

Substituted Diphenylmethyl Cations. Part I. Acid-Base Equilibria

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The ionisation of several alkyldiphenylmethanols in sulphuric acid is examined. Evidence is presented which confirms the conjecture that where possible equilibrium in these systems exists between carbonium ion and olefin. α -Substitution in the alkyl group is shown to strongly destabilise the carbonium ion through steric effects on solvation and on the planarity necessary for resonance. It is also shown that internal 'solvation' by a hydroxy-substituent in the alkyl group causes an unusually high slope for a plot of log (ionisation ratio) versus $-H_R$.

THE ionisation of triarylmethanols in aqueous mineral acids has been extensively studied,¹ and used as the basis for the H_R acidity function. The carbonium ions formed in the ionisation are in general very stable, vary markedly in basicity on substitution, permitting a large range of acidity to be studied, and their electronic spectra show very small solvent shifts, making them ideal for indicator studies.

Diarylmethanols undergo the same type of ionisation,² although in acid the equilibrium is believed to be between the cation and the olefin,^{3,4} where this is possible (*i.e.* where there exists an α -hydrogen in the carbonium ion).

calculated from equation (1) rather than (2). The latter is a more general type of equation⁵ in which m is the

$$pK_{R^+} = H_R - \log a_{H_2O} + \log \{[RH^+]/[R]\} \quad (1)$$

slope of log (ionisation) versus $-H_R$ plot, the H_R acidity function being used as the best established acidity function involving carbonium ions.

$$pK_{R^+} = mH_R + \log \{[RH^+]/[R]\} \quad (2)$$

In the course of a systematic study of the decomposition of diarylcarbonium ions it was therefore decided to

TABLE I

Physical data for alkyldiphenylmethanols (RPh₂COH)

Indicator	R	M.p. (°C)	Lit. m.p. (°C)	B.p. (°C)	Lit. b.p. (°C)
(I)	H	69	69 ^a		
(II)	Me	80	81 ^b		
(III)	Et	93—94	94 ^b		
(IV)	Pr ⁱ			153—154 at 10 mmHg	148 at 7 mmHg ^c
(V)	Bu ^t			175—176 at 10 mmHg	179—180 at 11 mmHg ^d
(VI)	CH ₂ Ph	88—89	91 ^e		
(VII)	Cyclopropyl	83.5—84.5	82—83 ^f		

^a 'Handbook of Chemistry and Physics,' The Chemical Rubber Co., Cleveland, 1968, 49th edn. ^b A. Jung, *Bull. Soc. chim. France*, 1966, 269. ^c S. P. Lagerev, *J. Gen. Chem. U.S.S.R.*, 1936, **6**, 1766. ^d P. Lucas, *Compt. rend.*, 1910, **150**, 1058. ^e A. Gandini and P. H. Plesch, *J. Chem. Soc.*, 1965, 6019. ^f P. Lipp, J. Buchkremer, and H. Seeles, *Annalen*, 1932, **499**, 1.

Such systems have not been studied as extensively as the triarylmethanols, probably on account of the chemical instability of the carbonium ions generated, which frequently attack a molecule of the olefin to produce dimers.⁴ In the major study of these systems by Deno⁴ several substituted diaryl cations were investigated, but in most cases the degree of ionisation was only measured at three or four acid concentrations. pK_{R^+} Values were

re-examine the ionisation equilibria of some alkyldiphenylcarbonium ions, with a view to evaluating the effects of steric interactions on basicity.

EXPERIMENTAL

Diphenyl- and cyclopropyldiphenyl-methanol were commercial samples. Other alkyldiphenylmethanols were prepared by the addition of the required Grignard reagent to benzophenone. In each case the indicator was carefully purified by crystallisation or distillation before use. Physical data for the indicators are collected in Table I.

¹ V. Gold, B. W. V. Hawes, and F. L. Tye, *J. Chem. Soc.*, 1952, 2167.

² V. Gold and F. L. Tye, *J. Chem. Soc.*, 1952, 2172.

¹ (a) V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 1951, 2102 for mixtures of sulphuric acid, water, and acetic acid; (b) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, 1954, **19**, 155; *J. Amer. Chem. Soc.*, 1955, **77**, 3044 for aqueous sulphuric acid; (c) N. C. Deno, H. E. Berkenheimer, W. L. Evans, and H. J. Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 2344 for aqueous nitric and perchloric acids; (d) E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, 1966, **88**, 1177 for hydrochloric, phosphoric, and toluene-*p*-sulphonic acids.

⁴ N. C. Deno, P. T. Groves, and G. Saines, *J. Amer. Chem. Soc.*, 1959, **81**, 5790.

⁵ K. Yates and R. A. McClelland, *J. Amer. Chem. Soc.*, 1967, **89**, 2686.

1,1-Diphenylethylene was prepared from 1,1-diphenylethanol by the method of Deno,⁴ and purified by distillation, b.p. 136–137° at 12 mmHg (lit.,⁶ b.p. 134° at 10 mmHg).

Stock indicator solutions were prepared by dissolving the methanols in AnalaR methanol, and then transferring portions (0.05 ml) to 10 ml volumetric flasks containing sulphuric acid of the required strength. Where possible [indicators (I)–(III), (VI), and (VII)] the flask was weighed before and after each addition, allowing a correction to be made⁷ for small differences in indicator concentration and changes in acid strength. Where decomposition of the carbonium ion was too rapid for this method to be practicable [indicators (IV) and (V)], sample solutions were made up by volume, shaken and quickly transferred to cells in the spectrophotometer. The fall in optical density (at λ_{\max}) with time was recorded, and the plot extrapolated back to the time of mixing, usually an extrapolation of *ca.* 15 s. Although an average correction was made to the acid strength of 0.2%, no allowance was made for slight differences in indicator concentration, and results obtained with this method should be regarded as less accurate than results obtained by the former method.

Spectra were recorded on a Unicam SP 1800 spectrophotometer, using 1 cm cells. An acid solution of comparable strength to the test solution was used as a reference in the spectrophotometer.

The spectra of all the carbonium ions examined showed small medium effects, an increase in intensity accompanying a bathochromic shift as the acidity was increased. The method of Katritzky⁸ was therefore used to evaluate the degree of ionisation at different acid concentrations. The logarithms of the ionisation ratio ([carbonium ion]/[free base]) were plotted against $-H_R$ ^{1b} to give the slope *m*, and the pK_{R^+} values calculated from equation (2).

Care was taken to keep the temperature constant ($25 \pm 1^\circ$) since the pK_{R^+} values of carbonium ions have been shown⁹ to vary considerably with temperature.

RESULTS AND DISCUSSION

A preliminary examination was made to confirm the identity of the species in equilibrium with the carbonium ion in sulphuric acid. The spectra of diphenylmethanol, 1,1-diphenylethanol, and 1,1-diphenylethylene were recorded in methanol and in sulphuric acid solutions of strength just below that required for ionisation. In methanol the alcohols showed identical spectra (λ 208 nm), and differed markedly from the olefin (λ 207, 230, and 252 nm). In 60% sulphuric acid 1,1-diphenylethanol and 1,1-diphenylethylene showed identical spectra (λ 198, 232sh, and 262sh nm), very similar to that of the olefin in methanol and dissimilar to that of diphenylmethanol in 60% sulphuric acid (λ 198 and 220sh nm). This would seem to confirm Deno's deductions,⁴ based on recovery experiments, that where possible equilibrium exists between carbonium ion and olefin.

The spectrum of cyclopropyldiphenylmethanol in 60%

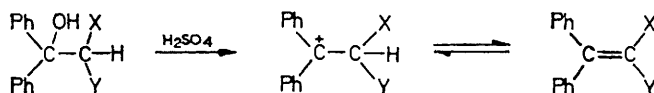
⁶ G. W. Lebedew, *Ber.*, 1923, **56**, 2349.

⁷ C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, 1969, **91**, 6654.

⁸ C. D. Johnson, A. R. Katritzky, B. J. Ridgeway, N. Shakir, and A. M. White, *Tetrahedron*, 1965, **21**, 1055.

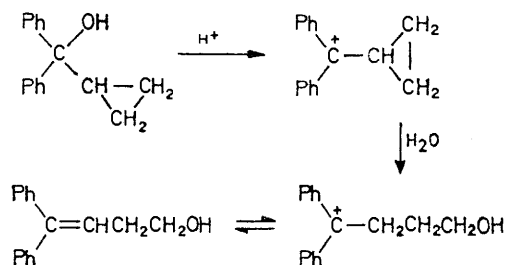
⁹ M. J. Cook, N. L. Dassanayaka, C. D. Johnson, A. R. Katritzky, and T. W. Toone, to be published.

sulphuric acid (λ 194 and 252 nm), when compared with that in methanol (λ 206 nm) indicated that the free base species in the equilibrium was an olefin. Recovery



experiments on this compound, after treatment for 2 min in 90% sulphuric acid, gave a 68% yield of 4,4-diphenylbut-3-en-1-ol, b.p. 133–134° at 0.3 mmHg (lit.,¹⁰ b.p. 135–137° at 0.6 mmHg); λ_{\max} (methanol) 252 nm (lit.,¹⁰ 250 nm); $\bar{\nu}$ 3400, 1600, and 1497 cm^{-1} (lit.,¹⁰ 3335, 1600, and 1500 cm^{-1}). This ring opening is analogous to that observed in acidic methanol by Roberts¹¹ and in trifluoroacetic acid in dichloromethane by Carey and Tremper.¹²

It was confirmed by n.m.r. that the ring-opening occurred in concentrated sulphuric acid and not in the work-up. In 96% sulphuric acid the spectrum of cyclopropyldiphenylmethanol shows a broad multiplet in the aromatic region, δ 8.0–9.0, and three additional fairly broad peaks at δ 4.3, 3.8, and 2.1 with relative intensities 1.00, 0.98, and 0.92 (the average from three spectra measured with a planimeter). In deuteriosulphuric acid the peak at δ 3.8 disappeared, but the other two non-aromatic peaks appeared in the same positions with the same relative intensities. The peak at δ 2.1 showed a slight decrease in intensity when the solution was warmed. This is consistent with an ion containing an opened cyclopropyl ring in which the three different carbons in the chain are each bonded to two hydrogens. The protons on the α -carbon exchange rapidly through equilibrium with the olefin, while those on the β -carbon exchange slowly through reversible dehydration of the terminal alcohol.



Basicity data are recorded in Table 2. Examination of the pK_{R^+} values reveals two opposing trends. In the increased stability of the 1,1-diphenylethylcarbonium ion over the diphenylmethylcarbonium ion, the stability endowed through the inductive effect of an alkyl group is observed. However, as increasingly large alkyl groups are introduced, the stability of the cation drops markedly. Decreases of δ 1.5, 2.9, and 1.9 *pK* units are observed

¹⁰ J. F. Vozza, *J. Org. Chem.*, 1959, **24**, 720.

¹¹ A. Maercker and J. D. Roberts, *J. Amer. Chem. Soc.*, 1966, **88**, 1742.

¹² F. A. Carey and H. S. Tremper, *J. Amer. Chem. Soc.*, 1969, **91**, 2967.

with successive methyl substitutions on the α -carbon atom. Deno⁴ has suggested that the effect of steric crowding in the carbonium ion-olefin equilibrium is to reduce the solvation energy of the cation and so destabilise it relative to the olefin. This is indicated by the increase in slope of \log (ionisation) *versus* $-H_R$ as the central carbon is successively substituted with methyl, ethyl, and isopropyl. Lee and Cameron¹³ have pointed out that increasing slopes of \log (ionisation) *versus* any given acidity function indicates decreased solvation of

The slope of greater than unity implies that $(m + n' - \chi') > (m + n + 1 - \chi)$ or $(n' - \chi') > (n + 1 - \chi)$. This condition can be met if the olefin is much more solvated than the triaryl methanol. This is possible, since the hydroxy-group in the olefin molecule is more accessible to solvent, but it is unlikely to be a large effect. The alternative is that the diarylcarbonium ion is less solvated than the triarylcarbonium ion. This is unlikely to occur through accessibility of the solvent to the positive charge, and a more likely explanation is a form

TABLE 2
Basicity data for RPh_2C^+

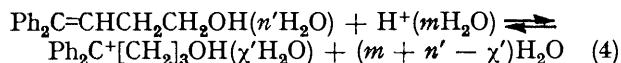
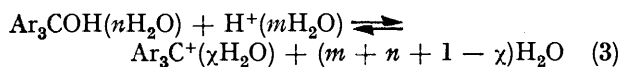
R	$\lambda_{max.}/nm$	$\log \epsilon$	H_R^a (half-protonation)	Slope of \log (ion) <i>versus</i> $-H_R^a$	pK_{R^+}	Lit. pK_{R^+}
H	443	4.63	-13.80	0.83	-11.5	-13.3 ^a
Me	428	4.51	-12.90	0.77	-9.9	-10.4 ^b
Et	430	4.49	-14.18	0.81	-11.4	-11.5 ^b
Pr ^t	432	4.22	-15.85	0.90	-14.3	-12.8 ^b
Bu ^t	434	4.12	-16.24	1.00	-16.2	
CH_2Ph	430	4.32	-16.52	0.80	-13.2	
$[CH_2]_3OH^c$	437	4.53	-14.02	1.14	-16.0	

^a N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044. ^b N. C. Deno, P. T. Groves, and G. Saines, *J. Amer. Chem. Soc.*, 1959, **81**, 5790. ^c In view of the surprising results obtained for this compound, all measurements were repeated. The results given are the average of two similar sets of measurements.

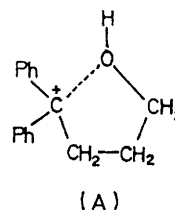
the cation relative to the free base. (The unsubstituted compound and the *t*-butyl compound must be excluded from the preceding argument since both equilibria involve the alcohol as the free base; also the diphenylmethyl cation has a hydrogen atom attached directly to the central carbon, and this is likely to interact strongly with the solvent.)

However, another effect is probably also involved in producing the large changes in stability of the cations. The effect of steric crowding will be to force the phenyl groups to twist out of plane, thereby reducing their ability to disperse the positive charge through resonance.

The ion generated from cyclopropyldiphenylmethanol shows unusual behaviour in having an exceptionally high slope of \log (ionisation) *versus* $-H_R$. As the equilibrium studied was between an olefin and a carbonium ion, a slope of less than unity is expected. The unusual result may be explained in terms of hydration theories of acidity functions.¹³ Equation (3) describes the ionisation of triarylmethanols and equation (4) that of the olefin.



of internal solvation as shown in structure (A). Such internal interactions would also account for the remarkable chemical stability of this ion. Polymerisation *via*



the cation-olefin mechanism is very slow, and the ion does not react with 2,6-dimethylphenol, a nucleophile commonly used for scavenging carbonium ions, at an appreciable rate. The pK_{R^+} value is nevertheless the smallest of the series, partly due to the electron-withdrawing effect of the hydroxy-group, and perhaps partly due to increased steric interactions between alkyl and aromatic (*ortho*) hydrogens in this conformation forcing the phenyl rings to twist further out of plane.

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¹³ D. G. Lee and R. Cameron, *J. Amer. Chem. Soc.*, 1971, **93**, 4724.