194. *Unstable Intermediates. Part VI.* Spectra of Certain Aryl Carbinols and Olefins in Strongly Acidic and Weakly Acidic Media.*

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An attempt has been made to find conditions under which reactive carbonium ions have sufficient life for spectrophotometric study. It is concluded that stable dilute solutions in sulphuric acid can be prepared provided precautions are taken to avoid interaction between carbonium ions and parent molecules during preparation. The compounds studied include benzyl alcohol and styrene, α-methylstyrene, and the corresponding carbinols. Under certain conditions these compounds give rise to intense absorption in the visible region of the spectrum in weakly acidic media. These spectra, which are quite different from those attributed to carbonium ions, are recorded and the nature of the solutions discussed.

Carbonium ions are frequently postulated as being transient intermediates in chemical reactions, their presence being inferred from studies on the course of the reactions.[1] Stable carbonium ions, such as the triarylcarbonium ions and certain protonated fused ring aromatic compounds,[2] have been studied extensively in a variety of solvents. Diarylcarbonium ions are also known, though they are reported to be unstable, but very few monoarylcarbonium ions have been studied as such.

Our main purpose has been to prepare monoarylcarbonium ions in conditions such that they can be studied by spectrophotometric and other methods, the basic assumption being that the reason for their usual transient life-time is not that they are unstable, but that they are highly reactive electrophils.

Several of the compounds selected form coloured solutions in solvents such as acetic–sulphuric acid mixtures. The spectra of these solutions are recorded and some properties listed.

Experimental and Results

Materials.—Sulphuric acid and oleums were purified as described earlier.[3] "AnalaR" benzene was shaken repeatedly with sulphuric acid, then washed with purified water, dried with sodium, and distilled. *cyclo*Hexane and chloroform (B.D.H. Spectrograde) were purified similarly.

αα-Dimethylbenzyl alcohol, prepared from acetone and phenylmagnesium bromide, had b. p. 52°/3 mm. α-Ethyl-α-methylbenzyl alcohol, prepared similarly, had b. p. 75°/2 mm. Anthracene (B.D.H. microanalytical reagent) was not further purified. 9-Methylanthracene, prepared from anthracene-9-aldehyde, had m. p. 79·5°.[4] Other solvents and solutes were high-grade commercial products further purified by standard methods.

Preparation of Solutions in Sulphuric Acid.—An 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. The reactants selected were olefins and the corresponding alcohols; both are attacked by electrophils and a preparative procedure was sought in which contact between carbonium ions and reactants was avoided. This was finally achieved by procedures (1*a* and *b*) (below), and hence reactions such as disproportionation and polymerisation were avoided. Sulphonation was likewise avoided since the rate of sulphonation of carbonium ions, in contrast to that of the corresponding alcohols or olefins, is slow.

The only other reaction likely to give coloured species is oxidation, by sulphuric acid, to the corresponding radical-ions [8] or carbonyl compounds. Electron spin resonance studies

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* Part V, preceding paper.

[1] (*a*) Bethell and Gold, *Quart. Rev.*, 1958, **12**, 173; (*b*) Gillespie and Leisten, *ibid.*, 1954, **8**, 40.

[2] Reid, *J. Amer. Chem. Soc.*, 1954, **76**, 3264.

[3] Symons, *J.*, 1957, 387.

[4] Phillips and Cason, *J. Amer. Chem. Soc.*, 1952, **74**, 2934.

showed that the solutions were not paramagnetic, thus eliminating the former, and an examination of the spectra of relevant carbonyl compounds eliminated the latter. (Bands having $\varepsilon_{max.} \simeq 10^4$ were detected, with maxima at 345, 347, 352, and 411 mμ for benzophenone, acetophenone, anthrone, and anthraquinone respectively, in sulphuric acid.)

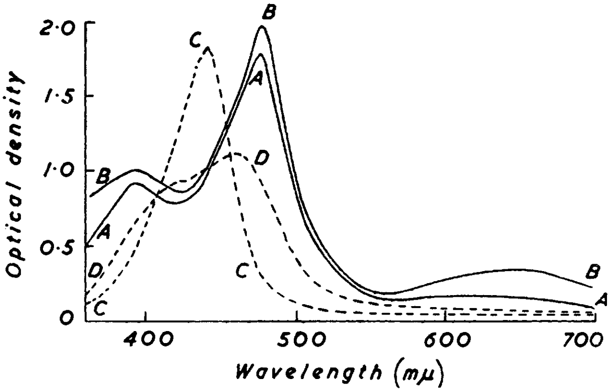
Procedure (1*a*). Dilute solutions of the reactant in acetic acid were treated with a hundredfold excess of cold sulphuric acid so that rapid mixing was ensured.

Procedure (1*b*). Solutions of reactant in *cyclo*hexane (10^{-4}M) were cooled in ice and extracted with cold sulphuric acid.

Solutions of benzyl alcohol in sulphuric acid (10^{-5}M) obtained by procedure (1*a*) had spectra which showed little change after 30 min. However, procedure (1*b*) gave solutions which were cloudy and had a rising absorption in the 400 mμ region, not found for the former solutions. The ultraviolet absorption increased slowly and the original orange colour changed to brown on standing. It seems probable that, despite the precautions taken, polymerisation was occurring.[5]

FIG. 1. *Absorption spectra for acid solutions of diphenylmethanol.*

A, By use of procedure (2*a*) after 5 min.
B, By use of procedure (2*a*) after 3 hr.
C, By addition of acetic acid to a solution in sulphuric acid after 5 min.
D, By addition of acetic acid to a solution in sulphuric acid after 6 hr.



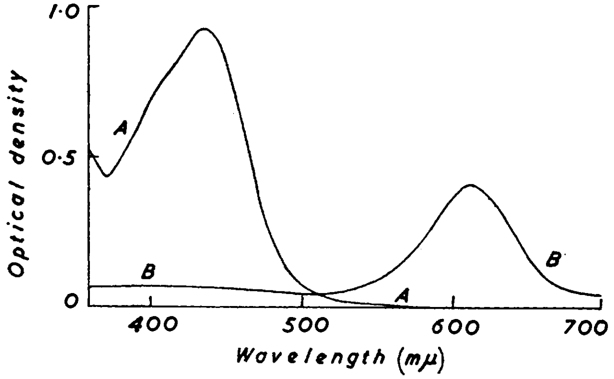


FIG. 2. *Absorption spectra of styrene in sulphuric acid* (100%) (*A*), *and in sulphuric–acetic acid mixtures* [*procedure* (2*b*)] (*B*).

The usual procedures for obtaining solutions in sulphuric acid, such as direct solution of the parent compound or extraction from more concentrated solutions, proved unsatisfactory.

Extinction coefficients could not always be measured accurately, but in all cases they were established to within 10% of the true value. The high values obtained (*ca.* 10^4) are of the same order as those found for carbonium ions by other workers. Such values preclude the possibility that traces of impurities are responsible for the spectra recorded.

Preparation of Solutions in Weakly Acidic Media.—Solutions in benzene containing trichloroacetic acid (*ca.* 2 mole $l.^{-1}$) were prepared by direct dissolution of the carbinol or hydrocarbon, the resulting solutions being exposed to light for a minimum period. Solutions in acetic–sulphuric acid mixtures were prepared as follows:

Procedure (2*a*). A mixture of sulphuric and acetic acids (1 : 1 v/v) was added dropwise,

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[5] Shiner and Berger, *J. Org. Chem.*, 1941, **6**, 305.

with stirring, to a cooled dilute solution of the compound in acetic acid. Spectra were recorded at intervals during the addition.

Procedure (2*b*). Ice-cold solutions of the compound in sulphuric acid, prepared by procedure (1*a*) or (1*b*) but somewhat more concentrated than usual, were poured into cold acetic acid or acetic–sulphuric acid, the solutions being cooled in a bath at −80° during the addition. When solutions were prepared by procedure (2*b*) comparison with the corresponding spectra of solutions in sulphuric acid was possible (see Fig. 2). From such comparisons we conclude that the extinction coefficients for the bands in the 500—600 mμ region recorded in Table 2 are $\doteqdot 10^4$, and generally greater than the extinction coefficients for bands recorded in Table 1 and attributed to carbonium ions.

Results are recorded in Table 2. Details for certain compounds are as follows: When anthracene was subjected to procedure (2*b*) only colourless solutions resulted. Procedure (2*a*) gave very pale blue colours unless nearly saturated solutions were used, when, at times, remarkably intense blue colours resulted, the intensity increasing with time. It seemed possible that this colour was due to anthracene positive ions,[8, 15] but no electron spin resonance absorption was detected at either room or liquid-oxygen temperatures. [Checks were made on other coloured solutions obtained by procedures (2*a*) and (2*b*), with similar results.]

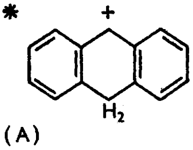
Styrene and α-methylbenzyl alcohol, treated by procedure (2*a*), gave cloudy, colourless solutions. In contrast, the blue solutions obtained by procedure (2*b*) were quite clear, and stable in the absence of light, though the colour was discharged on adding water.

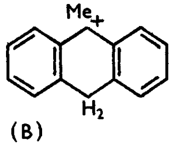
Solutions of α-methylstyrene and αα-dimethylbenzyl alcohol became red when either procedure was used. However, a band at 390 mμ, attributed to the ion $\mathrm{PhC^+(Me)_2}$, was found in addition to the 480 mμ band when procedure (2*a*) was used.

TABLE 1. *Absorption maxima for long-wavelength bands of solutions of various carbinols and hydrocarbons in sulphuric acid, prepared by procedures* (1*a*) *and* (1*b*).

Compound	Possible carbonium ion *	$\lambda_{max.}$ (mμ) †	$\varepsilon_{max.}$	Compound	Possible carbonium ion *	$\lambda_{max.}$ (mμ) †	$\varepsilon_{max.}$
Anthracene	A	427	3×10^4	$\mathrm{Ph{\cdot}CMe_2{\cdot}OH}$	$\mathrm{Ph{\cdot}\overset{+}{C}Me_2}$	390	$\doteqdot 10^4$
		425[a]	$3{\cdot}1 \times 10^4$	$\mathrm{Ph{\cdot}CMe{\cdot}CH_2}$	,,	390	$\doteqdot 10^4$
9-Methylanthracene	B	412	3×10^4	$\mathrm{Ph{\cdot}CHMe{\cdot}OH}$	$\mathrm{Ph{\cdot}\overset{+}{C}HMe}$	435	$\doteqdot 10^4$
				$\mathrm{Ph{\cdot}CH{=}CH_2}$	—	435	$\doteqdot 10^4$
$\mathrm{Ph_2CH{\cdot}OH}$	$\mathrm{Ph_2\overset{+}{C}H}$	442	4×10^4	$\mathrm{Ph{\cdot}CMeEt{\cdot}OH}$	$\mathrm{Ph{\cdot}\overset{+}{C}MeEt}$	405	$\doteqdot 10^4$
		442[b]	$5{\cdot}3 \times 10^4$	$\mathrm{Ph{\cdot}CH_2OH}$	$\mathrm{Ph{\cdot}\overset{+}{C}H_2}$	÷ 470	$>3 \times 10^3$
$\mathrm{Ph_2C{=}CH_2}$	$\mathrm{Ph_2\overset{+}{C}Me}$	429[a]	$3{\cdot}1 \times 10^4$	9-Hydroxyfluorene	C	660 and 480	$3{\cdot}1 \times 10^3$ and 2×10^3
		425[c]	$3{\cdot}1 \times 10^4$				
$\mathrm{Ph_2CMe{\cdot}OH}$	,,	429[a]	$3{\cdot}1 \times 10^4$				

[a] Ref. 10. [b] Branch and Walba, *J. Amer. Chem. Soc.*, 1954, **76**, 1564. [c] Evans, *J. Appl. Chem.*, 1951, **1**, 240.


(A)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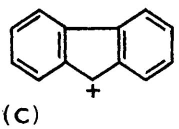
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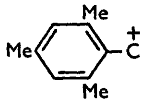
(D)

† Carbonium ions in solvent HF have similar spectra, but there is a solvent shift of about 15 mμ to shorter wavelengths compared with spectra in H_2SO_4 (cf. ref. 2).

Diphenylmethanol in benzene–trichloroacetic acid gave spectra which closely resembled 1 : 1-diphenylethylene in the same solvent.[6] Fresh solutions were colourless, but a peak at 660 mμ slowly developed which, together with a rising absorption in the 400 mμ region, imparted an emerald-green colour to the solution. As with 1 : 1-diphenylethylene, the band in the 430 mμ region ascribed to the carbonium ion was not observed.

Fig. 1 gives a typical spectrum for solutions of diphenylmethanol obtained by procedure (2*a*). The band at 650 mμ corresponds to the band at 660 mμ for solutions in benzene–trichloroacetic acid, but the bands at 480 and 395 mμ are not characteristic of the carbonium ion (see

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[6] Evans, Jones, and Thomas, *J.*, 1957, 104.

Table 1). Treatment of a solution in sulphuric acid with a small quantity of acetic acid gave a solution whose spectrum slowly changed from that of the carbonium ion to that displayed in Fig. 1, which has bands at 480, 440, and 395 mμ, but no band at 650 mμ. Addition of more acetic acid further increased the 480 and 395 mμ bands at the expense of the 440 mμ band.

In order to learn more about these involved changes in spectra the following experiments were devised: (*a*) Green solutions of diphenylmethanol in benzene–trichloroacetic acid, which had been kept until there was no further change in the spectrum, were shaken with a excess of purified water and the colourless benzene layer separated, dried (Na_2SO_4), and filtered. On addition of a solution of trichloroacetic acid in benzene an intense green colour developed *immediately*, and a spectrophotometric examination showed that the spectra of the original solutions were quantitatively reproduced.

TABLE 2. *Absorption maxima for long-wavelength bands of solutions of various carbinols and hydrocarbons in weakly acidic media.*

	$\lambda_{max.}$ (mμ) in solvent			$\lambda_{max.}$ (mμ) in solvent	
Compound	$CCl_3{\cdot}CO_2H + C_6H_6$	$AcOH + H_2SO_4$	Compound	$CCl_3{\cdot}CO_2H + C_6H_6$	$AcOH + H_2SO_4$
Anthracene ...	750, 590	615 (2*a*)	$Ph{\cdot}CMe{=}CH_2$	No visible bands	480 (2*a*)
$Ph_2CH{\cdot}OH$ ...	660	650, 480, 395 (Fig. 1)	$Ph{\cdot}CHMe{\cdot}OH$	,, ,,	610 (2*a*, 2*b*)
$Ph_2C{=}CH_2$ ...	607 -	600 *	$Ph{\cdot}CH{=}CH_2$ ...	,, ,,	615 (2*a*)
$Ph{\cdot}CMe_2{\cdot}OH$	No visible bands	480 (2*a*, 2*b*)	$Ph{\cdot}CH_2{\cdot}OH$ ...	,, ,,	†

* Ref. 6. † Cloudy solution.

TABLE 3. *Effect of methyl substitution on trigonal carbon.*

$$\Delta\ (m\mu) = (\lambda_{max.} \text{ for } R_2C\overset{+}{H}) - (\lambda_{max.} \text{ for } R_2C\overset{+}{M}e).$$

$R_2\overset{+}{C}H$	$Ph_2\overset{+}{C}H$	A *	$Ph{\cdot}\overset{+}{C}HMe$	$Ph{\cdot}\overset{+}{C}H_2$	D* †	$(p\text{-}Me{\cdot}C_6H_4)_2\overset{+}{C}H$	$(p\text{-}MeO{\cdot}C_6H_4)_2\overset{+}{C}H$	$(p\text{-}Cl{\cdot}C_6H_4)_2\overset{+}{C}H$
Δ	15	15	45	≒ 35	100	15	17	19

* See footnote to Table 1. † Ref. 12 gives data for $R\overset{+}{C}H_2$ and $R\overset{+}{C}Me_2$ (R = mesityl). Hence the Δ value of 100 should be halved to give a rough measure of the effect for a single methyl group.

(*b*) A solution of diphenylmethanol in sulphuric–acetic acid, whose spectrum was dominated by the 480 and 395 mμ bands, was poured on ice, and the colourless solution extracted with benzene. After separation and drying, the benzene extract was added to trichloroacetic acid–benzene, and the spectrum of the resulting pink solution recorded. The peaks at 480 and 395 mμ were still present, and there was no absorption in the 660 mμ region. The identity of the species absorbing at 480 mμ is unknown, and will not be considered at this stage. This experiment establishes that the species absorbing at 660 mμ is not derived from the former compound.

(*c*) Bisdiphenylmethyl ether was prepared from diphenylmethanol as crystals from acetic–perchloric acid.[7] On dissolution in benzene–trichloroacetic acid the ether behaved in just the same way as the carbinol.

Stable solutions of benzyl alcohol could not be obtained by any of the procedures outlined above.

Spectra.—The spectra were recorded on a Unicam S.P. 600 glass or S.P. 500 quartz spectrophotometer, pure solvents being used as reference solutions. Generally, solutions were kept in stoppered 1 cm. quartz cells. The results are summarised in Tables 1—3, and representative examples are displayed in the Figures. Generally, only the low-energy band maxima are recorded in the Tables. In many cases other bands were detected in the near-ultraviolet region, but they were not studied systematically.

DISCUSSION

Although several of the carbonium ions are thought to be important intermediates in a variety of reactions, no direct study has previously been reported. The postulate that the spectra (Table 1) are due to carbonium ions can be supported as follows: (*a*)

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[7] Burton and Praill, *J.*, 1953, 986.

[8] Carrington, Dravnieks, and Symons, *J.*, 947.

Identical spectra were obtained from alcohols and corresponding olefins, (*b*) extinction coefficients and wavelengths are very similar to those of stable carbonium ions, (*c*) characteristic changes in spectra on methyl substitution (Table 3) parallel the trends for more stable carbonium ions. Other evidence is given in the Experimental section. The reproducibility of the spectra shows that complete conversion is achieved under our conditions.

Effect of Methyl Substitution.—We consider only ions which have the chromophore $>\overset{+}{C}\text{–Ph}$, and the substitution is of the type $\text{R–}\overset{+}{C}\text{H–Ph} \longrightarrow \text{R–}\overset{+}{C}\text{Me–Ph}$.

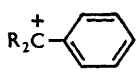
For diarylcarbonium ions, whose structure can be assumed, the trends are all very similar, involving a shift of about 15 mμ to shorter wavelengths. For anthracene and 9-methylanthracene the fact that a similar shift is observed can be understood in terms of Gold and Tye's concept, who pointed out that anthracene protonated at position 10 closely resembles the diphenylmethyl carbonium ion.[10,11]

By analogy, we expected a similar shift for monoaryl carbonium ions. In fact, the shift is in the same direction but considerably larger (Table 3).

These trends make a consistent picture. Without considering the nature of the long-wavelength transition in detail it seems reasonable to suggest that there is a partial transfer of charge from the ring to the tervalent carbon atom, so that the structure (I) contributes considerably to the ground state, whilst structures such as (II) are of greater importance in the excited state. In that case when R is methyl, both ground and excited states will be more stable than when R is hydrogen, but the stabilisation will be greater for the ground than for the excited state and hence the transition energy will be greater.

In accord with this pictorial representation is the fact that replacement of hydrogen by methyl in the *para*-position of the aromatic ring results in a shift of the band to *lower* energies.[6,12] Replacement of hydrogen by methyl in the *ortho*-positions leads to steric interactions which add greatly to the complexity of the problem.[13]

(I)



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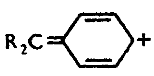

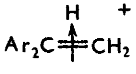

(III)

Spectra in Weakly Acidic Media.—This section has only reached a preliminary stage and is still being studied. However, in view of current interest in π-complex formation, and the postulate by Evans and his co-workers[6] that the bands in the 600 mμ region of certain diarylethylenes in weakly acidic solvents are due to complexes in which protons are π-bonded to the olefinic bonds, we consider that the present results should be reported. The structure proposed[6] (III) was arrived at by a process of elimination. One cannot be certain that all possibilities were considered, and the properties reported[6] are not in accord with current theories about such complexes. The remarkable similarity between the behaviour of 1 : 1-diphenylethylene[6] and diphenylmethanol suggests that there may be some alternative explanation, since there is no way of deriving a complex of the type shown above from the latter compound.

The phenomenon seems to be broad, requiring a comprehensive interpretation; many have been examined but none has proved comprehensive.

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[9] Weissman, Conradi, and de Boer, *J. Chem. Phys.*, 1957, **26**, 963.
[10] Gold and Tye, *J.*, 1952, 2172.
[11] Lewis and Symons, *Quart. Rev.*, 1958, **12**, 230.
[12] Deno, Jaruzelski, and Schrieshein, *J. Org. Chem.*, 1954, **19**, 155.
[13] Newman and Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 3648.