( \varepsilon_{430} \) and of the corresponding observed optical density \( D \) :

\[
x = \frac{D_{308}}{\varepsilon_{308}} = \frac{D_{420}}{\varepsilon_{420}}
\]

or in terms of the equivalent conductivity \( \Lambda_0 \) and of the observed specific conductivity \( \kappa \) :

\[
x = \frac{1000 \kappa}{\Lambda_0}
\]

The use of the last two relations requires a knowledge of \( \varepsilon_{308} \), \( \varepsilon_{420} \), and \( \Lambda_0 \), which cannot be deduced from the initial
concentration of styrene, because the ionisation is never quantitative since variable amounts of polymer are formed even in the best conditions. These parameters were eventually determined from pure ions, formed quantitatively directly from their precursors (Sec. 3.6.3), and are: $\varepsilon_{308} = 12,000$, $\varepsilon_{420} = 35,000$, and $\Lambda_0 = 137$ (Mhos cm$^{-2}$ mole$^{-1}$).

All data relevant to the kinetic investigation of the interaction of styrene with a large excess of HClO$_4$ are displayed in Table 2.

The second order rate constants found for the spectroscopic runs described above (carried out at 25$^\circ$) show an excellent agreement between PRV10St and PRV11St, both runs concerned with the 420 m$\mu$ peak increase, where $k_2$ was respectively 1,100 and 1,090 lit. mole$^{-1}$ sec.$^{-1}$. When the increase of the 308 m$\mu$ peak is considered (PRV7St and PRV8St), the second order rate constants are found to be respectively 1,500 and 300 lit. mole$^{-1}$ sec.$^{-1}$, quite in disagreement apparently, and showing a bad reproducibility. However, if the arithmetic mean of the last two values $(1,500 + 300)/2 = 900$ is taken, a much better agreement with the rate constants for the 420 m$\mu$ runs (1,100 and 1,090) is found.

Although the values of the second order rate constants found for the spectroscopic runs above appear to be of similar order of magnitude, they show that the reaction investigated is poorly reproducible, as confirmed by the variable magnitude of the final
Table 2.
(ref. page 72)

<table>
<thead>
<tr>
<th>PRVSt</th>
<th>Temp.</th>
<th>$10^4[St_.]$</th>
<th>$10^2[HC10_4]$</th>
<th>$[HC10_4]_{o}/[St.]$</th>
<th>$10^6[ions]_f$</th>
<th>$k_2(420)$</th>
<th>$k_2(308)$</th>
<th>$k_2(K)$</th>
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<tr>
<td>7</td>
<td>25°</td>
<td>1.9</td>
<td>1.34</td>
<td>70</td>
<td>9.6</td>
<td>1,500</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>25°</td>
<td>1.08</td>
<td>1.87</td>
<td>173</td>
<td>15.8</td>
<td>300</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>25°</td>
<td>1.59</td>
<td>1.57</td>
<td>100</td>
<td>8.45</td>
<td>1,100</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>25°</td>
<td>1.19</td>
<td>0.835</td>
<td>70</td>
<td>5.7</td>
<td>1,090</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>25°</td>
<td>0.272</td>
<td>0.12</td>
<td>44</td>
<td>2.59</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>25°</td>
<td>0.934</td>
<td>1.06</td>
<td>114</td>
<td>11.6</td>
<td>288</td>
<td>224</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>8°</td>
<td>1.09</td>
<td>1.2</td>
<td>110</td>
<td>10.1</td>
<td>132</td>
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<tr>
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<td>4°</td>
<td>0.615</td>
<td>1.54</td>
<td>250</td>
<td>8.9</td>
<td>153</td>
<td>154</td>
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</tr>
<tr>
<td>22</td>
<td>2°</td>
<td>1.36</td>
<td>2.05</td>
<td>150</td>
<td>20.5</td>
<td>117</td>
<td>194</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>2°</td>
<td>0.97</td>
<td>1.5</td>
<td>155</td>
<td>16.9</td>
<td>220</td>
<td>170</td>
<td></td>
</tr>
<tr>
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<td>2°</td>
<td>0.88</td>
<td>2.24</td>
<td>255</td>
<td>16.5</td>
<td>183</td>
<td>203</td>
<td></td>
</tr>
</tbody>
</table>

All concentrations are in moles per litre

The dimensions of the second order rate constants $k_2$ are lit. mole^{-1} sec^{-1}
apparent extinction coefficients, which are: 605 and 1,760 for the 308 µm peak (PRV7St and PRV8St respectively), and 1,860 and 1,680 for the 420 µm peak (PRV10St and PRV11St respectively). Again, the reproducibility appears to be better for the 420 µm peak than for the 308 µm peak. This can in part be accounted for by the fact that the optical density in the 420 µm region can be measured with a higher accuracy than the optical density in the 308 µm region, where a variable background absorption is observed (due to polymer formation and to the HClO₄ absorption).

As no adequate information appeared to be obtainable from separate optical experiments, I decided to build the device described in Section 2.2.2.1, with which simultaneous conductivity and spectroscopic measurements could be made. The conductivity was recorded, and the increase of the 308 and 420 µm peaks was plotted point by point by continually changing the wavelength setting of the spectrophotometer.

The results by these simultaneous measurement are discussed in the following section.

3.2.3.2 Conductivity and simultaneous conductivity and spectroscopic measurements. Electrical conductivity measurement of $10^{-5}$ to $10^{-4}$ M styrene solutions in methylene dichloride interacting with a high excess of perchloric acid ($10^{-3}$ to $10^{-2}$ M) were carried out at temperatures ranging from $+25^\circ$ to $-61^\circ$. Simultaneous conductivity
and spectroscopic measurement were made in similar conditions, but only between 25° and 2°. The results showed that:

a) The specific conductivity gave second order plots, with approximately the same rate constant as for the absorbance increase (Fig. 12 B and PRV18, 19, 21-24St in Table 2). Moreover, the conductivity reached its maximum in the same time as the absorbance.

b) Clean and more complete reactions were obtained at 2° than at 25°, as shown by the higher values attained by $\Lambda'_M$ and $\varepsilon'$ (apparent molar conductivity and extinction coefficient) at the lower temperature:

25° (PRV18St) : $\varepsilon'_{308} = 1,500$; $\Lambda'_M = 16.9$ Mhos cm.² mole⁻¹

2° (PRV23St) : $\varepsilon'_{308} = 2,600$; $\Lambda'_M = 23.7$ " " "

(the concentrations of styrene and HClO₄ are shown in Table II).

c) In the cleanest runs, made at 2°, the conductivity, the 308 μ peak, and the 420 μ peak increased at very nearly the same rate. Thus, for instance, in PRV23St ([styrene] = 9.7 x 10⁻⁵ M, [HClO₄] = 1.5 x 10⁻² M) the second order rate constants for the increase of the 308 and 420 μ peaks, and the conductivity were respectively 220, 170, and 175 lit. mole⁻¹ sec⁻¹

d) After the mixing of the reagents, there was an induction period, during which the specific conductivity was zero within the range of experimental error (Fig. 13), after
Second order plots (equal initial conc.) of reaction curves representing the increase of the 308 and 420 m\(\mu\) peaks, and of the conductivity, measured simultaneously. (Interaction of styrene with high excess of HC1O\(_4\), at 2\(^\circ\)).

The arrows show 50% increase of optical density or specific conductivity.
$D \uparrow = 50\%$ increase

$\mu Mhos$

0.4
0.3
0.2
0.1

$D_{420}$

$D_{308}$

PR V23St

0

0.1

0.5

1

1.5

2

Fig. 12 B

time (min.)

$K$

$10^{-4}(1 - \frac{x_f - x_0}{x_f - x_t})$

lit. mole$^{-1}$ sec$^{-1}$

0

4

8

12

16

20

0

2

4

6

8

10

12

time (min.)

$K$

$D_{308}$

$D_{420}$
subtraction of the solvent and $\text{HClO}_4$ conductivities, which are both low. This induction period increased when the styrene concentration and the temperature were lowered, and was about 3 sec. when $5.45 \times 10^{-5}$M styrene interacted with $5.6 \times 10^{-3}$M $\text{HClO}_4$ at $17^\circ$, and about 100 sec. with $5.45 \times 10^{-5}$M styrene and $7 \times 10^{-3}$M $\text{HClO}_4$ at $-61^\circ$.

3.2.3.3 Recovery experiments. At time intervals from 10 sec. to 1 hr. after the mixing I recovered the reaction products, as described in Sec. 3.2.2, and analysed them by u.v. spectroscopy and g.l.c. The results can be summarized as follows:

a) Styrene (or 1-phenylethanol) was never recovered.

b) In the early stages of the reaction a very small amount of 1,3-diphenylbut-1-ene was recovered.

c) Cyclic dimer was recovered in amounts which decreased as the reaction proceeded further; at the end of a reaction, when absorbance and conductivity had reached the maximum value, no saturated dimer was recovered at all.

d) Two unknown compounds were recovered in similar amounts, which increased as the reaction proceeded. The first of these compounds was later tentatively identified by g.l.c. as 1-methyl-3-phenylindene (same retention time, same peak shape); the second, unidentified but probably a saturated compound (u.v. spectroscopy and retention time on the g.l.c.), could
be 1,3-diphenylbutane.

e) A quantitative comparison of the gas-chromatographic results with the u.v. spectra of the extracts showed that these contained variable amounts of non volatilisable oligomers. Thus, the concentration of cyclic dimer in the extract (cyclohexane) of a particular run (VB34B) was $2.8 \times 10^{-4}$ M as computed from $D_{273}$ and $E_{273}$, and about $10^{-4}$ M, when determined by g.l.c.

Table 3 shows the variation of recovered product distribution with increasing reaction time. Styrene (or 1-phenylethanol) = VII, unsaturated dimer = VIII, saturated dimer = IX, 1-methyl-3-phenyl-indene = XXIII, unknown = U:

<table>
<thead>
<tr>
<th>time</th>
<th>VII</th>
<th>VIII</th>
<th>IX</th>
<th>XXIII</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 sec.</td>
<td>0</td>
<td>+</td>
<td>+++</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>1 min.</td>
<td>0</td>
<td>0</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>5 min.</td>
<td>0</td>
<td>0</td>
<td>+</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>45 min.</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>+++</td>
<td>+++</td>
</tr>
</tbody>
</table>
3.2.4 Interaction of styrene with equimolar or small excess of perchloric acid.

When $[\text{HClO}_4]$ was between ca. 1 and 10 times $[\text{C}_8\text{H}_8]$, the latter being in the range of $10^{-4} \text{M}$, the following pattern of reactions was observed, as determined by u.v. spectroscopy, electrical conductivity and analysis of recovered products:

a) Even with the lowest concentration of $\text{HClO}_4$ (equimolar) styrene dimerised to 1,3-diphenylbut-1-ene in a matter of seconds. The unsaturated dimer formed in the first step cyclised very rapidly to 1-methyl-3-phenylindane. No reliable kinetic information was obtained for the second step, considering its high rate and its simultaneity with the first step; nevertheless the spectroscopic data suggested that the second reaction (cyclisation) was rather slower than the first (dimerisation).

b) At the end of the reaction sequence (as shown in Fig. 14 A) the cyclic dimer is formed quantitatively (molar extinction coefficient of the 273 $\text{m} \mu$ peak: found 1,270, expected 1,250), and remained stable for 24 hr. even in presence of tenfold excess of $\text{HClO}_4$.

c) No ions appeared at any stage of the reaction, as shown by the absence of peaks above 300 $\text{m} \mu$ and by the absence of conductivity increase. This does not exclude the possibility that carbonium ions existed in too low concentration to be detected.
d) At the end of the reactions a very weak absorption band developed near 400 μm. The concentration of the species responsible for this absorption was certainly less than $10^{-6}$ M (assuming an extinction coefficient of $10^4$).

e) When more acid was added, or when the initial excess of HClO$_4$ was larger than about 10, ions were formed, the rate of increase of $D_{308}$, $D_{420}$, and $K_C$ (specific conductivity) being identical; the final spectrum had the usual two peaks at 308 and 420 μm. Fig. 14 B shows u.v. spectra at successive stages of the ionisation of the cyclic dimer.

f) Recovery experiments at successive times after the mixing of the reagents confirmed the spectroscopic findings (summarized in table 4): styrene reacting too quickly, was never recovered; unsaturated dimer was recovered in the early stages of the reactions; pure cyclic dimer was recovered at the end of the reactions.

g) In a run in which $7.3 \times 10^{-4}$M styrene reacted with $2.2 \times 10^{-2}$M HClO$_4$ (30/1 excess), a fast cyclisation occurred, and subsequently about 20% of the resulting cyclic dimer ionised.

<table>
<thead>
<tr>
<th>time</th>
<th>styrene</th>
<th>unsat. dimer</th>
<th>sat. dimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 sec.</td>
<td>0</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>1 min.</td>
<td>0</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>30 min.</td>
<td>0</td>
<td>0</td>
<td>+++++++++</td>
</tr>
</tbody>
</table>
Typical conductivity record, showing the induction period.

Interaction of styrene with a small excess of HClO₄, u.v. spectra at different time intervals (styrene 1.67 x 10⁻⁴ M, HClO₄ 7.15 x 10⁻⁴ M, temperature 2°C).

(a) Styrene before reaction.

(b) 1 min. after the mixing; note the smearing out of the 282 mµ peak, and the shift of the 291 mµ peak to 293 mµ. This spectrum is characteristic of 1,3-diphenylbut-1-ene containing some cyclic dimer (273 mµ shoulder).

(c) After 5 min., the cyclic dimer peak, at 273 mµ, becomes prominent; the unsaturated dimer peak, at 293 mµ, is very shallow.

(d) After about one hour, the spectrum of pure cyclic dimer is formed; note the complete disappearance of the unsaturated dimer peak, at 293 mµ.

U.v. spectra showing the interaction of 1-methyl-3-phenylindane (1.1 x 10⁻⁴ M) with HClO₄ (1.8 x 10⁻² M) at 2°C.

(a) Before reaction, spectrum of pure cyclic dimer.

(b) 1 min. after mixing; appearance of 308 mµ peak.

(c) After 5 min. (d) After 1 hr.; complete disappearance of the cyclic dimer spectrum, replaced by the usual peak at 308 mµ and the shoulder at about 290 mµ.
\[ K (\text{\textmu }\text{Mho}) \]

\[
[\text{Styrene}] = 5.45 \times 10^{-5} \text{ M}
\]

\[
[\text{HClO}_4] = 5.5 \times 10^{-3} \text{ M}
\]

Temp. = 17°C

---

Fig. 13

---

\[ D \]

\[ \lambda (\text{m\mu}) \]

---

Fig. 14 A

---

\[ D \]

\[ \lambda (\text{m\mu}) \]

---

Fig. 14 B
3.2.5 Interaction of an excess of styrene with perchloric acid.

The interaction of styrene with anhydrous perchloric acid in methylene dichloride solution under polymerisation conditions (large excess of styrene) was investigated in this work with a dual purpose: a) to attempt to trace any ionic species which may have escaped the observation of previous researchers; b) to observe the reaction sequence leading to polystyrene and finally to the ionic species appearing at the end of the polymerisation.

a) Styrene, $10^{-3}$ to 2.5 M, was polymerised at 20 using $10^{-5}$ to $5 \times 10^{-3}$ M HClO$_4$, and the whole spectrum was repeatedly examined, from 600 m$\mu$ down to the styrene cut-off (300 to 310 m$\mu$, according to the concentration). No absorption band was observed in this region (four experiments) during the polymerisation, the lowest detection limit being in the range of $10^{-6}$ M of ionic species, assuming an extinction coefficient of $5 \times 10^3$ for these. The usual spectrum with maxima at 308 and 420 m$\mu$ appeared as expected only at the end of the polymerisation, and at this moment only the solution turned yellow.

When at the end of the first polymerisation more styrene was added, the yellow colour (and associated spectrum) disappeared immediately and a second polymerisation proceeded. A very careful examination of the spectrum during the second polymerisation revealed (in all the three runs made in these conditions) the
appearance of a very shallow band at 377 m$\mu \pm 2$ m$\mu$. Assuming an extinction coefficient of $10^4$, the concentration of the species related to this absorption should have been of the order of $2 \times 10^{-6}$ M.

As the kinetic pattern for both first and second polymerisations is the same (in agreement with Gandini and Plesch's results$^{13}$), the species responsible for this new absorption do not seem to take any measurable part in the reaction, and might be generated by rearrangement reactions of the ionic species appearing at the end of the first polymerisation.

b) When the spectrum of polymerising styrene was observed in the region of 240 to 300 m$\mu$, it was seen that as styrene was consumed, its sharp absorption peaks at 282 and 291 m$\mu$ decreased and were replaced by a single sharp peak at 293 m$\mu$, showing the formation of styrene oligomers with unsaturated end groups.

When all styrene had reacted, as shown by the disappearance of its major absorption at 249 m$\mu$ ($\varepsilon 15,500$), the unsaturated end group peak (293 m$\mu$) started decreasing, and the spectrum of low molecular weight polystyrene with indane end groups (characteristic peak at 273 m$\mu$) built up.

The spectrum with 308 and 420 m$\mu$ peaks (yellow colour) appeared only at the end of the reaction sequence, when the indane end groups started to be formed.

Results under b) agree with the independent and simultaneous findings by Bywater and Worsfold.$^{11}$
3.2.6 Interaction of the saturated and unsaturated dimers
of styrene with perchloric acid.

3.2.6.1 1-Methyl-3-phenylindane. The cyclic dimer was made to
react in $10^{-5}$ to $10^{-3}$ M solution in CH$_2$Cl$_2$ with an excess (100 to
500 fold) of HClO$_4$, and yielded ionic species exhibiting the same
spectrum as styrene under similar conditions (308 and 420 m$_\mu$ peaks).

In a reaction performed at $2^\circ$, with $5 \times 10^{-5}$ M cyclic dimer
and $2 \times 10^{-2}$ M HClO$_4$, it was possible to follow the increase of the
420 m$_\mu$ peak, starting 30 sec. after the mixing and up to the virtual
completion of the reaction, in about 1 hr, where the absorbance
reached the final value of 0.310, giving $\varepsilon'_{420} = 6,200$. The absorbance
increase gave a good second order plot up to at least 60% conversion
(Fig. 15). The second order rate constant computed on the basis of
the ionic concentration deduced from $\varepsilon$ (Section 3.2.3.1) was
126 lit. mole$^{-1}$ sec.$^{-1}$

In similar experiments, the cyclic dimer ($6.9 \times 10^{-5}$M) prepa-
red in-situ by interaction of styrene with a small excess of HClO$_4$
(Sec. 3.2.4) was subsequently treated with a 260 fold excess of
HClO$_4$ ($1.8 \times 10^{-2}$M), at $2^\circ$, and the increase of the 308 m$_\mu$ peak
recorded. The absorbance increase gave again a second order plot
up to at least 65% conversion; $k_2$ (computed as above) was
365 lit.mole$^{-1}$ sec.$^{-1}$ and $\varepsilon'_{308} = 5,300$. 
Kinetic analysis of the 420 m\(\mu\) peak increase during the interaction of 1-methyl-3-phenylindane (5 \(\times\) 10\(^{-5}\)M) with HClO\(_4\) (2 \(\times\) 10\(^{-2}\)M) at 2\(^{\circ}\).

The second order plot implies equal initial concentration.
Fig. 15

- First graph:
  - $D_{420}$ vs. time (min.)
  - $D_f = 0.310$
  - 420 μ peak
  - VB 110

- Second graph:
  - $\text{lit mole}^{-1}\text{sec}^{-1}$ vs. time (min.)
  - $10^{-4}(\frac{1}{x-x_f} - \frac{1}{1-x_f})$
  - VB 110
3.2.6.2 1,3-Diphenylbut-1-ene. Treated with a small excess of perchloric acid (1 to 10 fold) the unsaturated dimer cyclised quantitatively and the reaction stopped at the cyclic dimer.

When treated with a large excess of acid, the unsaturated dimer gave the same spectrum as styrene or the cyclic dimer in the same conditions (308 and 420 m\(\mu\) peaks, with \(D_{420}/D_{308}\approx 2.5\)).

In the cleanest runs, it was possible to see that the 308 and 420 m\(\mu\) peaks appeared only when the indane end groups started to be formed.

The acid catalysed cyclisation of the unsaturated dimer of styrene has been investigated by Barton and Pepper.\(^{22}\)
3.2.7 **Summary and discussion.**

The results described in sections 3.2.1 to 3.2.6 can be summarized as follows:

a) Methylene dichloride solutions of styrene (VII), 1,3-diphenylbut-1-ene (VIII), or 1-methyl-3-phenylindane (IX) exhibit, after interaction with a large excess of anhydrous perchloric acid, the same u.v. spectrum, with absorption maxima at 308 and 420 m\(\mu\), \(D_{420}/D_{308}\) being between 2 and 3. Moreover, these two peaks increase at very nearly the same rate.

The final apparent molar extinction coefficients (\(\varepsilon'\)) and conductivities (\(\Lambda'_M\)) are of same order of magnitude in all three systems (computed on the basis of dimer concentration), as shown in Table 5 by representative runs at 2\(^\circ\), with VII, VIII, and IX about \(10^{-4}\)M and HClO\(_4\) about \(2 \times 10^{-2}\)M:

<table>
<thead>
<tr>
<th></th>
<th>VII</th>
<th>VIII</th>
<th>IX</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{-3}\varepsilon'_{420})</td>
<td>13.1</td>
<td>14</td>
<td>14.9</td>
</tr>
<tr>
<td>(10^{-3}\varepsilon'_{308})</td>
<td>5.2</td>
<td>5.4</td>
<td>5.7</td>
</tr>
<tr>
<td>(\Lambda'_M)</td>
<td>51.5</td>
<td>52</td>
<td>49</td>
</tr>
</tbody>
</table>

b) With styrene, both under "protonation" and under polymerisation conditions, the ionic species appear only after the formation of cyclic (indane) end-groups.
As the formation of ions proceeds, the concentration of cyclic end groups decreases, to reach zero when the absorbance and conductivity have attained their maximum value (Fig. 14 B).

c) Absorbance and conductivity increase give second order plots, showing that the ionic species cannot be formed by direct protonation. 17,21

d) The second order rate constants are of similar magnitude in all three systems (308 m\(\mu\) peak, 420 m\(\mu\) peak, and conductivity increase), when expressed in ionic concentration (Sec. 3.2.3.1). This indicates that the rate controlling step is the ionisation of the cyclic dimer, and that therefore dimerisation and cyclisation are much faster.

I conclude that the 308 and 420 m\(\mu\) peaks cannot be attributed to the 1-phenylethyl cation (or to any linear oligostyryl cations). Every evidence shows moreover that these cations cannot be stable in any measurable amount in the systems studied here.

The identity of the spectra of styrene or its cyclic dimer ionised by HClO\(_4\), and of the cyclic dimer in H\(_2\)SO\(_4\) solution (Fig. 11) shows that in both cases the ionic species derive from the cyclic dimer, or from oligomers with cyclic end-groups.

When styrene or its unsaturated dimer interact with concentrated strong acids (such as H\(_2\)SO\(_4\) and HS\(_2\)O\(_3\)Cl) the resulting solutions have spectra with a prominent peak at 315 m\(\mu\), and variable absorption
in the 430 m\(\mu\) region (sections 3.1.2 and 3.1.3). I have shown, in agreement with suggestions in recent publications\textsuperscript{9–11} that only the low wavelength peak can be attributed to linear oligostyryl cations. Bywater and Worsfold\textsuperscript{11} demonstrated that when the medium, in which the spectrum derived from styrene was formed, is made less acidic by diluting the sulphuric acid to 1–10\% with trifluoroacetic acid, the final absorption is found to be similar to the spectrum obtained when styrene reacts with a high excess of perchloric acid in methylene dichloride solution (308 and 420 m\(\mu\) peaks, with \(D_{420} > D_{308}\)).

It appears that in such weakly acidic systems, the linear oligostyryl cations cannot be stabilised, cyclisation occurs, and the cyclic end-groups are finally ionised.
3.3 Working hypotheses used in the identification of ions derived from styrene and from 1-methyl-3-phenylindane.

Having ascertained that the spectrum of styrene in weakly acidic solutions (absorption maxima at 308 and 420 m\(\mu\), with \(D_{420} > D_{308}\)) is due to ions formed from the indane end-groups formed as reaction intermediates, three important questions remained to be answered:

a) Which are these ions?
b) Which is the mechanism leading to their formation?
c) Which are the species responsible for the 430 m\(\mu\) region absorption, found when styrene reacts with concentrated strong acids?

To answer the first two questions, the following reaction routes were considered, bearing in mind that the strong absorption above 400 m\(\mu\) suggests the presence of cations of the diphenylmethyl type:

A) Opening of the indane ring with protonation in one or more of four possible ways (Fig. 16 A) which would give the ions X to XIII:

\[(X)\quad 1,1\text{-diphenyl-}n\text{-butyl}\]
\[(XI)\quad 1\text{-phenyl-}1\text{-}(2'\text{-ethylphenyl})\text{ethyl}\]
\[(XII)\quad 1\text{-phenyl-}(2'\text{-isopropylphenyl})\text{methyl}\]
\[(XIII)\quad 1\text{-methyl-}1,3\text{-diphenylpropyl}.\]
B) Hydride-ion abstraction from 1-methyl-3-phenylindane
to yield the 3-methyl-1-phenylindanyl cation (XIV), as
shown in Fig. 16 B.

A partial answer to the third question could be found in the
fact that the protonation of the unsaturated oligomers of styrene
is never quantitative, and even in the cleanest reaction some
cyclisation occurs, with subsequent ionisation of the indane end-
groups following routes A and B. Variable proportions of cations
X to XIV could explain possibly the drift of the absorption maximum
anywhere from 415 to 450 m\(\mu\), from one run to the next.

A further reaction path was considered, which was thought to
involve interaction (in the simplest case) between 1,3-diphenylbut-
l-ene, present as a transient species, and the 1,3-diphenyl-n-butyl
cation, to form a tertiary cation of the tribenzyl type, as shown
in Fig. 17.

Before attempting to investigate experimentally the hypotheses
discussed here, I considered that it would be sensible to compare the
behaviour of styrene and its dimers, with that of another apparently
similar system, \(\alpha\)-methylstyrene and its dimers. The cyclisation of
the unsaturated dimer of \(\alpha\)-methylstyrene catalysed by HClO\(_4\) has
already been investigated\(^{22}\) and was not considered any further here.
Reaction schemes for ionisation of 1-methyl-3-phenylindane

**A) Ring opening**

- $\text{X}$
- $\text{XI}$
- $\text{XII}$
- $\text{XIII}$

Fig. 16 A

**B) Hydride ion abstraction**

- $\text{CH}_3$
- $\text{XIV}$

Fig. 16 B
3.4 **Interaction of α-methylstyrene and related compounds with strong acids.**

3.4.1 **Introduction.**

My aim was to investigate as thoroughly as possible the interaction of the following compounds with dilute and concentrated strong acids: α-methylstyrene (XV), 2-phenylpropan-2-ol (XVI), 4-methyl-2,4-diphenylpent-1-ene (V), 2-phenyl-2-propyl acetate (XVII), and 1,1,3-trimethyl-3-phenylindane (XVIII).

The acids used were anhydrous perchloric acid in methylene dichloride solution, 98% sulphuric acid, chlorosulphonic acid and 30% SO₃ in sulphuric acid. The experimental procedure was as described for styrene (sections 3.1.2). All reactions were carried out at 0° and the spectra were measured at 2°, with 10⁻⁵ to 10⁻⁴ M solutions.

To facilitate the exposition of the experimental results, the same compound numbering as above will be used throughout the following sections.
3.4.2 Interaction with 98% sulphuric acid.

Compounds XV, XVI, and V gave, when dissolved in 98% H₂SO₄, the u.v. spectra shown in Fig. 18, with a major peak at 327 m\(\mu\) (± 1 m\(\mu\)) and a shallow one at around 380 m\(\mu\). The apparent molar extinction coefficients (\(\varepsilon'\)) increased as follows:

\[ \varepsilon'_{327} = 5,200 \text{ (XV), 7,200 (XVI), 8,600 (V)}. \]

All spectra were formed in less than 10 sec. after the mixing, and the absorption maxima decreased with a half-life of about 30 min. (for 2 x 10⁻⁵ M solutions) at 2⁰. In order to obtain the full spectra at zero time, the original values of D at several wavelengths were derived by the zero time extrapolation of Gold and Tye.²³

A few runs made with 100% H₂SO₄ gave identical results. Variable absorption in the 270 m\(\mu\) region showed that in all cases uncontrollable amounts of polymer (with cyclic end-groups) were formed.

The spectrum of the cations formed from XV and XVI showed exactly the same 327 m\(\mu\) peak as protonated V; the 380 m\(\mu\) region peaks were not considered, being too shallow and wide to allow any accurate wavelength determination.

Analysis of the products from recovery experiments, made at time intervals from 10 sec. to 1 hr. after the mixing, revealed mainly the presence of unsaturated and saturated dimers and oligomers (g.l.c. and u.v. spectroscopy). 1 to 5% of \(\alpha\)-methylstyrene was recovered from the H₂SO₄ solutions of XV and XVI, when the
neutralisation was made 30 sec. after the mixing.

The clear-cut conclusion is that in all cases the major ionic species formed are at least dimeric cations, together with variable amounts of polymeric cations. No more than 5% (if any) of monomeric 2-phenylprop-2-yl cation was formed in these conditions, in agreement with recent publications\textsuperscript{12,24} showing that this ion needs an acidity level of 30\% oleum to be stabilised.

"Note: Bywater and Worsfold\textsuperscript{11} report the following apparent molar extinction coefficients for solutions of compounds XV, XVI, and V in 96\% H\textsubscript{2}SO\textsubscript{4}: XV (10\textsuperscript{-3}M), \( E_{327} = 1,400 \); XVI (10\textsuperscript{-3}M), \( E_{327} = 800 \); V (2 \times 10\textsuperscript{-4}M), \( E_{327} = 1,900 \). And for compound V only (4 \times 10\textsuperscript{-4}M) in 30\% oleum, \( E_{327} = 700 \). In all runs, the acid was added to the neat precursor; the mode of stirring is not indicated; spectra were scanned at room temperature. The low extinction coefficients reported by these authors constitute a good illustration of the need to use low concentrations and fast dispersal techniques in order to increase the yield of carbonium ions (as discussed in Section 2.2.8.3 of this thesis)."

Compound XVIII (cyclic dimer) did not react with H\textsubscript{2}SO\textsubscript{4}. As the cyclic dimer of styrene reacts easily both with concentrated and dilute acids, it was sensible to assume that the reactive diphenyl substituted carbon atom in the cyclic dimer is blocked by the extra methyl in compound XVIII, as suggested by Bywater and
I shall show below (Sec. 3.6.7.2) that the real reason for the unreactivity of XVIII is the lack of hydrogen atoms on the diphenyl substituted carbon atom.

Mixed with HS$_3$Cl and 30% oleum, XVIII was sulphonated (as shown by recovery experiments) without any unambiguous formation of carbonium ions.

I attempted to ionise in the same way 1-methyl-1,3,3-triphenylindane, the cyclic dimer of 1,1-diphenylethylene, without any succes

(in HClO$_4$/CH$_2$Cl$_2$, 100% H$_2$SO$_4$, HS$_3$Cl, and 30% oleum).

A surprising feature was revealed by the behaviour of 2-phenyl-2-propyl acetate (XVII). When dissolved in 98% or 100% H$_2$SO$_4$ to form $10^{-5}$ to $10^{-4}$ M solutions, this compound gave, by the time the first spectroscopic reading was made (15 to 30 sec. after the mixing) the spectrum shown in Fig. 18, with absorption maxima at 324 and 380 m$\mu$. The apparent molar extinction coefficient of these peaks was the higher, the lower had been the initial concentration of XVIII and reached a ceiling value of $\varepsilon_{324}=15,200$ and $\varepsilon_{380}=1,300$, as determined by the zero time extrapolation method, for $10^{-5}$ M solutions.

The intensity of the peaks decreased with a half-life of about 33 min. ($2 \times 10^{-5}$ M solution at 2$^\circ$), and the 324 m$\mu$ peak drifted to 327 m$\mu$. The 380 m$\mu$ peak being very broad and shallow, no drift was observed with certainty.
Formation of a tribenzyl type cation by reaction of the 1,3-diphenyl-n-butyl cation with 1,3-diphenylbut-1-ene.

U.v. spectra of the ionic species formed by dissolution in 98% H$_2$SO$_4$ of:

- $\alpha$-methylstyrene (XV), $1.9 \times 10^{-5}$ M;
- 2-phenylpropan-2-ol (XVI), $2.2 \times 10^{-5}$ M;
- 4-methyl-2,4-diphenylpent-1-ene (V), $2.45 \times 10^{-5}$ M;
- 2-phenyl-2-propyl acetate (XVII), $2.4 \times 10^{-5}$ M.

Refer to Section 3.4.2 for variation of the extinction coefficients.
G.l.c. analysis of extracts after recovery showed the presence of α-methylstyrene in amounts inversely proportional to the time interval between the addition of XVII to H₂SO₄, and the recovery by dilution into an excess of alkali. No accurate estimate of the amount of α-methylstyrene recovered was possible, because of the very fast polymerisation of this olefin in regions of intermediate acidity during the dilution process.

Considering all the information given above, there is fairly strong circumstantial evidence that the spectrum exhibited by compound XVII in 98-100% H₂SO₄ belongs to the dimethylphenylcarbocation ion. This assignment need not necessarily be at variance with the presently accepted view⁰¹ that the dimethylphenylcarbocation ion is not stable in 100% H₂SO₄, considering that here the half-life of the ionic species is only of the order of 33 min., and the drift of the 324 mμ peak to 327 mμ showing that the monomeric cations dimerise and polymerise with the same 33 min. half-reaction time.

The dimethylphenylcarbocation ion cannot be formed from the olefin or the corresponding carbinol, not only for reasons of intrinsic instability in H₂SO₄, but also because polymerisation becomes highly competitive in regions of intermediate acidity, during the mixing step, when ions are in presence of excess olefin.

My explanation of why it is possible to obtain almost quantitatively the dimethylphenylcarbocation ion when XVII is mixed with
98-100% H₂SO₄, is based on the assumption of a very fast protonation of XVII to form an acylium ion,¹²,²⁵ which then gives the tertiary carbonium ion, without any possible intermediate polymerisation, via an unimolecular heterolysis reaction of conventional type,¹⁷,²⁵ as shown below:

As said before, the yield of this protonation decreases with increasing concentration of XVII: nearly 100% with 10⁻⁵ M, about 20% with 10⁻⁴ M, and about 1% with 5 x 10⁻² M.

A logical extension of the protonation of XVII was to investigate in similar conditions the behaviour of 1-phenylethyl acetate, with the heretical hope of obtaining some 1-phenylethyl cations. This was attempted, unsuccessfully, as described in Sec. 3.5.
3.4.3 Interaction with a large excess of $\text{HClO}_4$.

All compounds were made to react as $10^{-5}$ to $10^{-4}$M solutions with generally hundredfold excess of anhydrous $\text{HClO}_4$, in $\text{CH}_2\text{Cl}_2$, and in semi-open or in vacuum systems. Only spectroscopic measurements were made.

When $\alpha$-methylstyrene is made to react with a large excess (hundredfold) of $\text{HClO}_4$, fast dimerisation occurs, followed by a slower cyclisation to 1,1,3-trimethyl-3-phenylindane. The latter remains unaltered, as opposed to 1-methyl-3-phenylindane which is ionised in similar conditions (Sec. 3.2.6.1).

Treated the same way, 2-phenylpropan-2-ol is very rapidly dehydrated to $\alpha$-methylstyrene, and subsequently dimerises and cyclises.

Pure unsaturated dimer, treated with any amount of $\text{HClO}_4$, cyclises, as described by Barton and Pepper.\textsuperscript{22}

Pure cyclic dimer remains perfectly stable even in presence of 1 M $\text{HClO}_4$ (10% in $\text{CH}_2\text{Cl}_2$).

2-Phenyl-2-propyl acetate treated with 200 fold excess of $\text{HClO}_4$ yielded the cyclic dimer. (One single run).

No kinetic data are available for the experiments described above, as only qualitative information was sought.
Two interesting features were revealed by the investigation of \( \alpha \)-methylstyrene and related compounds:

a) The \( \alpha \)-methylstyrene cyclic dimer is not ionised by \( \text{HClO}_4 \) or by 100\% \( \text{H}_2\text{SO}_4 \), confirming that the ionisation of 1-methyl-3-phenylindane must depend on the presence of a hydrogen atom on the diphenyl substituted carbon atom.

b) The 2-phenylprop-2-yl cation can be formed in 98-100\% \( \text{H}_2\text{SO}_4 \) as a fairly stable species (half-life 33 min. at 2\( ^\circ \) for 2 \( \times 10^{-5} \)M solutions), when an indirect method is used in conjunction with conventional rapid dispersal techniques at low concentration and temperature.
3.5 Interaction of l-phenylethyl acetate, ethyl benzoate, 
β-methylstyrene, 2,6-dimethylstyrene and pentafluorostyrene with 98-100% sulphuric acid.

3.5.1 Introduction.

l-Phenylethyl acetate and ethyl benzoate were considered in relation to the investigation of the 2-phenyl-2-propyl acetate system (Sec. 3.4.2).

Pentafluorostyrene, β-methylstyrene and 2,6-dimethylstyrene were studied with the hope of obtaining information which would shed light on the behaviour of styrene.

All reactions were performed at 0° and the spectra were scanned at 2°.

3.5.2 l-Phenylethyl acetate and ethyl benzoate.

AcOH solutions of l-phenylethyl acetate, $10^{-4}$ to $10^{-3}$M, were diluted to $10^{-4}$ to $10^{-5}$M in 100\% \( \text{H}_2\text{SO}_4 \). The clean u.v. spectrum exhibited a peak at 262 m\( \mu \) which reached its maximum ($\varepsilon_{262} = 10,400$) in about 10 min., with $5 \times 10^{-5}$M acetate, and remained stable for days.

The relatively slow growth of the absorption (as compared to 2-phenyl-2-propyl acetate, with which the reaction is completed in less than 15 sec.) suggested that the spectrum was not due to directly formed ionic species. Recovery experiments did not reveal the formation of any l-phenylethyl or related oligomeric cations.
Increasing the initial or final concentration of the acetate led to formation of the carbinol and then the same reaction pattern as with styrene.

In an attempt to identify the species responsible for the 262 mμ absorption, and bearing in mind that arylacyl cations absorb strongly in this region,12 I protonated in identical conditions ethyl benzoate, which gave exactly the same 262 mμ peak, but with an extinction coefficient twice as high: 20,600, belonging to the benzoyl cation12 Ph-C=O (phenyloxocarbonium ion). Benzyl benzoate behaved in the same way, whilst ethyl and benzyl acetate did not show any ionic u.v. absorption in the region investigated (200 - 500 mμ).

I did not investigate any further the 1-phenylethyl acetate/H2SO4 system or look for any evidence establishing with certainty the identity of the species responsible for the 262 mμ absorption. Considering that the ε of this peak is one-half of the ε of the pure benzoyl cation, and excluding a sheer coincidence, a bimolecular rearrangement mechanism with formation of 50% carbonium ions could be suggested. Similar carbonium ion rearrangement reactions with alkyl and aryl migration are well known and reviewed.26

3.5.3 Pentafluorostyrene, β-methylstyrene, and 2,6-dimethylstyrene.

A dilute solution of pentafluorostyrene (10^-5 - 10^-4 M) in H2SO4 exhibited a single u.v. peak at 266 mμ, shifting slowly (4 days) to 257 mμ, with the apparent molar extinction coefficient growing
from $2 \times 10^3$ to $2.5 \times 10^4$. The very slow increase of the absorbance showed that there was no direct protonation and therefore this compound was not investigated any further.

Propenylbenzene ($\beta$-methylstyrene) dissolved in 98% H$_2$SO$_4$ to form $10^{-4}$M solutions exhibited a spectrum with two major absorption peaks, at 416 and 310 m$\mu$. Extensive polymerisation prevented any estimation of the extinction coefficients. This spectrum being similar to the spectrum exhibited by ionised 1-methyl-3-phenylindane, the following reaction mechanism leading to the formation of ionic species seems plausible: propenylbenzene dimerises to 2-methyl-1,3-diphenylpent-1-ene, which cyclises to form 1-ethyl-2-methyl-3-phenylindane. The latter compound having a reactive hydrogen on the diphenyl substituted carbon is then ionised in the same way as 1-methyl-3-phenylindane.

The dimerisation and cyclisation of propenylbenzene have been investigated by van der Zanden and Rix, by Erdmann, and by Müller and Körnendy. However, these authors did not consider the ionisation reaction.

2,6-Dimethylstyrene ($10^{-4}$M) polymerised extensively in H$_2$SO$_4$ and no clean u.v. spectra were obtainable. When treated with hundredfold excess of HClO$_4$ in CH$_2$Cl$_2$, this compound ($10^{-4}$M) exhibited an absorption with a broad peak at 350 m$\mu$ reaching in 15 hr. an extinction coefficient of $10^4$. The very slow increase of absorption made
it seem likely that this was not due to direct protonation, and therefore the identification of the species responsible for this spectrum was not attempted.

3.5.4 Conclusion.

Although little useful information was gained from the experiments discussed in sections 3.5, one finding deserves some attention:

Propenylbenzene solutions in $\text{H}_2\text{SO}_4$ give very nearly the same spectrum as 1-methyl-3-phenylindane in the same conditions. Considering that none of the following compounds: pentafluorostyrene, 2,6-dimethylstyrene, and 1,1,3-trimethyl-3-phenylindane (Sec. 3.4.2) give any immediately formed ionic species stable in conc. $\text{H}_2\text{SO}_4$, it becomes clear that the only stable cations obtained easily from styrene and related compounds are those which derive from the ionisation of the cyclic end-groups formed as reaction intermediates. This ionisation is made possible only by the presence of a reactive hydrogen on the diphenyl substituted carbon.

The cyclic dimer of $\alpha$-methylstyrene cannot ionise for lack of reactive hydrogen. Pentafluorostyrene and 2,6-dimethylstyrene cannot give any indane end-groups, and hence no ionisation by this route is possible.
3.6 U.v. spectra of carbonium ions derivable from
1-methyl-3-phenylindane and styrene.

3.6.1 Introduction.

The reasons for investigating the ions derivable from the
cyclic dimer of styrene have been discussed in Section 3.3.

I have already shown in the appropriate sections of this
thesis (under 3.1 and 3.2) that 1-methyl-3-phenylindane, as well
as styrene, give clean reactions with excess of strong acids only
at the highest dilutions. This makes impracticable straightforward
identification methods, such as n.m.r. spectroscopy of the carbonium
ions, and unreliable any conventional structural analysis of products
recovered after killing the ions.

One must bear in mind too, that recovery experiments with such
low concentrations (order of $10^{-5}$M) of highly reactive species must
introduce a further uncertainty, due to destruction and rearrangement
reactions in media of intermediate acidity during the dilution
(killing) in excess alkali.$^{14,30}$

The only identification route left was to synthesise compounds
corresponding to structures logically derivable from the compounds
investigated, and to compare the u.v. spectra of their carbonium ions
with the spectra of the unknown.

I prepared accordingly the compounds XIX to XXIII, shown in
Table 6, next page:
Compound XXI was synthesised in place of phenyl-(2'-isopropylphenyl)methanol, for reasons of starting material availability. Theoretical and experimental evidence shows that the u.v. spectra of carbonium ions derived from the last two compounds must be very similar (Section 3.7.3.b).
3.6.2 Protonations.

Compounds XIX, XX, XXI, and XXIII were protonated at 0° in 98% H₂SO₄, and the u.v. spectra of the 10⁻⁵M solutions were scanned at 2°. Compound XXII which gave polymers with H₂SO₄, was protonated in HSO₃Cl, with partial polymerisation, and then diluted with H₂SO₄.

The u.v. and visible spectra of the carbonium ions formed from these compounds are shown in Fig. 19, along the extinction coefficients observed.

In all instances the protonations were completed by the time the first spectrometric reading was made (within about 15 sec.), and the spectra of the products remained stable at 0° from hours to many days, for 10⁻⁵M solutions.

N.m.r. spectra made with 5 to 10% solutions in 98% H₂SO₄ of all compounds (except XXII) confirmed the expected structures, shown in Fig. 16 A and B. These concentrated carbonium ion solutions remained stable, when kept at 0°, for many weeks with IXX, XX, and XXI, and for many months with XXIII. Further details on the n.m.r. spectra of these ions, along with those of other ions, will be given later on in this thesis (sections 3.7.4). Attempts to protonate XXII in concentrations useful for n.m.r. spectroscopy (1 to 10%) yielded extensive polymerisation and sulphonation.

The expected precursors were recovered by dilution of the 10% (by weight) acid solutions into excess cold alkali (Sec. 2.2.9).
Fig. 19 (page 102)

U.v. spectra of cations X (a), XI (b), XXVI (c), XIII (d), and XIV (e), formed by dissolution of precursors XIX, XX, XXI, XXII, and XXIII in 98% H\textsubscript{2}SO\textsubscript{4}, at 0°.

The spectra were scanned at 2°, with 10^{-5}M solutions.
Fig. 19
It is worth stressing that with protonated XX the recovered precursor was the corresponding olefin, 1-phenyl-1-(2'-ethylphenyl)ethylene. This behaviour is by no means an anomaly. When any carboxonium ion derived from a carbinol is killed with aqueous alkali, the olefin obtainable by normal dehydration of the carbinol is recovered. Thus, the 1,1-diphenylethyl cation regenerates 1,1-diphenylethylene. 

As the carboxonium ion derived from XXII was not identifiable by n.m.r. spectroscopy, the extracts after killing were analysed by g.l.c.; a single peak was detected, corresponding to the expected precursor, 1,3-diphenylbut-2-ene. Thus, there is very little doubt that the protonation of XXII (or of the corresponding olefin) in HSO₃Cl - 98% H₂SO₄, and with dilute solutions, yields the 1-methyl-1,3-diphenylpropyl cation. The maximum absorption at 311 mμ, and the magnitude of the extinction coefficient (10⁴) confirmed further that the ion is of the monoarylalkyl type, and that few polymeric ions are formed.

The 1-methyl-1,3-diphenylpropyl cation was however rather short lived, and in a matter of one or two days its u.v. spectrum changed completely, with decrease of the 311 mμ peak, and formation of a new peak at around 420 mμ. The new spectrum was fairly similar to the spectrum of the 3-methyl-1-phenylindanyl cation (as shown in Fig. 20) suggesting possibly rearrangement, oxidation and cyclisation reactions leading to the latter ion.
As stated before (Sec. 3.1.2.2), the 315 \( \text{m} \mu \) peak of the 1,3-diphenyl-n-butyl cation slowly drifts to about 310 \( \text{m} \mu \). This could now be accounted for (tentatively) by a rearrangement, via an internal 1 - 3 hydride ion shift, to the more stable tertiary 1-methyl-1,3-diphenylpropyl cation (XIII).

As I wanted to obtain more information about the behaviour of XIII, I attempted to protonate 1,2-diphenylpropan-2-ol in 98 and 100\% H\(_2\)SO\(_4\) or HSO\(_3\)Cl, with concentrations ranging from 1M down to 10\(^{-5}\)M. My aim was to obtain the corresponding 1,2-diphenylprop-2-yl cation, which should exhibit a u.v. spectrum resembling that of XIII, both cations having a similar structure, as shown below:

![Diagram of 1-methyl-1,3-diphenylpropyl cation (XIII) and 1,2-diphenylprop-2-yl cation](image)

No direct protonation of 1,2-diphenylpropan-2-ol was observed however. On mixing 10\(^{-4}\)M carbinol in AcOH (1 ml.) with 98\% H\(_2\)SO\(_4\) (9ml.) to form a 10\(^{-5}\)M solution, an intense yellow colour appeared for about 1 sec. and then disappeared again. The solution remained colourless for about 10 sec., then slowly (minutes) became pink and then pale.
red, and the spectrum exhibited a peak at 544 m\textmu, with an apparent extinction coefficient of 3,000. Absorption at 266 and 272 m\textmu showed formation of oligomers with cyclic end-groups. The reaction pattern appears to be dehydration of the carbinol to methylstilbene (cis and trans 1,2-diphenylprop-1-ene) with subsequent oligomerisation and cyclisation. A similar reaction pattern was observed by Brackman and Plesch\textsuperscript{31} in the polymerisation of trans-stilbene in hexane-benzene mixtures, catalysed by TiCl\textsubscript{4}-CCl\textsubscript{3}COOH.

Another carbonium ion showing an interesting behaviour is the 1,1-diphenyl-n-butyl cation. Although the 10% solution of the latter in 98% H\textsubscript{2}SO\textsubscript{4} remained stable for many weeks at 0\degree, its 10\textsuperscript{-5}M solutions in 100% H\textsubscript{2}SO\textsubscript{4} appeared to be completely altered within a few days. The final u.v. spectrum was similar to the 3-methyl-1-phenyl-indanyl spectrum, as shown in Fig. 21. A tentative interpretation of this modification will be given in the discussion section (3.6.7.3).
Fig. 20 (page 103)

Spectrum produced by 1,3-diphenylbutan-3-ol in a mixture of 90% $\text{H}_2\text{SO}_4$ and 10% $\text{HSO}_3\text{Cl}$ (vol./vol.) after 15 min. (full curve) and after 7 days (dashed curve).

Fig. 21 (page 105)

Spectrum produced by 1,1-diphenylbutene in 100% $\text{H}_2\text{SO}_4$, after 15 min. (dashed curve) and after 48 hr. (full curve).
Fig. 20

XXII \((3 \times 10^{-5} \text{ M})\) in 90\% \(\text{H}_2\text{SO}_4\) and 10\% \(\text{HSO}_3\text{Cl}\)

15 min.

7 days

Fig. 21

XIX \((10^{-5} \text{ M})\) in 100\% \(\text{H}_2\text{SO}_4\)

15 min

48 hr.
3.6.3 Identification of the cation obtained by ionisation of 1-methyl-3-phenylindane.

The spectra exhibited by 1-methyl-3-phenylindane and compounds IXX – XXIII in 98% H₂SO₄ are compared in Fig. 22 and 23. It appears immediately that two spectra are nearly identical; they belong to ionised 1-methyl-3-phenylindane (IX) and to the 3-methyl-1-phenylindanyl cation (XIV), and exhibit exactly the same maxima, and 304 and 415 mμ, and a shoulder at 291 mμ. The only minor difference noticeable is an extra shoulder at 315 mμ with ionised IX. I will show later on that this difference not only does not contradict the identity assignment, but supplies a fundamental clue regarding the ionisation mechanism of IX (Section 3.6.7.2).

In order to investigate further the similarity of these spectra, I protonated XXIII (10⁻⁵ M) with 10⁻³ M anhydrous HClO₄ in CH₂Cl₂, at 0⁰, under high vacuum conditions, and measured simultaneously the spectrum and the conductivity, at 2⁰. As shown in Fig. 24, the whole spectrum was shifted bathochromically to 308 and 421 mμ, as predictable in a solvent of lower acidity and dielectric constant; the molar extinction coefficient however remained unaffected: \( \varepsilon_{308} = 12,000; \ \varepsilon_{421} = 35,000. \)

The molar conductivity at 2⁰ was 137 Mhos cm.²mole⁻¹.

The very fast protonation was completed even at the highest dilution (6 x 10⁻⁶ M olefin and 10⁻³ M HClO₄) in less than 30 sec.
Fig. 22 (page 106)

Qualitative comparison of the spectra in 98% $\text{H}_2\text{SO}_4$ solution produced by compounds IX, XIX, XX, XXI, and XXII.

Fig. 23 (page 106)

Comparison of the spectra in 98% $\text{H}_2\text{SO}_4$ solution produced by compounds IX and XXIII; the latter compound gives the 3-methyl-1-phenylindanyl cation (XIV). The only difference noticeable is the shoulder at 315 m$\mu$ in IX.
Fig. 22

D all comps. $10^{-5}M$
in 98% $H_2SO_4$

Fig. 23

$cation~XIV$

$\frac{XXIII}{(10^{-5}~M)}$

98% $H_2SO_4$

$\frac{IX}{(3\times10^{-5})}$

98% $H_2SO_4$
The complete ionisation of the cyclic dimer in similar conditions required about 1 hr., and the final apparent molar extinction coefficients and conductivity were: \( \varepsilon_{308} = 5,300; \varepsilon_{420} = 15,000; \)
\[ \Lambda_M = 49 - 52 \text{ Mhos cm.}^2\text{mole}^{-1} \] (Sections 3.2).

The spectra of 1-methyl-3-phenylindane and 1-methyl-3-phenylindene ionised by HClO\(_4\) in CH\(_2\)Cl\(_2\) are compared in Fig. 24. The identity is here complete, no 315 m\(\mu\) shoulder being present in the spectrum of IX.

I have shown before (sections 3.2) that styrene, its unsaturated dimer and its cyclic dimer give the same spectrum with large excess of HClO\(_4\) in CH\(_2\)Cl\(_2\), the latter compound (or oligomers with cyclic end-groups) being in all instances the final species ionised. This has been confirmed independently by Bywater and Worsfold.\(^{11}\)

The clear-cut conclusion resulting from my work is that the ions formed (almost exclusively) from styrene and perchloric acid under the cleanest conditions, as described in previous sections (low temperature, lowest concentrations) is the 3-methyl-1-phenylindanyl cation. The fact that when the latter is formed from the pure cyclic dimer the \( \varepsilon \) and \( \Lambda_M \) have about one half of the values obtained when the ion is formed from 1-methyl-3-phenylindene, indicates a mechanism involving formation of 50% ions and 50% of neutral compound (Sec. 3.6.7.2). It is also now apparent that the different values of \( \lambda_{\text{max}} \) and \( \varepsilon \) obtained by various investigators who used less rigorous experimental conditions (see Table 2 of Ref. 1) must have
been due to variable quantities of one or more of the ions derivable by ring opening having been formed along with the 3-methyl-1-phenyl-indanyl cation (XIV).

Four precursors yielded quantitatively XIV in \(98\% \text{ H}_2\text{SO}_4\):
- 1-methyl-3-phenylindene,
- 1-methyl-3-phenylindan-3-ol,
- 1,1-diphenylbuta-1,3-diene,
- 1,1-diphenylbut-3-ene-1-ol,

and exactly the same spectrum, qualitatively and quantitatively, was obtained from all four compounds. The protonation of the first two compounds to give the indanyl cation was structurally and theoretically predictable: a diaryl substituted unsaturated carbon can be expected to form easily the corresponding diarylcarbonium ion, particularly when no steric factors prevent formation of the planar trigonal carbonium ion.

What may appear fairly puzzling on the other hand is the formation of the indanyl cation from the last two compounds (the butadiene and the butenol), which are by no means direct precursors. I will discuss this particular feature in Section 3.6.7.3.
3.6.4 Formation of the l-phenylindanyl cation.

Using the same technique as in Section 3.6.2, I protonated 3-phenylindene in 98% H$_2$SO$_4$, with concentrations ranging from $10^{-5}$M to 1M. In all instances the l-phenylindanyl cation was formed quantitatively, as established by u.v. and n.m.r. spectroscopy, and instantaneously (or at least within 15 sec., time of the first spectroscopic reading). Once formed, this cation appeared to be stable for many months at 0$^\circ$, and at any concentration.

The u.v. spectrum exhibited two peaks, at 302 m$\mu$ ($\varepsilon=13,000$) and 412 m$\mu$ ($\varepsilon=37,000$), and a shoulder at 290 m$\mu$ ($\varepsilon=7,500$). Apart from the slight hypsochromic shift and increase of the extinction coefficients, the spectra of this cation and of the 3-methyl substituted cation XIV are identical (Fig. 25).

The n.m.r. spectrum is shown and discussed in the appropriate section of this thesis (3.7.4.2).

The only reference to this cation found in the literature is in a publication by Deno et al. who studied diarylolefin-diarylalkyl cation equilibria in sulphuric acid, and only mention the long wavelength peak of the l-phenylindanyl cation at 418 m$\mu$, in 97% H$_2$SO$_4$, with $\log_{10} \varepsilon=4.32$ (20,900). As these authors did not study the n.m.r. spectrum of the cation, there is no certainty whether they obtained the monomeric or the dimeric cation. The much lower value of $\varepsilon$ in their case, actually one half my value, suggests that they observed the
Comparison of the spectra produced in HClO₄/CH₂Cl₂ by compounds IX and XXIII; the latter compound gives the 3-methyl-1-phenylindanyl cation (XIV). Clearly, in both cases the cation formed is XIV. Note the absence of the 315 μ shoulder in IX, as compared to IX in H₂SO₄ solution in Fig. 23.

Comparison of the spectra of the 1-phenylindany1 and the 3-methyl-1-phenylindany1 cations in 98% H₂SO₄. Both cations are in 10⁻⁵ M solution.
dimeric cation; this should account also for the higher wavelength, 418 μ instead of 412 μ, although the latter minor difference could be well within the range of experimental error (the spectrometer I used was carefully calibrated, both in wavelength and in absorbance, as described in Section 2.2.1.1). Another possible, and more probable, explanation for the lower extinction coefficient could lie in a non quantitative protonation, accompanied by oligomerisation, yielding eventually a mixture of monomeric and oligomeric cations.

Although it is Prof. Deno's group which recommended for the first time,14 in 1963, the use of appropriate fast dispersal techniques for better yield of carbonium ions in protonations, it is not clearly stated that such techniques were used in the work discussed above, published in 1959.

These authors also report33 the 1-phenyl-3,4-dihydronaphthyl cation (very similar to the 1-phenylindanyl cation) whose spectrum has a major peak at 420 μ with ε = 21,400.

As I was able to prepare 3-phenylindene before 1-methyl-3-phenylindene, for reasons of availability of starting materials (Sec. 2.1.4.12), the study of the 1-phenylindanyl cation supplied me with the first serious clue showing that I was on the right way in the identification of the ions observed when styrene interacts with dilute acids. I stress the plural, ions, for the obvious reason that even in the best conditions styrene yields a mixture of monomeric and polymeric indanyl cations.
3.6.5 **Ions possibly contributing to the 430 μm region absorption of styrene ionised in concentrated strong acids.**

I have shown (sections 3.1.2) that the interaction of styrene with concentrated H₂SO₄ yields the 1,3-diphenyl-n-butyl cation (accompanied by variable amounts of homologous polymeric ions) exhibiting only one major peak, at 315 μm. I demonstrated also that the erratic absorption appearing at around 430 μm, and growing in importance as the experimental conditions became less rigorous, could not be attributed to linear polystyryl cations (monoarylalkylcarbonium ions). The only plausible hypothesis was that the latter absorption could belong to diarylcarbonium ions formed by extensive oligomerisation and rearrangement reactions.

The preparation and characterisation of the five cations X to XIV (Fig. 16 A and B, and Sec. 3.6.2) derivable from 1-methyl-3-phenylindane made available the experimental evidence substantiating this hypothesis. The 1-methyl-1,3-diphenylpropyl cation (XIII) being ruled out (monoarylalkylcarbonium ion, hence no important absorption above 400 μm), all the four remaining carbonium ions exhibit strong absorption in the 415 - 447 μm region. Comparison of the spectra of these cations with the high wavelength absorption of styrene ionised in different conditions (Fig. 26) shows that all four cations (or their higher homologues) can be present in variable amounts, accounting thus for the wide fluctuations of position and
intensity of the latter absorption from one experiment to the next. Shoulders corresponding to the absorption of these ions in the 315 μ region further support this, and the final clue comes from the variable presence of their precursors in the recovery products (Section 3.1.2.3).
Qualitative comparison of different spectra shown by styrene dissolved in 98% H₂SO₄, with the spectra of cations X, XI, XIII, XIV, and XXVI. Evidently, all these cations could contribute, as suggested by the reaction scheme in Fig. 16A and 16B.
Fig. 26
3.6.6 Interaction of tribenzylcarbinol with $\text{H}_2\text{SO}_4$ and $\text{HClO}_4$.

The reasons for protonating this compound have already been discussed in Section 3.3.

$10^{-4}$M solutions of tribenzylmethanol in conc. $\text{H}_2\text{SO}_4$ exhibited a single shallow and broad peak at around 440-450 m$\mu$, and another smaller one at around 320 m$\mu$. The extremely low extinction coefficients (900 for the former and 150 for the latter) showed that not more than a few per cent, if any, of the original carbinol can have been ionised, via polymerisation and rearrangement reactions leading to species very different from the expected tribenzylcarbinium ion.

When $10^{-4}$M tribenzylmethanol was made to react with at least a hundredfold excess of anhydrous perchloric acid in methylene dichloride, the resulting solution exhibited a slowly growing spectrum with peaks at 340, 425, and 504 m$\mu$, with extinction coefficients of 6,800, 8,000, and 9,200 respectively, 20 min. after the mixing of the reagents. After this, the 504 m$\mu$ peak continued to grow, whilst the 340 and 425 m$\mu$ peaks started decreasing to one half their value. The final extinction coefficient of the 504 m$\mu$ peak, after about one hour was $10^4$.

Considering the slow increase of the absorbance, and the comparatively low extinction coefficients reached, it was evident that the species under observation could not have been formed by
direct protonation. Hence, some products other than the tribenzyl- 
carbonium ion were formed. Moreover, the latter cannot be expected 
to absorb at such high wavelengths, where only highly conjugated 
polyarylmethyl ions absorb.

A tentative mechanism leading to similar ions, in presence 
of strong acids in large excess, should be the following:

Tribenzylmethanol dehydrates$^{34}$ to the corresponding olefin, 
2-benzyl-1,3-diphenylprop-1-ene, which could cyclise to 2-benzyl-
1-phenylindane via the secondary 2-benzyl-1,3-diphenylpropyl cation, 
itsel itself deriving, by a 1-2 hydride ion shift, from the tertiary 
tribenzymethyl cation formed by direct protonation of the olefin, 
as shown in Fig. 27. The formation of a secondary (anti- Markownikow) 
ion from a tertiary ion is made possible by the stabilisation 
gained by conjugation with the phenyl ring. Olah and Pittman$^{63}$
(and Ref. 24, p. 342) have similarly obtained the secondary (but 
phenyl conjugated) phenylisopropylmethyl cation by ionisation of 
the tertiary benzyldimethylcarbinol, followed by 1-2 hydride ion 
shift.

2-Benzyl-1-phenylindane should behave in the same way as the 
cyclic dimer of styrene, and yield diarylmethyl cations by ring 
opening or hydride ion abstraction. The same mechanism should apply to 
oligomers with cyclic end-groups.

One cannot completely rule out the possibility that similar
ions formed from distyryl cation and unsaturated dimer, via
tetramerisation, cyclisation, and ionisation, contribute to some
extent to the final ionic population in solutions derived from
styrene (Fig. 17).
Cyclisation mechanism of the olefin formed by dehydration of tribenzylmethanol:

(a) 2-benzyl-1,3-diphenylprop-1-ene is protonated to the tribenzylmethyl cation;

(b) the latter isomerises to the secondary (anti-Markownikow) 2-benzyl-1,3-diphenylpropyl cation, by a 1-2 hydride ion shift; the formation of the secondary cation from the tertiary cation is made possible by the stabilisation gained by conjugation with the phenyl ring;

(c) cyclisation to 2-benzyl-1-phenylindane (in the same way as the 1,3-diphenyl-n-butyl cation gives 1-methyl-3-phenylindane).
Fig. 27

(a) $\text{C} \quad - \quad \text{H}^+$

(b) 1-2 hydride shift

(c) $-\text{H}^+$
3.6.7 Discussion.

3.6.7.1 Summary. I have established that the u.v. spectrum exhibited when styrene interacts with dilute strong acids, and attributed to the 1-phenylethyl cation and its higher homologues, is due to the 3-methyl-1-phenylindanyl cation and its homologues (3-arylalkyl-1-phenylindanyl cations).

Moreover, the variable absorption at around 430 m\textmu\textmu exhibited by styrene solutions in concentrated strong acids is due not to polystyryl cations, but to diarylalkyl cations formed most probably by ring opening and ionisation of the indane end-groups.

This is the plain experimental evidence. Considering however the great variety and, sometimes, complexity of the experimental results described in the previous few sections, a more detailed discussion is now required.

3.6.7.2 Ionisation mechanism of 1-methyl-3-phenylindane (IX). When the 3-methyl-1-phenylindanyl cation is formed from IX, the molar extinction coefficients and the molar conductivity are about one half their values when the cation is formed from the direct precursor, 1-methyl-3-phenylindene. Moreover, a qualitative comparison of the spectra in concentrated H\textsubscript{2}SO\textsubscript{4} reveals a minor difference, which is the presence of an extra shoulder at 315 m\textmu\textmu, exhibited only when the precursor has been the saturated dimer (IX).
I have already shown (sections 3.1.2 to 3.1.4) that the only ion derivable from styrene or its oligomers and exhibiting a peak at 315 μ is the 1,3-diphenyl-n-butyl cation. If one assumes that this is the ion responsible for the 315 μ shoulder, the ionisation mechanism of IX can tentatively be established as follows:

a) In presence of an excess of strong acid, IX is slightly ionised to the 1,3-diphenyl-n-butyl cation (XXIV), and an equilibrium heavily shifted towards IX is established. This ionisation by ring opening should not be surprising, considering that the indane ring is formed by the reverse reaction.

b) As soon as formed, XXIV abstracts a hydride ion from the No 3 carbon of IX, to generate the more stable 3-methyl-1-phenyl-indanyl cation (XIV), and is reduced itself to 1,3-diphenyl-n-butane (XXV).

c) The disappearance of XXIV shifts the equilibrium towards more ionisation of IX to XXIV, with a subsequent new hydride ion abstraction step.

d) At the end of the reaction equal quantities of XIV and XXV have been formed, no more IX is left to reduce XXIV, and this remains in small amounts, as attested by the 315 μ shoulder, in H₂SO₄ solutions.

Obviously, all reactions described above proceed simultaneously, although following different rates, and no separate steps
are discernable. Moreover, as the rates of the ring-opening and hydride transfer are unknown, the rate controlling reaction cannot be determined.

Many similar hydride transfer reactions described in recent reviews\textsuperscript{35-37} favour the mechanism suggested above.

In HClO\textsubscript{4} solution, no clearly apparent shoulder is observed at 315 m\textmu. This shows that the 1,3-diphenyl-\textit{n}-butyl cation is stabilized appreciably only in strong concentrated acids.

3.6.7.3 Stability of indanyl cations. Olah and Pittman pointed out in a very recent review\textsuperscript{24} the outstanding stability of alkylindanyl cations, as compared to similar monoarylalkyl cations. Thus, the 1-methylindanyl cation is perfectly stable in 85-100\% H\textsubscript{2}SO\textsubscript{4}. The electronically very similar dimethylphenylcarbonium ion requires at least 30\% oleum, or even more drastic solvents such as SO\textsubscript{2}-Sbf\textsubscript{5}-FSO\textsubscript{3}H, to be stabilised at low temperature.

These authors suggest that the stability of indanyl cations can be partly attributed to the inherent planarity locked in the system, favouring a maximum \textit{\Pi} overlap of the p-orbital of the carbonium carbon with the ring orbitals. Thus, the 1-methyltetrahydronaphthyl cation, which must be strained in order to achieve 120\textdegree bond angles at planarity, is definitely less stable and requires higher acidity to be generated.

The unsuccessful attempts to protonate indene (this work and
Olah et al.\textsuperscript{24,38} to monomeric ions emphasizes the stabilising effect of electron donating substituents at the ionic carbon.

It now becomes clear why the 3-methyl-1-phenylindanyl cation appears to be such an ubiquitous entity. Its very high stability (diphenylcarbonium ion with locked in planarity) will favour its formation even via the most twisted paths, to the great bewilderment of the investigator. For instance, as shown before (Section 3.6.2), the u.v. spectra of the 1-methyl-1,3-diphenylpropyl and 1,1-diphenyl-n-butyl cations in \(10^{-5}\text{M }\text{H}_2\text{SO}_4\) solutions change slowly to become nearly identical to the spectrum of the 3-methyl-1-phenylindanyl cation. I cannot for the moment suggest any simple mechanism leading to the cyclisation of XIII. As far as the cyclisation of the 1,1-diphenyl-n-butyl cation is concerned, it requires the action of an oxidising agent (two hydrogen atoms to be removed) and proceeds only in 100\% \(\text{H}_2\text{SO}_4\), in which traces of \(\text{SO}_3\) are always present, but not in 98\% \(\text{H}_2\text{SO}_4\). The tentative cyclisation mechanism of the latter cation, reduced to its simplest expression, is shown in Fig. 28.

Considering the oxidative cyclisation of the 1,1-diphenyl-n-butyl cation to the 3-methyl-1-phenylindanyl cation, I thought it worth while to investigate the behaviour of a compound in which an already present unsaturation would favour particularly the cyclisation, that is 1,1-diphenylbuta-1,3-diene, and the corresponding
carbinol 1,1-diphenylbut-3-ene-1-ol.

The dissolution of these two compounds in 98% H₂SO₄ yielded quantitatively the 3-methyl-1-phenylindanyl cation (XIV), as already stated in Sec. 3.6.3. A more detailed investigation of the interaction with increasing concentrations of aqueous sulphuric acid revealed the following sequence of reactions, leading finally to the indanyl cation XIV (at temperatures between 0°C and 25°C, all acid concentrations expressed in weight %, and with very vigorous stirring):

a) 50-65% H₂SO₄, the carbinol is quantitatively dehydrated to the diolefin, 1,1-diphenylbuta-1,3-diene.

b) 70% H₂SO₄, very slow cyclisation (about one week to reach 80% conversion) to 1-methyl-3-phenylindene (XXIII), temp. 25°C.

c) 75% H₂SO₄, nearly quantitative cyclisation to the indene XXIII, within 48 hr. at 25°C; if the temperature is raised to 45°C, formation of minor quantities of 1-phenyl-3,4-dihydronaphthalene is observed.

d) 80% H₂SO₄, increased formation of dihydronaphthalene and probably some dimerisation of XXIII (n.m.r. spectrum).

e) 85-100% H₂SO₄, formation of the indanyl cation XIV; in 98% acid, the latter is formed quantitatively (at 0°C).

It is accordingly established that in regions of intermediate acidity both precursors give 1-methyl-3-phenylindene, which can be isolated in nearly quantitative yield.
These cyclisation reactions could provide a general route to substituted indenes and dihydronaphthalenes, as illustrated in Fig. 29A.

Deno et al. \(^{39}\) have recently prepared the 1,3,3-trimethyl-indanyl cation by a cyclisation protonation reaction, by adding 4-phenyl-2-methyl-1,3-pentadiene to either 96% \(\text{H}_2\text{SO}_4\) or 23% oleum. In a final experiment seeking to evaluate the stability of the 3-methyl-1-phenylindanyl cation, I attempted a hydride transfer reaction between 1-methyl-3-phenylindane and triphenylmethyl perchlorate, in \(\text{CH}_2\text{Cl}_2\) solution, at 25\(^\circ\). When equimolar reagents were used (10\(^{-4}\)M), no reaction was observed. With a tenfold excess of the indane, the absorption of the trityl cation decreased noticeably, and a new peak appeared at 308 m\(\mu\), together with a corresponding relative increase (unbalancing) of the 410 m\(\mu\) trityl peak. All these changes could be accounted for by the formation of about 10% of indanyl cation. Altogether, it appears that the trityl cation is more stable than the indanyl cation, but not much more.

In analogous experiments, the trityl cation is quantitatively reduced to triphenylmethanol by hydride ion donation from cycloheptatriene, \(^{40}\) 1,3-dioxolane, \(^{41}\) and tribenzylamine, \(^{41}\) among others, with, respectively, formation of the tropylium, dioxolenium, and benzylidenedibenzylammonium ions.

Fig. 29B shows a tentative cyclisation and ionisation scheme for 1,1-diphenylbuta-1,3-diene.
Tentative oxidation mechanism of ion $X$ to ion $XIV$, in
100% $H_2SO_4$ (presence of traces of $SO_3$).

General route to:

(a) 1,1,3-trisubstituted indenes, by cyclisation of the corresponding dienes in 75% aqueous $H_2SO_4$, at 25°;

(b) 1,4-disubstituted-1,2-dihydronaphthalenes by cyclisation of the corresponding dienes in 75% $H_2SO_4$ at 50°, or in 80% $H_2SO_4$ at 30°.

Note: $H_2SO_4$ concentrations in weight per cent.
FIG. 28

\[
\text{SO}_2
\]

\[
\text{H}_2\text{O}
\]

FIG. 29A
Fig. 29B (page 121)

Tentative reaction pathways leading to 1-methyl-3-phenylindene and to the corresponding cation, when 1,1-diphenylbuta-1,3-diene is treated with $\text{H}_2\text{SO}_4$ at different concentrations.
3.7 Spectroscopic investigation of diphenylcarbonium ions.

3.7.1 Introduction.

In my investigation of the ionic species derivable from styrene and its cyclic dimer I prepared (Sec. 3.6) four diphenylcarbonium ions which had not yet been characterised: the 1,1-diphenyl-n-butyl (X), 1-phenyl-1-(2'-ethylphenyl)ethyl (XI), 3-methyl-1-phenylindanyl (XIV), and phenyl-(2'-ethylphenyl)methyl (XXVI).

It appeared that these carbonium ions, and especially the two ortho-alkyl substituted diphenylcarbonium ions, showed some interesting features requiring further investigation by n.m.r. and u.v. spectroscopy.

In order to obtain as much information as possible within the limits of this work, I synthesised two more precursors: phenyl-(2'-methylphenyl)methanol and 1-phenyl-1-(2'-methylphenyl)ethanol. These, together with diphenylmethanol and 1,1-diphenylethylene, made up two parallel series, each of three diphenylmethyl and three 1,1-diphenylethyl cations, whose electronic and n.m.r. spectra were to be compared.

Several diphenylcarbonium ions have been extensively studied by u.v. spectroscopy in $H_2SO_4$ solution by Newman,42 Gold,23 Branch,43 Deno,33,44 Evans,45 Symons5 and their co-workers, and in $SO_2-SbF_5-FSO_3H$ at $-60^\circ$ by Olah et al.12
The proton shifts in the n.m.r. spectra of the diphenylmethyl and the 1,1-diphenylethyl cations have been discussed in two communications, by Farnum\textsuperscript{18} and by Olah;\textsuperscript{46} the solvent used by these authors were respectively HSO\textsubscript{3}Cl at -20\textdegree{} and SO\textsubscript{2}-SbF\textsubscript{5} at -30\textdegree{}. Kingsbury\textsuperscript{47} studied by n.m.r. the hydrogen-deuterium exchange in para- and meta-substituted 1,1-diphenylethyl cations, and Volz et al.\textsuperscript{48} gave a qualitative account of their n.m.r. and visible spectroscopic observations of several diphenylmethyl cations with methyl substituted ring hydrogens, in N\textsubscript{2}CH\textsubscript{3}-SbCl\textsubscript{5} solutions.

However, none of these works deal with series of identically substituted carbonium ions, nor can such comparison be established by cross-referencing. This was a sufficient reason to go ahead with my investigation of diphenylcarbonium ions. The interesting qualitative and quantitative information gained regarding both the u.v., visible, and n.m.r. spectra showed that the work was worth performing.

As time was limited, I concentrated only on a few parameters, attempting to establish them with the highest possible accuracy; they were: wavelength and extinction coefficients of the u.v. and visible absorption spectra, oscillator strength (f) of separate peaks and of whole spectra, n.m.r. spectra and relative downfield shifts (deshielding) of all relevant protons.

The aim was to establish any spectroscopically apparent effects due to hyperconjugation or to steric hindrance.
3.7.2 Procedure.

3.7.2.1 Protonation and recovery of products. Considering the wide range of concentrations used (10^{-5} M to about 0.5 M), due care was required to assure quantitative protonations and to avoid any misleading side reactions.

All protonations for u.v. and visible spectroscopy were made by adding 1 ml. of a 10^{-4} M acetic acid solution of the precursor to 9 ml. of 98% H_{2}SO_{4} at 0^\circ (both acids AnalaR grade). In a few comparative runs, 0.1 ml. of 10^{-3} M precursor in AcOH was added to 9.9 ml. of 98% H_{2}SO_{4}; at 0^\circ; within the limits of experimental error, the same extinction coefficients were found as above, showing that in both cases the protonation reached the same degree of completion.

Protonations for n.m.r. spectroscopy were performed in 98% H_{2}SO_{4} and in HS0_{3}Cl (unless otherwise stated) at temperatures from -30 to 0^\circ.

Both protonation and recovery runs were performed by fast dispersal techniques, as described in sections 2.2.8 and 2.2.9.

Precursors recovered from carbonium ion solutions were analysed by n.m.r. and i.r. spectroscopy when the concentration was suitable, and by u.v. spectroscopy and g.l.c. with the low concentrations.
3.7.2.2 Measurement of the spectra. The u.v. and visible spectra were measured at 20°, with $10^{-5}$ to $10^{-4}M$ solutions, in 1 and 0.1 cm. silica cells. The blank (background) spectra were determined with matched cells and subtracted when necessary (quite seldom, in the 250-300 μm range); even in the most unfavourable cases, the background remained less than 10% of the total absorption. The concentrated carbonium ion solutions, for n.m.r. study, were checked by u.v. spectroscopy after dilution in 98% $H_2SO_4$. The resulting extinction coefficient was in all cases, within the limits of experimental error (2 to 5%), the same as directly determined with $10^{-5}M$ solutions, showing that all protonations were clean and quantitative.

The spectrophotometer was calibrated as described in Section 2.2.1.1.

The n.m.r. spectra of the cations were calibrated with TMAS (tetramethylammonium sulphate) as internal standard $^{14}$ (Sec.2.2.1.3).

All n.m.r. spectra were measured satisfactorily at 35°; some of the carbonium ion solutions, kept at 0° between the runs, displayed identical n.m.r. spectra after several weeks.

3.7.2.3 Determination of the oscillator strength ($f$). The most conventionally used expression of the intensity of an absorption band, the molar extinction coefficient $\varepsilon_{\text{max}}$, does not necessarily give the total absorption strength. $^{32,49}$ A broad band with a comparatively small value of $\varepsilon_{\text{max}}$ may involve more energy than a narrow
band with a greater value of $\varepsilon_{\text{max}}$.

A more convenient measure for the intensity of the total absorption due to electronic transitions is given by the oscillator strength, or $f$ value, which is directly related to the integrated intensity, and in terms of classical electromagnetic theory is determined by the number of oscillating units per molecule (or ion), as follows:

$$f = (10^3mc^2\log e 10/\pi e^2N)\int \varepsilon d\nu$$

where $e$ and $m$ are the charge and the rest mass of the electron, $c$ is the velocity of light, $N$ is Avogadro's number, and $\varepsilon d\nu$ is the band area. In the case of symmetrical and smooth absorption bands, the area may be obtained in good approximation by the relation:

$$\int \varepsilon d\nu = \varepsilon_{\text{max}} \Delta \nu$$

where $\Delta \nu$ is the band width at half maximum extinction (in cm$^{-1}$).

Introducing the numerical values in the term within brackets of the first equation gives:

$$f = 4.317 \times 10^{-9} \varepsilon_{\text{max}} \Delta \nu$$

To compute the constant term above I used the physical constants as recommended by the National Bureau of Standards (U.S.).

When the oscillator strength is computed from spectroscopic data determined in solution, $f$ is multiplied by a correction factor $F$ related to the refractive index $n$ of the solvent. Unfortunately
there is no agreement regarding the equation relating $F$ to $n$. Thus, Lewis and Kasha\textsuperscript{53} suggest the simple relation:

$$(1) \quad F = n^2$$

whilst Rubinowicz\textsuperscript{54} recommends the more elaborate relation:

$$(2) \quad F = \frac{9n}{(n^2 + 2)^2}$$

Both equations give $F = 1$ for $n = 1$. When $n$ increases, (1) gives $F > 1$ and (2) $F < 1$, the deviation increasing with $n$. The general practice being\textsuperscript{32,52} to consider $F = 1$ for most common solvents ($n = 1.3$ to $1.6$), I conformed to this and suppressed the $F$ term.

Although in modern quantum mechanics\textsuperscript{49} the oscillator strength is rather seen in statistical terms, as related to the transition probabilities for induced emission and absorption, the above treatment remains valid\textsuperscript{50} for determining experimental oscillator strengths, and was used as such in this work.

Considering that the absorption peaks of the carbonium ions studied here were seldom symmetrical, their area was determined (after plotting the spectrum on a linear $\mathcal{E}$ and cm.\textsuperscript{-1} scale) either by graphical integration, or by cutting and weighing the spectrum plotted on paper of uniform thickness.
3.7.3 Ultraviolet and visible spectroscopy.

Note: For reasons of simplicity, a new numbering (Tables A and B) has been adopted for compounds and cations considered in this and the following sections.

The compounds (NoP) in Table A were protonated by 98% \( \text{H}_2\text{SO}_4 \) to the corresponding cations (NoC) in Table B:

<table>
<thead>
<tr>
<th>Table A</th>
<th>Table B</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP  diphenylmethanol</td>
<td>IC  diphenylmethyl</td>
</tr>
<tr>
<td>IIIP phenyl-(2'-methylphenyl)-methanol</td>
<td>IIC phenyl-(2'-methylphenyl)-methyl</td>
</tr>
<tr>
<td>IIIP phenyl-(2'-ethylphenyl)-methanol</td>
<td>IIIC phenyl-(2'-ethylphenyl)-methyl</td>
</tr>
<tr>
<td>IVP 1,1-diphenylethylene</td>
<td>IVC 1,1-diphenylethyl</td>
</tr>
<tr>
<td>VP  1-phenyl-1-(2'-methylphenyl)-ethanol</td>
<td>VC 1-phenyl-1-(2'-methylphenyl)-ethyl</td>
</tr>
<tr>
<td>VIP 1-phenyl-1-(2'-ethylphenyl)-ethanol</td>
<td>VIC 1-phenyl-1-(2'-ethylphenyl)-ethyl</td>
</tr>
<tr>
<td>VIIP 1,1-diphenylbut-1-ene</td>
<td>VIIC 1,1-diphenyl-n-butyl</td>
</tr>
<tr>
<td>VIIIIP 3-phenylindene</td>
<td>VIIIC 1-phenylindanyl</td>
</tr>
<tr>
<td>IX  1-methyl-3-phenylindene</td>
<td>IX  3-methyl-1-phenylindanyl</td>
</tr>
</tbody>
</table>

The structures of ions IC to IXC are shown in Table 7.
Table 7 (p. 123)

<table>
<thead>
<tr>
<th>Code</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC</td>
<td>Diphenylmethyl</td>
</tr>
<tr>
<td>IIC</td>
<td>Phenyl-(2'-methylphenyl)methyl</td>
</tr>
<tr>
<td>IIIC</td>
<td>Phenyl-(2'-ethylphenyl)methyl</td>
</tr>
<tr>
<td>IVC</td>
<td>1,1-Diphenylethyl</td>
</tr>
<tr>
<td>VC</td>
<td>1-Phenyl-1-(2'-methylphenyl)ethyl</td>
</tr>
<tr>
<td>VIC</td>
<td>1-Phenyl-1-(2'-ethylphenyl)ethyl</td>
</tr>
<tr>
<td>VIIC</td>
<td>1,1-Diphenyl-n-butyl</td>
</tr>
<tr>
<td>VIIIC</td>
<td>1-Phenylindanyl</td>
</tr>
<tr>
<td>IXC</td>
<td>3-Methyl-1-phenylindanyl</td>
</tr>
</tbody>
</table>
Spectra were scanned with $10^{-5}$ and $10^{-4}$M solutions (Sec. 3.7.2.2) from 700 mµ down to 220 mµ. In order to ensure the best accuracy, each compound was protonated at least two times and separate spectra run. The protonations were virtually instantaneous, and the ions remained stable for many days, when kept at 0°, and even for many months (cations VIIIC and IXC).

All spectra exhibited two well shaped maxima, one at around 300 mµ and one between 412 and 447 mµ; the latter absorption always having the higher extinction coefficient and being responsible for the colour of the solutions. Carbonium ions absorbing only at around 300 mµ and below give colourless solutions; for instance the tropylium cation, $\lambda_{\text{max}}^{20} 274$ and 217 mµ and the dimethylphenylmethyl cation, $\lambda_{\text{max}}^{30} 325$ mµ (this work and Ref. 12).

The colour of dilute solutions ($10^{-5}$M) was from pale yellow to greenish yellow, as the wavelength increased. In the same way, the colour of more concentrated solutions ($10^{-2}$M and above) went from greenish yellow (cations VIIIC and IXC) to yellow ochre (IVC to VIIC) and deep red (IC to IIIC). Chichibabin$^{55}$ observed already in 1909 that sulphuric acid solutions of IIP were red.

Table 8 summarises the spectroscopic data obtained, in the order: short and long wavelength maxima in millimicrons and in cm.$^{-1}$, extinction coefficients, oscillator strength $f$ of separate peaks, ratio $f_{\text{sh.}}/f_{\text{l.}}$, and total $f$. ($f_{\text{sh.}}/f_{\text{l.}}$ = ratio $f$ short wavelength to $f$ long wavelength).
Table 8
(ref. page 129)

<table>
<thead>
<tr>
<th>Cation</th>
<th>m(\mu)</th>
<th>(10^{-3}\text{cm}^{-1})</th>
<th>(10^{-3}\varepsilon)</th>
<th>(f)</th>
<th>(f_{\text{sh.}}/f_{\text{l.}})</th>
<th>(f_{\text{tot.}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC</td>
<td>304</td>
<td>32.9</td>
<td>2.8</td>
<td>0.060</td>
<td>0.085</td>
<td>0.766</td>
</tr>
<tr>
<td></td>
<td>442</td>
<td>22.6</td>
<td>60.6</td>
<td>0.706</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IIIC</td>
<td>306</td>
<td>32.7</td>
<td>3.4</td>
<td>0.070</td>
<td>0.106</td>
<td>0.730</td>
</tr>
<tr>
<td></td>
<td>446</td>
<td>22.4</td>
<td>48.5</td>
<td>0.660</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IIIIC</td>
<td>307</td>
<td>32.6</td>
<td>4.2</td>
<td>0.086</td>
<td>0.135</td>
<td>0.722</td>
</tr>
<tr>
<td></td>
<td>447</td>
<td>22.4</td>
<td>47.6</td>
<td>0.636</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IVC</td>
<td>314</td>
<td>31.8</td>
<td>12</td>
<td>0.189</td>
<td>0.36</td>
<td>0.713</td>
</tr>
<tr>
<td></td>
<td>427</td>
<td>23.4</td>
<td>39</td>
<td>0.524</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VC</td>
<td>320</td>
<td>31.25</td>
<td>10.3</td>
<td>0.182</td>
<td>0.4</td>
<td>0.634</td>
</tr>
<tr>
<td></td>
<td>431</td>
<td>23.2</td>
<td>26</td>
<td>0.452</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIC</td>
<td>323</td>
<td>30.95</td>
<td>11</td>
<td>0.185</td>
<td>0.42</td>
<td>0.624</td>
</tr>
<tr>
<td></td>
<td>434</td>
<td>23.05</td>
<td>27</td>
<td>0.439</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIIC</td>
<td>321</td>
<td>31.15</td>
<td>13</td>
<td>0.180</td>
<td>0.36</td>
<td>0.680</td>
</tr>
<tr>
<td></td>
<td>431</td>
<td>23.2</td>
<td>40</td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIIIC</td>
<td>302</td>
<td>33.1</td>
<td>13</td>
<td>0.148</td>
<td>0.23</td>
<td>0.790</td>
</tr>
<tr>
<td></td>
<td>412</td>
<td>24.3</td>
<td>37</td>
<td>0.642</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IXIC</td>
<td>304</td>
<td>32.9</td>
<td>12</td>
<td>0.157</td>
<td>0.275</td>
<td>0.752</td>
</tr>
<tr>
<td></td>
<td>415</td>
<td>24.1</td>
<td>35</td>
<td>0.595</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A first look at this table shows that the oscillator strength is much more informative than the extinction coefficient (Sec. 2.7.2.3). For instance, the ratio of the long wavelength peak extinction coefficients of cations IC and VIIIC is $60,600/37,000 = 1.64$; on the other hand the $f$ ratio for the same peaks is $0.706/0.642 = 1.10$; finally, the $f$ ratio for the entire spectra is $0.766/0.790 = 0.97$. Thus, while the ratio of $\varepsilon$ suggested that the absorption of cation IC is higher than the absorption of cation VIIIC, the $f$ ratio shows that the opposite is true.

A closer examination of Table 8 reveals the following features (refer also to Fig. 30 - 38):

a) In homologous series of cations (IC-IIIC, IVC and VIIIC, IVC-VIC, VIIIC-IXC) the wavelength of all peaks increases when alkyl substituents are introduced.

b) In the series IC-IIIC and IVC-VIC, the wavelength increase appears to be more related to the substitution itself, than to the chain length of the substituent (when moderate). Thus, when a methyl is substituted for an ortho hydrogen in IC and IVC to give respectively IIC and VC, the bathochromic shift of the low wavelength peak is $200 \text{ cm}^{-1}$ for IIC and $600 \text{ cm}^{-1}$ for VC. When the ortho-ethyl monosubstituted cations IIIC and VIC are compared to IIC and VC, the low wavelength bathochromic shift becomes 100 and 300 cm.$^{-1}$ respectively, which is one
half of the above figures. This experimental finding confirms the hypothesis (Section 3.6.1) that the u.v. spectra of IIIC and of the phenyl-(2'-isopropylphenyl)methyl cation must be very similar, as predictable from published data on symmetrically disubstituted\textsuperscript{44} and polysubstituted\textsuperscript{48} diphenylmethyl cations.

c) Considering the same series of cations, it clearly appears that the total oscillator strength decreases with substitution. Again, as for the wavelength variation above, the decrease of $f$ is much greater at the first step (appearance of substitution) that at the second (increasing chain length of substituent). (An analogous variation pattern of the extinction coefficient of unsubstituted and ortho-methyl, ethyl and isopropyl $N,N$-dimethylanilines has been observed by Burgers et al.$^{56}$). Moreover, the decrease of $f$ is more important in the diphenylethyl than in the diphenylmethyl cations series.

Thus, when going from IC to IIC and IIIC, $\Delta f$ is respectively $-36$ and $-8$ ($-5.7\%$ together); when going from IVC to VC and VIC, $\Delta f$ is $-79$ and $-10$ ($12.5\%$ together).

The disparity of the variation of the oscillator strength could become clear if hindrance to planarity were held responsible for it. Steric crowding is higher in the diphenylethyl cations, and hence planarity is more hindered.
However, Deno et al.\textsuperscript{33} have claimed that absorption spectra cannot be used to measure steric inhibition of resonance in arylmethyl cations. These authors calculated oscillator strengths for mono-, di-, and triphenylmethyl cations using the approximation that the oscillator strength is proportional to the square of the difference in dipole moment between the first excited state and the ground state (as suggested by Murrell and Pople\textsuperscript{57}), and found that the vectors contributing over 96\% of the dipole moment are invariant to rotation of the phenyl rings. The calculations predicted also that the oscillator strength of mono-, di-, and triphenylmethyl cations will be respectively 0.25, 0.94, and 1.60. The predicted $f$ for diphenylcarbonium ions is in satisfactory agreement with my experimental values, which vary from 0.624 to 0.790.

d) Another interesting feature appears when the oscillator strength ratio of the short to the long wavelength peaks is established. This ratio increases in all the series considered above, showing a relative increment of the contribution from the high energy transitions. Moreover, this ratio is much higher in the diphenylethyl cation series IVC-VC-VIC (respectively 0.36, 0.4, and 0.42) than in the diphenylmethyl cation series IC-IIIC-IIIC (respectively 0.085, 0.106, and 0.135). This could show a higher phenylalkylcarbonium ion
character in the former (due to hyperconjugation) than in the latter cations, in consistence with the well established fact that monophenylalkylcarbonium ions exhibit their major peak $^{12,24}$ in the low wavelength region, around 300-350 m$\mu$.

The spectra of cations IC-VIC, VIIIC, and IXC are displayed in Fig. 30 to 33.

Fig. 34 and 35 illustrate the variation of $\lambda_{\text{max}}$ and $f$ in the two diphenylmethyl and diphenylethyl cation series.

The spectra of increasingly substituted diphenylcarbonium ions and diphenylmethylcarbonium ions are compared in Fig. 36 A, B, and C.

Fig. 37 shows the extensive spectroscopic modification brought about by cyclisation, in otherwise identically substituted diphenylalkylcarbonium ions. The higher oscillator strength observed for the cyclic cation: 0.752, as compared to 0.624 for the open homologue, is well consistent with the suggestion (Olah and Pittman$^{24}$ and Section 3.6.7.3 of this work) that the locked-in planarity is responsible for the higher stability of indanyl cations. The same comparison can be established for the two homologous cations VC (open) and VIIIC (cyclic).

Fig. 38 shows the spectral changes brought in by a lengthening of the alkyl substituent directly attached to the ionic carbon. More information about similar changes was made available in a recent
publication by Olah and co-workers. These authors report the spectra of diphenylalkylcarbonium ions in \( \text{FSO}_3\text{H-SbF}_5 \) solution; the alkyl substituents being: methyl, ethyl, isopropyl, cyclopropyl, cyclobutyl, and cyclohexyl.
Fig. 30 (page 133)

Spectra of the diphenylmethyl (dashed) and the 1,1-diphenyl-ethyl (full) cations plotted on linear $\varepsilon$ and cm.$^{-1}$ scales in order to allow determination of the oscillator strength.
Spectra of the phenyl-(2'-methylphenyl)methyl (dashed) and the 1-phenyl-1-(2'-methylphenyl)ethyl (full) cations, plotted on linear $\varepsilon$ and cm.$^{-1}$ scales in order to allow determination of the oscillator strength.
Fig. 32 (page 133)

Spectra of the phenyl-\((2'\text{-ethylphenyl})\)methyl (dashed) and the 1-phenyl-1-\((2'\text{-ethylphenyl})\)ethyl cations, plotted on linear \(\varepsilon\) and cm.\(^{-1}\) scales in order to allow the calculation of the oscillator strength.
Fig. 33 (page 133)

Spectra of the 1-phenylindanylid and the 3-methyl-1-phenylindanylid cations, plotted on linear $\varepsilon$ and cm.$^{-1}$ scales in order to allow the calculation of the oscillator strength.
Fig. 34 (page 133)

Spectra of the three diphenylmethy1 cations, showing the sharp decrease of ε when substitution on the ring is brought in. Note that the area under the peaks is much less altered than ε.

Fig. 35 (page 133)

Series of three diphenylethyl cations. Same remarks as above.
Spectra of homologous diphenylmethyl and diphenylethyl cations compared. Note the decrease of the long wavelength peak and the corresponding increase of the short wavelength absorption when going from the diphenylmethyl to the corresponding diphenylethyl cations.
Fig. 37 (page 133)

Illustration of the effect of cyclisation on the u.v. spectrum exhibited by two otherwise identically substituted carbonium ions.

Fig. 38 (page 133)

This Fig. shows the very minor change in the spectrum of diphenylcarbonium ions when the alkyl substituent (on the ionic carbon) is made longer.
3.7.4 Proton magnetic resonance spectroscopy.

3.7.4.1 Foreword. Compounds IP to IXP (Table A, page 128) were protonated to the corresponding cations IC to IXC (Table B, page 128), as 5-10% solutions in $\text{H}_2\text{SO}_4$, $\text{D}_2\text{SO}_4$, or $\text{HSO}_3\text{Cl}$. Cation VIIIC was also formed from VIIIP in $\text{HClO}_4 - \text{CH}_2\text{Cl}_2$.

Although all compounds (except IP, IIP, and IXP) were protonated satisfactorily when added undilute to the acid, the best results were obtained when the precursor was extracted by the acid from a carbon tetrachloride solution (sections 2.2.8 and 3.7.2).

Fig. 39 to 47 show the good resolution obtained with a Perkin-Elmer Model R 10, 60 Mc. spectrometer equipped with a probe thermostatted at $35^\circ$. In a general way, slightly better resolution was obtained in $\text{HSO}_3\text{Cl}$ than in $\text{H}_2\text{SO}_4$, probably because of the lower viscosity of the former.

All spectra are given in $\tau$ (Tau) units, with the TMS peak at 10 $\tau$ (in p.p.m.) and the TMAS (tetramethylammonium sulphate) peak at 6.90 $\tau$. The integrated areas corresponded to the assigned structure in every case. For the sake of clarity and compactness, the integration trace has been omitted from most spectra.

All precursor spectra were scanned using 1 M solutions in carbon tetrachloride (unless stated otherwise).

The deshielding of protons in the carbonium ions is expressed
in p.p.m. downfield relative to the position of the same protons in the spectra of the corresponding carbinols. No variation of the chemical shifts was observed when comparing spectra in H_2SO_4 and HSO_3Cl, and when changing the concentration of the precursor (to be protonated) from 5 to 10%.

All n.m.r. data are summarized in Table 9.

3.7.4.2 Phenylindanyl cations. Spectra of the 1-phenylindanyl cation in H_2SO_4, HClO_4·CH_2Cl_2, HSO_3Cl, and D_2SO_4 are displayed in Fig. 39, along with the spectra of 3-phenylindene, and of the same compound recovered from the H_2SO_4 solution. The stability of the cation is best shown by comparing the spectra in H_2SO_4 run 10 min. after the protonation and after 15 days: no change is observed. The four indanyl ring protons form a clean and simple A_2B_2 spectrum with peaks at 5.87 and 6.35  \( \tau \), the low field peak belonging to the protons on the carbon  n° 2 (carbon n° 1 bearing the positive charge), as shown by the smearing out of this peak in D_2SO_4 and in HClO_4·CH_2Cl_2. Deno et al.\textsuperscript{39} studied the 1-methylindanyl cation in 96% H_2SO_4 and found a similar shift for the indanyl protons on carbon 2 and 3, respectively 6.16 and 6.44 \( \tau \). The slightly lower Tau values in the 1-phenylindanyl cation are consistent with a higher deshielding due to the extra phenyl ring.

Fig. 40 shows the spectra of 1-methyl-3-phenylindene before protonation, 3-methyl-1-phenylindanyl cation, and the indene
<table>
<thead>
<tr>
<th>Cation</th>
<th>$\mathcal{T}$ in carbinol</th>
<th>$\mathcal{T}$ in cation</th>
<th>Downfield shift in p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph[C^+\text{-CH}_3] (a)</td>
<td>(a) 8.13</td>
<td>6.33</td>
<td>1.80</td>
</tr>
<tr>
<td>(b)</td>
<td>8.20</td>
<td>6.36</td>
<td>1.84</td>
</tr>
<tr>
<td>Ph[C^+\text{-H}] (a)</td>
<td>(a) 4.3</td>
<td>-0.15</td>
<td>4.45</td>
</tr>
<tr>
<td>(b)</td>
<td>7.9</td>
<td>7.12</td>
<td>0.78</td>
</tr>
<tr>
<td>CH[CH_3] (b)</td>
<td>(c) 8.98</td>
<td>8.6</td>
<td>0.38</td>
</tr>
<tr>
<td>Ph[C^+\text{-H}] (a)</td>
<td>(a) 4.3</td>
<td>-0.13</td>
<td>4.43</td>
</tr>
<tr>
<td>(b)</td>
<td>7.53</td>
<td>6.75</td>
<td>0.78</td>
</tr>
<tr>
<td>(c)</td>
<td>8.98</td>
<td>8.6</td>
<td>0.38</td>
</tr>
<tr>
<td>CH[CH_2CH_3] (b) (c)</td>
<td>(c) 9.25</td>
<td>8.82</td>
<td>0.43</td>
</tr>
<tr>
<td>Ph[C^+\text{-CH}_3] (a)</td>
<td>(a) 8.22</td>
<td>6.33</td>
<td>1.89</td>
</tr>
<tr>
<td>(b)</td>
<td>7.63</td>
<td>7.34</td>
<td>0.29</td>
</tr>
<tr>
<td>(c)</td>
<td>9.25</td>
<td>8.82</td>
<td>0.43</td>
</tr>
<tr>
<td>Ph[C^+\text{-CH}_2\text{-CH}_2\text{-CH}_3] (a) (b) (c)</td>
<td>(a) 7.8</td>
<td>6.1</td>
<td>1.70</td>
</tr>
<tr>
<td>(b)</td>
<td>8.80</td>
<td>8.06</td>
<td>0.74</td>
</tr>
<tr>
<td>(c)</td>
<td>9.12</td>
<td>8.9</td>
<td>0.22</td>
</tr>
</tbody>
</table>
N.m.r. spectra of the 1-phenylindanyl cation in different acids and at various time intervals.

The precursor 3-phenylindene (top) was recovered (bottom) using fast dispersal methods.14
N.m.r. spectra of 1-methyl-3-phenylindene, of the 3-methyl-1-phenylindanyl cation (5\% solution in HSO₃Cl) and of the precursor recovered in nearly quantitative yield.

Note: the 3-methyl-1-phenylindanyl cation exhibits exactly the same spectrum as above when formed in 98\% H₂SO₄.
Fig. 40

Precursor recovered from the cation
recovered from the 5% HSO₃Cl solution of the carbonium ion.

The perfectly clean spectrum of the 3-methyl-1-phenylindanyl cation illustrates the good resolution obtained even when complex proton interactions occur. Thus, the central part of this spectrum (Fig. 40), between 5.3 and 6.5 Tau, represents the interaction of the three magnetically non-equivalent indanyl protons A, B, and C, separated from each other by chemical shifts of the same order of magnitude as the coupling constants between them, and constituting a typical ABC system. The full analysis of such a spectrum would involve elaborate computer techniques and is beyond the scope of this work. The only parameter which can be directly determined here is the spin-spin coupling constant Jₐₑ₃ for the protons A and B, and this is 24 c.p.s. Although unusually large, this value compares with the geminal coupling constant of the same methylene protons in 3-methylindan-1-one, which is 19 c.p.s., as determined in this work; Maréchal, Basselier, and Sigwalt have performed the full analysis of the spectrum of this ketone, and give the slightly lower value of 18.5 c.p.s. for Jₐₑ₃.

The comparison of the p.m.r. of 3-methylindan-1-one and of the 3-methyl-1-phenylindanyl cation (Fig. 41) can be justified, at least as far as the system formed by the methyl and the three indane ring protons is concerned: both structures have a built-in planarity, due to the trigonally (sp²) hybridised carbon atom in position 1. If the relation established between the geminal coupling
constant and the H−C−H angle is assumed to be valid for the two systems discussed above, the bond angle between the methylene hydrogens is found\(^{60}\) to be 105.5° for the indanone and 103° for the indanyl cation. The bond angle difference, 2.5°, is small enough to be accounted for by conventional steric factors brought in by the extra phenyl ring in the carbonium ion. Alternatively, the increase of \(J_{\text{gem}}\) HH in the cation could be due to a combination of bond angle decrease and stereo-electronic interaction which is inherent to the charge delocalisation.

Fig. 41 shows the p.m.r. spectra of the 1-phenylindanyl (VIIIC) and 3-methyl-1-phenylindanyl cations as compared to the spectra of the corresponding ketones: indan-1-one (XXVII) and 3-methylindan-1-one (XXVIII). The \(A_2B_2\) spectrum formed by the four methylene protons of XXVII is shifted downfield without any major alteration, in cation VIIIC. More extensive changes are observed when considering the spectra of IXC and XXVIII. The simple ABX spectrum\(^{59}\) formed by the three indane ring protons of XXVIII is transformed to an ABC spectrum in cation IXC. This modification is due to the fact that the methylene protons experience a higher deshielding than the proton in position 3, with a consequence that all three protons resonate at much closer frequencies and thus generate a more complex interacting system, ABC.
The n.m.r. spectra of the 1-phenylindany1 and 3-methyl-1-phenylindany1 cations are compared to the spectra of the corresponding ketones, in order to illustrate the similarity of the spectra of the protons in position 2 (considering the downfield shift). Both cations are as 5% solution in HSO\textsubscript{3}Cl, and the ketones as 10% solutions in CCl\textsubscript{4}.
3.7.4.3 Diphenylmethyl and diphenylethyl cations. The p.m.r. spectra of the three diphenylmethyl cations IC, IIC, and IIIC, and the three 1,1-diphenylethyl cations IVC, VC, and VIC (Section 3.7.3) are displayed along with the spectra of their precursors in Fig. 42-46.

Fig. 42 compares the spectra of the diphenylmethyl and 1,1-diphenylethyl cations with the spectra of the corresponding diphenyl and methyldiphenyl carbinols. The n.m.r. spectra of both cations have been investigated by Olah (using SO₂-SbF₅ at -30°C) and Farnum (using HSO₃Cl at -20°C and measuring the spectrum at room temperature). These authors were interested in studying the chemical shifts and the long range shielding effects, and did not attempt to establish any spectroscopic correlation with the precursors. The agreement between the published spectroscopic data and the values found in my work is excellent, and shows the insensitivity of the chemical shifts to temperature variations and to solvent effects. Thus, the methyl protons of the methyldiphenylcarbonium ion are found at 6.33 Tau in 98% H₂SO₄ at 35°C (my work), at 6.30 Tau in SO₂-SbF₅ at -30°C (Olah), and at 6.33 Tau in HSO₃Cl at room temperature (Farnum). The actual value published by Farnum is 6.30 Tau, with reference to the tetramethylammonium ion peak at 6.87. The value for the TMAS peak taken in my work as 6.90 (as recommended by Deno et al.), Farnum's value is
to be increased by 0.03 Tau in order to make a fair comparison.

The agreement of these data confirms moreover the adequacy of the TMA ion as internal standard for strongly acidic solutions, considering the fact that Olah's value is referred to TMS as internal standard. The very small difference observed (0.03 p.p.m.) is well within the range of experimental scatter.

Fig. 43 shows the spectra of phenyl-(2'-methylphenyl)methanol in CCl₄ and the corresponding phenyl-(2'-methylphenyl)methyl cation in 98% H₂SO₄ and 98% D₂SO₄. As expected, the hydrogen directly bonded to the ionic carbon is highly deshielded (by 4.45 p.p.m. as compared to 4.28 p.p.m. in the diphenylmethyl cation, Fig. 42). In D₂SO₄ this hydrogen is exchanged in less than 2 min. at 35°. The methyl hydrogens exhibit the same peak in H₂SO₄ and D₂SO₄ and are deshielded by 0.78 p.p.m.

The spectra of 1-phenyl-1-(2'-methylphenyl)ethanol in CCl₄ and of the 1-phenyl-1-(2'-methylphenyl)ethyl cation in H₂SO₄ and D₂SO₄ are shown in Fig. 44. The perfect stability of the cation is shown by the identity of spectra run 10 min. and 15 days after its formation. The hydrogens of the methyl group attached to the ionic carbon are deshielded by 1.84 p.p.m. and those of the methyl group attached to the phenyl ring by 0.48 p.p.m. (0.30 p.p.m. less than the same hydrogens in IIC, Fig. 43). The validity of the
chemical shift assignment is confirmed by the disappearance of
the low field peak (6.36 Tau) in $D_2SO_4$, whilst the high field peak
remains unaltered.

Fig. 45 displays the spectra of phenyl-(2'-ethylphenyl)-
methanol in $CCl_4$, and of the phenyl-(2'-ethylphenyl)methyl cation in
$HSO_3Cl$. The clean $A_2X_3$ spectrum formed of the five ethyl protons in
IIIC illustrates the excellent resolution obtained in $HSO_3Cl$ at 35°;
slightly less sharp peaks are obtained in $H_2SO_4$. The hydrogen
bonded to the carbonium carbon is deshielded by 4.43 p.p.m. to
-0.13 Tau (as compared to 4.45 p.p.m. in IIC). The methylene protons
are deshielded by 0.78 p.p.m. (exactly the same value as for the
protons of the methyl group attached to the ring in IIC, Fig 43).
The methyl protons are deshielded by 0.38 p.p.m.

Fig. 46 displays the spectra of 1-phenyl-1-(2'-ethylphenyl)-
ethanol in $CCl_4$, and of the 1-phenyl-1-(2'-ethylphenyl)ethyl cation
in $H_2SO_4$ and $D_2SO_4$. The protons of the methyl group attached to the
ionic carbon are deshielded by 1.89 p.p.m. (as compared to 1.84
p.p.m. in VC and 1.80 p.p.m. in IVC, Fig. 44 and 42 respectively).
The methylene protons are deshielded by 0.29 p.p.m. (0.49 p.p.m. less
than the same hydrogens in IIIC, Fig. 45). The second methyl
protons are deshielded by 0.43 p.p.m.
N.m.r. spectra of the diphenylmethyl and the diphenylethyl cations (5% solutions in $\text{H}_2\text{SO}_4$) compared to the spectra of the corresponding carbinols. Note the high deshielding (4.28 p.p.m.) of the hydrogen attached directly to the ionic carbon.
N.m.r. spectra of the phenyl-(2'-methylphenyl)methyl cation (IIC) as 5% solution in H_2SO_4 and D_2SO_4, compared with the spectrum of the precursor.

Note the disappearance of the peak due to the hydrogen directly bonded on the ionic carbon (-0.15 ppm) when the cation is formed in D_2SO_4.
N.m.r. spectra of the 1-phenyl-1-(2'-methylphenyl)ethyl cation (VC) in H₂SO₄, 10 min. after its formation and after 15 days, and in D₂SO₄, after 10 min., compared to the spectrum of the corresponding carbinol. The remarkable stability of the cation is illustrated by the fact that the spectrum is unchanged after 15 days. Note the disappearance of the peak belonging to the hydrogens of the methyl group directly bonded to the ionic carbon when the cation is formed in D₂SO₄.
Fig. 44
N.m.r. spectrum of the phenyl-(2'-ethylphenyl)methyl cation (IIIC) as 5% solution in HSO₃Cl compared to the spectrum of the precursor (1 M sol. in CCl₄).

Note the high deshielding of the hydrogen directly bonded to the ionic carbon (-0.13 Tau), and the good resolution of the methylene quadruplet and the methyl triplet.
N.m.r. spectra of the 1-phenyl-1-(2'-ethylphenyl)ethyl cation (VIC) in H$_2$SO$_4$ and D$_2$SO$_4$, both scanned 10 min. after formation, compared to the spectrum of the corresponding carbinol.

Note the beautiful resolution obtained and the disappearance in D$_2$SO$_4$ of the hydrogens of the methyl group attached to the charged carbon atom.
Fig. 46
3.7.4.4 The 1,1-diphenyl-n-butyl cation, VIIC. The spectra of this cation and of its precursor are displayed in Fig. 47. The cation was obtained quantitatively both from the carbinol and from the corresponding olefin 1,1-diphenylbut-1-ene, in H₂SO₄ and in HSO₃Cl. The deshielding of the alkyl protons in VIIC resolves the A₂B₃ spectrum with overlapping peaks of VIIP into a clear A₂X₃ spectrum showing the methyl triplet and the median methylene hextuplet (hextuplet and not quadruplet, due to the further interaction with the α methylene protons); as expected for an A₂X₃ system, both groups are symmetrically distorted. The α methylene protons are deshielded by 1.70 p.p.m. (as compared to 1.80, 1.84, and 1.89 p.p.m. respectively, for the methyl protons of cations IVC, VC, and VIC).
N.m.r. spectrum of the 1,1-diphenyl-n-butyl cation
compared to the spectrum of the corresponding carbinol.
Note the resolving of the complex $A_2B_3$ spectrum (carbinol)
to a triplet and sextuplet (cation) due to the downfield
shift (deshielding).
3.7.4.5 Summary and discussion. With reference to Table 9 and Fig. 42 - 47, the following facts can be established:

a) Protons bound directly to the ionic carbon experience the highest deshielding, which is 4.45 p.p.m. for IIC and 4.43 p.p.m. for IIIC.

b) Protons belonging to methyl groups directly bound to the ionic carbon experience a very similar deshielding. Thus, in the series IVC, VC, and VIC the deshielding is respectively (in p.p.m.) 1.80, 1.84, and 1.89; these values are in further agreement with the deshielding of the methylene protons of VIIC (1.70 p.p.m.).

c) A linear relation is found between the number of bonds separating a proton from the ionic carbon and the log of its deshielding value in p.p.m., as shown in Fig. 48.

d) Hydrogens directly bound to the ionic carbon, or separated from it by two bonds (cases a and b above) exchange completely in D₂SO₄.

e) Hydrogens belonging to methyl and methylene groups directly linked to the phenyl rings, in ortho position, experience a higher deshielding in the diphenylmethyl cations (0.78 p.p.m. for IIC and IIIC) than in the diphenylethyl cations (0.48 p.p.m. for VC and 0.29 p.p.m. for VIC). The difference of deshielding for these hydrogens is thus 0.30 p.p.m.
Correlation between the number of bonds separating a proton from the ionic carbon and the deshielding (downfield shift) in p.p.m.

Point 1 refers to protons directly bound to the ionic carbon (in cations IC, IIC, and IIIC).

Points 2, 3, and 4 refer to protons a, b, and c of the 1,1-diphenyl-n-butyl cation (Fig. 47).
Fig. 48

downfield shift (in p.p.m.)

number of bonds
between IIIC and VIC, and 0.49 p.p.m. between IIIC and VIC.

f) Hydrogens belonging to methyl groups separated from the phenyl ring by a methylene (ethyl terminal hydrogens) experience a slightly higher deshielding in the diphenyl-ethyl cation VIC (0.43 p.p.m.) than in the diphenylmethyl cation IIIC (0.38 p.p.m.). Moreover, the deshielding sequence of the ortho-ethyl hydrogens is quite unexpectedly reversed for cation VIC (see Table 9): 0.29 p.p.m. for the methylene protons and 0.43 p.p.m. for the methyl protons. Normally, the low field shift (relative to the corresponding carbinol) should be the higher, the closer the protons are to the positive charge delocalised over the phenyl ring, and this is what actually happens for the ortho-ethylphenylphenylmethyl cation IIIC, where the deshielding is 0.78 p.p.m. for the methylene protons and 0.38 p.p.m. for the methyl protons.

g) Hydrogens of methyl and methylene groups directly bound to the phenyl ring of diphenylmethyl cations (respectively IIIC and IIIC) experience exactly the same deshielding, which is 0.78 p.p.m.

Some of the findings stated above fit with facts which have already been observed. Thus, the high deshielding of hydrogens directly bound to the ionic carbon was observed by Farnum and
and by Olah\textsuperscript{46}. The decrease of deshielding with increasing number of bonds separating a hydrogen from the ionic carbon was observed in alkylcarbonium ions by Olah et al.\textsuperscript{61} The fast exchange in D\textsubscript{2}SO\textsubscript{4} of hydrogens close to the ionic carbon was observed for the 1-methylindanyl cation and other monophenylcarbonium ions by Deno et al.\textsuperscript{39}

On the other hand, the findings related under the headings \textsuperscript{e}, \textsuperscript{f}, and \textsuperscript{g} have apparently been observed for the first time in this work, and may have a fairly interesting significance.

The fact that hydrogens attached to the ortho substituents experience a higher deshielding in the diphenylmethyl cations IIIC and IIID than in the diphenylethyl cations VC and VIC could be interpreted by assuming that the diphenylethyl cations exhibit a hyperconjugation effect,\textsuperscript{21,64} due to the methyl group directly bound to the ionic carbon, allowing more resonating forms, with a subsequent lower charge delocalisation over the phenyl rings (than in the diphenylmethyl cations), and hence a lower deshielding.

The reversed deshielding of the ethyl protons in VIC could be explained in terms of the hyperconjugation, creating a steric interaction effect, whose net results is a higher deshielding of proton (c) than of proton (b). In other words, the deshielding effect of the positive charge distributed over the phenyl rings
is counterbalanced by the effect of the positive charge distributed over the methyl group attached to the ionic carbon:

\[ \text{Ph} \xrightarrow{+} \text{CH}_3 \]

An indirect support for the hypothesis of hyperconjugation in the 1,1-diphenylethyl cations is found in the investigation of the electronic absorption spectra of cations ICl - VIC (Table 8). These spectra always exhibit two maxima: one in the 300 - 320 nm region, and one above 400 nm, the extinction coefficient and the oscillator strength of the latter peak being the higher. When the ratio of the oscillator strengths of the low wavelength peak to the high wavelength peak is considered, it appears that it is much higher (0.36 - 0.42) for the diphenylethyl cations than for the diphenylmethyl cations (0.085 - 0.135). The oscillator strengths of the low wavelength peaks follow the same pattern, and are respectively 0.182 to 0.189 and 0.06 to 0.085 (Table 8).

The well established fact\(^\text{12,24}\) that monophenylalkylcarbonium ions exhibit their major absorption peak in the 320 nm region may show the appearance of a partial monoaryl character (due to hyperconjugation and to steric factors) in the 1,1-diphenylethyl cations.
A last observation concerns the identical deshielding (0.78 p.p.m.) of protons (b) in cations IIC and IIIC. Unless this identity is attributed to coincidence, it should show that the charge delocalisation over the disubstituted phenyl ring is very nearly the same in both cations, i.e., the conjugation with the ionic carbon is not affected in this particular case by the introduction of a bulkier substituent. Again, reference to the electronic spectra of these cations supports the n.m.r. findings. Reference to Table 8 shows that the total oscillator strengths for cations IIC, IIC, and IIIC are respectively 0.766, 0.730, and 0.722. It clearly appears that the variation of \( f \) is of some importance (4.7%) when a substituent is introduced; moderate increase of the volume of the substituent causes a much smaller variation (1.1%).
SUGGESTIONS FOR FURTHER WORK

4.1 Ionisation mechanism of 1-methyl-3-phenylindane.

Although good circumstantial evidence supports the proposed hydride abstraction mechanism (Sec. 3.6.7.2), more experimental work is required for its unambiguous establishment (or rejection).

One point on which further experimentation should concentrate is the conductimetric study of the interaction of 1-methyl-3-phenylindane with a large excess of HClO₄ in CH₂Cl₂. I have shown that the induction period observed when styrene interacts with excess HClO₄ (Sec. 3.2.3.2) is due to the dimerisation and cyclisation reactions, during which no increase of conductivity is noticed. The logical deduction from this is that when the cyclic dimer is made to react directly with HClO₄ in protonation conditions, no induction period should be observed.

The induction period being very short (seconds) even at the lowest concentrations, this investigation should be carried out using the conductivity cell n°II (page 35) with which the time interval between mixing of the reagents and the recording of the conductivity is reduced to less than 1 sec.
4.2 Spectroscopy of carbonium ions.

The correlations deduced from u.v., visible, and n.m.r. spectroscopy discussed in sections 3.7.3 and 3.7.4.5 could constitute the experimental basis of a semi-quantitative evaluation of electron density repartition in arylalkylcarbonium ions, and should deserve further investigation.

The study should extend also to meta- and para-alkyl substituted diphenylmethyl and diphenylethyl cations. Thus, the anomalous deshielding sequence of the ortho-ethyl protons in cation VIC, as compared to cation IIIC was tentatively attributed in this work to a steric interaction effect, involving the methyl group directly bound to the ionic carbon. This hypothesis could be checked by investigating the degree of deshielding of protons belonging to ethyl groups in meta and para position in parallel series of diphenylmethyl and 1,1-diphenylethyl cations. If the space interaction hypothesis is correct, the anomalous deshielding should decrease (or disappear) in the meta-, and even more in the para-ethylphenylethyl cations.
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