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Origin of the Alleged, and Position of the Real, U.v. Absorption of the 1,3-Diphenyl-n-butyl Cation

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WHEN styrene (I), 1,3-diphenylbut-1-ene (II), or 1-phenylethanol (III) are treated with excess of anhydrous perchloric or sulphuric acid in dilute solution, or when these compounds are introduced into 98% 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 mμ (see Ref. 1 and references quoted there). The λ_{max}, the ϵ, the ratio $\epsilon_{430}/\epsilon_{310}$, 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 secondary cations.[1] This assignment was challenged[2-6] and as a result of the work reported here we now know it to have been wrong, and the criticisms to be (at least partly) justified. Here we elucidate the origin of these spectra and report the absorption of the 1,3-diphenyl-n-butyl cation (IV) derived from (II).

We studied methylene dichloride solutions 10^{-5} to 10^{-1}M in (I) and 10^{-4} to 1M in perchloric acid by the technique described,[7] using also a spectrometer cell fitted with electrodes. Simultaneous recording of spectra and conductivity (specific conductivity κ) showed that on mixing the reagents, (I) is converted very rapidly into linear unsaturated oligomers which are subsequently cyclised to 1-methyl-3-phenylindane (V) and the corresponding higher aralkylindanes. If [$HClO_4$] is between *ca.* 1 and 10 times [C_8H_8], (V) is formed almost exclusively, and the reaction stops at that stage. If more acid is added, or if the initial [$HClO_4$] is greater, ions are then formed, the rate of increase of D_{420}, D_{308}, and κ being identical; the final spectrum has the usual two peaks at 420 and 308 mμ. The interval between mixing the reagents and onset of ion formation increases with decreasing [$HClO_4$]/[styrene] ratio and with decreasing [styrene]; it is only readily observable when [styrene] is less than 10^{-4}M. When (V) is treated with an excess of perchloric acid in dilute solution, D_{420}, D_{308}, and κ increase immediately, again following identical courses. When (V) is dissolved in sulphuric acid the same spectrum, with a slight hypsochromic shift (λ_{max} 415 and 304 mμ) is found. Previously we reported[1] that (V) does not react with acids, and we have been unable to trace the reason for this discrepancy.

Having ascertained that the ions are formed, not directly from styrene, but from its cyclic oligomers we considered two routes for their formation, bearing in mind that the strong absorption above 400 mμ indicates that they are probably of the diphenylmethyl type. Route A comprises ring opening with protonation in one or more of four possible ways, which would yield the ions (VI) to (IX). Route B involves hydride ion-abstraction from (V) to give the ion (X). We synthesised compounds (XI) to (XVI) (see Table) and protonated them under the conditions shown in the Table. The clear-cut result is that the ion formed (almost exclusively) from styrene and perchloric acid under the cleanest conditions as described above (low temperature, lowest concentrations) is (X). The fact that when (X) is formed from (V)

TABLE. *Spectroscopic characteristics of carbonium ions*

All reactions were done at 0° in 98% H_2SO_4; the spectra of 10^{-5}M-solutions were measured at 2°.

Precursor	Cation	$\lambda_{max}(10^{-3}\ \epsilon)$ (mμ)	
(V) 1-Methyl-3-phenylindane	(X)	415 (15)	304 (5·3)[f]
(XI) 1,1-Diphenylbut-1-ene	(VI)[a]	431 (39)	321 (9)
(XII) 1-Phenyl-1-(2′-ethylphenyl)ethanol	(VII)	434 (27)	323 (11)
(XIII) Phenyl-(2′-ethylphenyl)methanol	[b]	447 (47·6)	307 (4·2)
(XIV) 1,3-Diphenylbutan-3-ol	(IX)[c]	408 (1·6)	311 (10)
(XV) 1-Methyl-3-phenylindene	(X)[d]	415 (35)	304 (12)
(XVI) 1,1-Diphenylbuta-1,3-diene[e]	(X)	415 (35)	304 (12)

[a] In dilute solution slowly cyclises to (X).

[b] The phenyl-(2′-ethylphenyl)methyl ion (XVII) which should have a spectrum very similar to that of (VIII), the corresponding 2′-isopropyl ion.

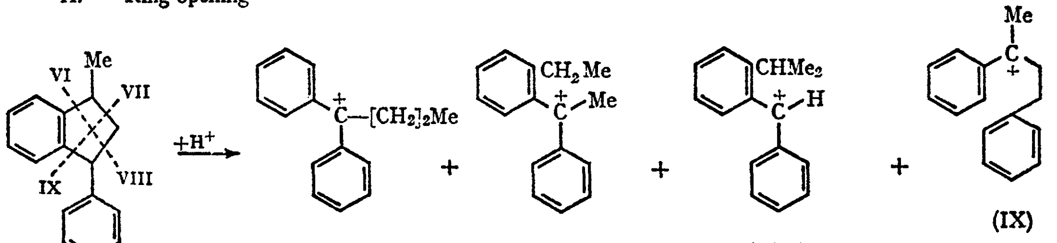
[c] Diluted from solution in HSO_3Cl; polymerises and rearranges to (X).

[d] With $HClO_4$ in CH_2Cl_2 the peaks are shifted to 421 and 308 mμ.

[e] In 70% (weight) H_2SO_4 this cyclises quantitatively to (XV).

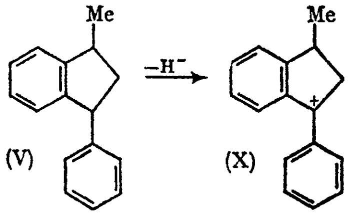
[f] Shoulder at 315 mμ.

A. Ring opening



(VI) (VII) (VIII) (IX)

B. Hydride ion-abstraction



(V) (X)

the ϵ-values are about one half of their values when the ion is formed from (XV) or (XVI) indicates that the abstracted hydride ion neutralises an equivalent of carbonium ions. It is also now evident that the different values for λ_{max} and ϵ 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 (VI) to (IX) having been formed along with (X). The n.m.r. spectra of (VI), (VII), (X), and (XVII) (10% solutions in 98% sulphuric acid) are clean and well resolved and correspond closely to expectations based on the structures shown in the reaction scheme.

We note with regret as a result of this work that the interpretations given in Ref. 1, like those of all previous authors cited there, are erroneous, though the facts reported (with the one exception noted above) agree closely with our subsequent findings.

After thus ascertaining the origin of the spectra previously assigned to ion (IV) and its homologues, we sought their real spectrum. The present view is that this would have only one important absorption above 240 mμ.

We studied the reaction of (I) and (III) with 98% sulphuric acid at *ca.* 0° using *ca.* 10^{-5}M-solutions, introducing the compounds by vacuum distillation[8] or through a capillary into rapidly stirred acid.[9] The u.v. spectrum of the solutions at 1—5 min. after mixing shows a peak at 315 mμ and one varying between 430 and 440 mμ, with a shoulder at 410—420 mμ; $D_{315} > D_{435}$. After 1—5 days the 315 mμ peak has been replaced by one at *ca.* 310 mμ; the peak at *ca.* 430 mμ decreases, and one at 415 mμ becomes prominent. From our assignments we deduce the initial presence of at least the ions (VI) and/or (VII), and (X), and one other absorbing at 315 mμ. Shoulders corresponding to the absorption of these ions in the 315 mμ region confirm this.

After measuring the u.v. spectrum, at time intervals from 5 sec. to 1 hr. after mixing, and in consecutive experiments, we recovered the reaction products by adding the reaction mixture to an excess of ice-cold aqueous sodium hydroxide, using rapid dispersal techniques,[9] and extracting the aqueous solution with carbon tetrachloride or hexane. The u.v. and i.r. spectra of the extract showed the presence of a mixture of unsaturated oligomers and of oligomers with indanyl end-groups.

Gas chromatography of the extracts showed that no detectable amounts of (I) or (III) were recovered. This agrees with the recent finding[6] that the 1-phenylethyl cation cannot be formed even in SO_2–SbF_5–FSO_3H at −60°. The gas chromatography of the extracts revealed only 3 components: (V), unknown (Y), and (II), in the order of increasing retention time. The first and third fractions were identified by the retention time of authentic specimens, and in the same way we ascertained that (Y) could consist of one or more of the following: (XI), (XV), and 1,3-diphenylbut-2-ene. A quantitative comparison of the gas-chromatographic results with the spectra of the extracts showed that these must have contained appreciable quantities of non-volatilisable oligomers.

The ratio [II]/[V] in the recovered products was the larger, the higher the 315 mμ peak had been in the sulphuric acid solution.

When (V) is dissolved in 98% sulphuric acid, the u.v. spectrum always shows a small shoulder at 315 mμ, which does not belong to ion (X), as direct protonation of (XV) shows (see Table).

Dissolution of (II) in 98% sulphuric acid yields the same 315 mμ peak, and variable absorption in the 430 mμ region.

We conclude that (IV) absorbs at 315 mμ and that it has no important absorption of comparable extinction coefficient at higher wavelength. Because of the multiplicity of products formed even under optimum conditions we can only say that the extinction coefficient of (IV) at 315 mμ is likely to be greater than 10^4. Our results and interpretations agree with those of Bywater and Worsfold[3] as far as they overlap.

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