Photolysis of Triphenylmethyl and Related Cations in Sulphuric Acid

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Photolysis of triphenylmethyl cation in 99% sulphuric acid in the absence of oxygen gives 9-phenylfluorenyl cation. When oxygen is present an additional product, 9-hydroxyfluoren-9-yl cation is formed. The effect of oxygen on the rate of reaction and on the distribution of products is described. As the sulphuric acid concentration is reduced to 88% the rate of reaction is increased. Further reduction is accompanied by the appearance of a new product, 4-hydroxyphenyldiphenylmethyl cation, which at 78% sulphuric acid becomes predominant. The effect of introducing a methyl or chloro-substituent into one or all of the *para*-positions of Ph_3C^+ is described.

ULTRAVIOLET and visible spectra of many carbonium ion species have been reported and some reviews have included theoretical treatments.[1,2] Photochemical reactions of carbonium ions however have been studied only in more recent years. Among the first systems investigated[3] from the standpoint of product development involved the conversion of the tropylium cation

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[1] S. F. Mason, *Quart. Rev.*, 1961, **15**, 335.

[2] G. A. Olah and P. von R. Schleyer, 'Carbonium Ions,' Interscience, New York, 1968, vol. 1.

[3] (*a*) E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, *J. Amer. Chem. Soc.*, 1968, **90**, 1372; (*b*) E. E. van Tamelen and T. M. Cole, *ibid.*, 1970, **92**, 4123; (*c*) T. M. Cole, *ibid.*, 1970, **92**, 4124.

in aqueous sulphuric acid solution intobicyclo [3.2.0]-hepta-3,6-dien-2-ol and a corresponding ether *via* a reactive valence-bond isomer. The same authors[3] reported the photochemical conversion of the triphenylcyclopropenyl cation into hexaphenylbenzene and the triphenylmethyl cation into a variety of products which depended on the solvent composition. Filipescu and Pavlik[4] have reported that irradiation of the delocalised cyclohexadienyl cations formed by oxygen protonation of 4-dichloromethyl-4-methylcyclohexa-2,5-dienone or 6-dichloromethyl-6-methylcyclohexa-2,4-dienone results in an efficient photorearrangement which leads to the same product, 5-hydroxy-2-methylbenzaldehyde. The mechanism proposed involves a type of bonding which has been shown to take place efficiently in the photolysis of hexa- and hepta-methylbicyclo-[3.1.0]hexenyl cations;[5,6] the cyclopropane migration of the kind observed in hydroxyhexamethylbicyclohexenyl cations[7] was absent however. van Tamelen and Cole[8] have described the photolysis of the triphenylmethyl cation in relatively concentrated (*ca.* 10^{-3}M) solutions and in various mixed solvent systems.

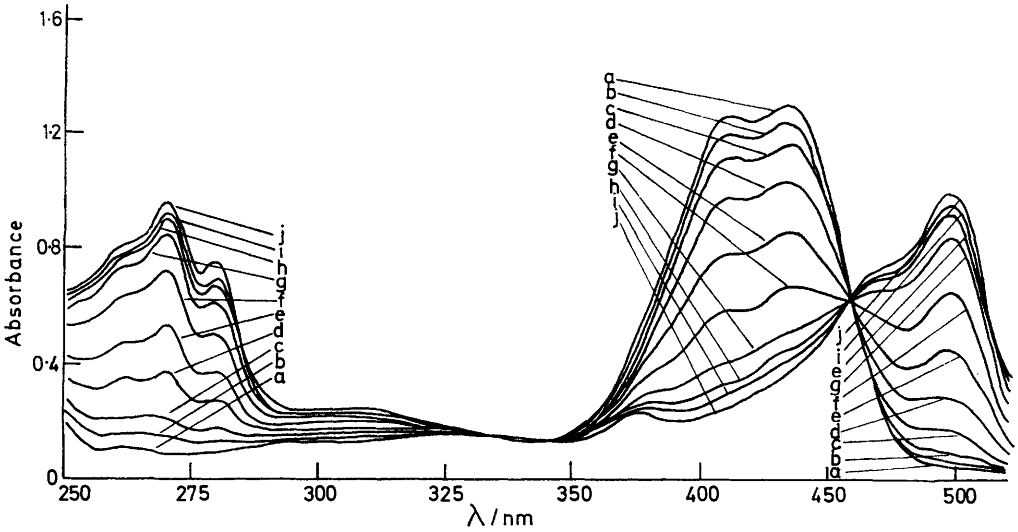


FIGURE 1 Absorption spectra of thoroughly outgassed solutions of triphenylcarbonium ion in 99% sulphuric acid after various times of photolysis: a, 0; b, 2; c, 5; d, 10; e, 17; f, 27; g, 40; h, 55; i, 75; j, 135 min

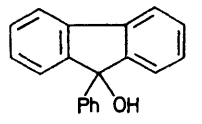
In a preliminary communication[9] we reported the results of the irradiation of dilute (*ca.* 10^{-5}M) solutions of triphenylmethyl cation in 99% sulphuric acid both in the absence and presence of oxygen. We now present details of this and related systems.

RESULTS

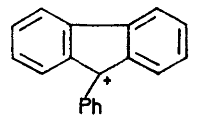
Triphenylmethyl Cation in 99% *Sulphuric Acid.*—When thoroughly outgassed solutions (*ca.* 10^{-5}M) of Ph_3·OH (I) in 99% AnalaR sulphuric acid were irradiated (Pyrex filter, high-pressure mercury lamp), the characteristic absorption of the carbonium ion ($\lambda_{max.}$ 430 nm, log ε 4·60) decreased and was replaced by an absorption with a maximum at 493 nm. Isosbestic points occurred at 453 and 340 nm (Figure 1). On completion of the reaction the sulphuric acid solution was diluted with a large excess of ice, extracted with benzene, and the product separated by preparative t.l.c. on silica gel. The product was shown to be 9-phenylfluoren-9-ol (II) by comparison of its u.v. and i.r. spectra with those of the authentic material. The visible and u.v. spectra of a solution of (II) in 99% sulphuric acid, *i.e.* of the carbonium ion (III) ($\lambda_{max.}$ = 493 nm, log ε 4·58) was identical with that of the solutions of (I) after irradiation. The rate of disappearance of (I) was the same as the rate of appearance of (III) and this together with the sharpness of the isosbestic points indicated a clean conversion of (I) into (III) with the absence of any detectable side-reactions.

$Ph_3C^+OH^-$

(I)



(II)



(III)

On introduction of varying amounts of oxygen to the outgassed system two significant changes were observed. Firstly the rate of disappearance of (I) was reduced (Figure 2) by a factor of 40 as the partial pressure of oxygen was increased from zero to 400 Torr. The graph of (R_0/R) against p_{O_2} (where R_0 and R represent the rates of photolysis in the absence and presence of oxygen) shows (Figure 3) that the decrease in rate is rapid at first and is followed

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[4] N. Filipescu and J. W. Pavlik, *J. Amer. Chem. Soc.*, 1970, **92**, 6062.

[5] R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, 1968, **90**, 7144.

[6] R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, 1968, **90**, 7146.

[7] D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, 1967, **89**, 5057.

[8] E. E. van Tamelen and T. M. Cole, *J. Amer. Chem. Soc.*, 1971, **93**, 6158.

[9] D. M. Allen and E. D. Owen, *Chem. Comm.*, 1971, 848.

by a region in which a linear relationship exists between (R_0/R) and p_{O_2}. The second effect of oxygen was on the nature of the products. The percentage of (III) decreased and a new product was detected. Following the work-up procedure described for the outgassed systems and separation by t.l.c., u.v., i.r. and mass spectral examination proved that this was fluoren-9-one (IV) and spectra of solutions photolysed while open to the atmosphere (Figure 4) showed absorptions which were characteristic of the oxonium ion (V) formed by protonation of the ketone (IV). Here again the constant proportion of the products is indicated by the sharpness of the isosbestic points and in this case the rate of disappearance of (I) is the sum of the rates of appearance of (III) and (V). In addition, as the concentration of oxygen is increased, the percentage of (V) in the product increases as (III) decreases (Figure 5).

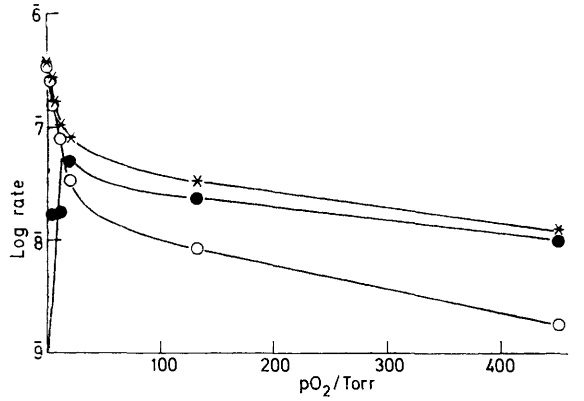
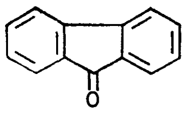
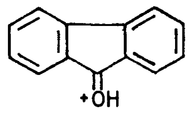


FIGURE 2 Effect of oxygen concentration on (a) rate of disappearance of (I) (✱) (b) rate of formation of (III) (○) and (c) rate of formation of (V) (●)



(IV)



(V)

Substituted Triphenylmethyl Cation in 99% Sulphuric Acid.—(a) *Diphenyl-*p*-tolylmethanol.* When aerated solutions of diphenyl-p-tolylmethanol in 99% sulphuric acid were photolysed the characteristic absorption of the carbonium ion ($\lambda_{max.}$ 450 nm, log ε 4·66) decreased in intensity and was replaced by an absorption with maxima at 508, 406, 267, and 259 nm and with isosbestic points at 468 and 364 nm. Products were isolated and separated as previously described. The least-polar compound (R_F = 0·55) was recrystallised from ligroin to yield a yellow solid. An i.r. spectrum in carbon tetrachloride (peaks at 2940, 2905, 2820, 1710, 1605, 1595, 1445, 1292, 1252, 1207,

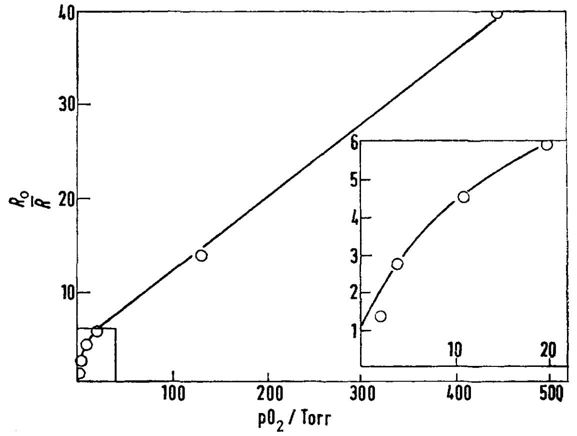


FIGURE 3 Variation of the relative rate of disappearance of (I) (R_0/R) with oxygen concentration

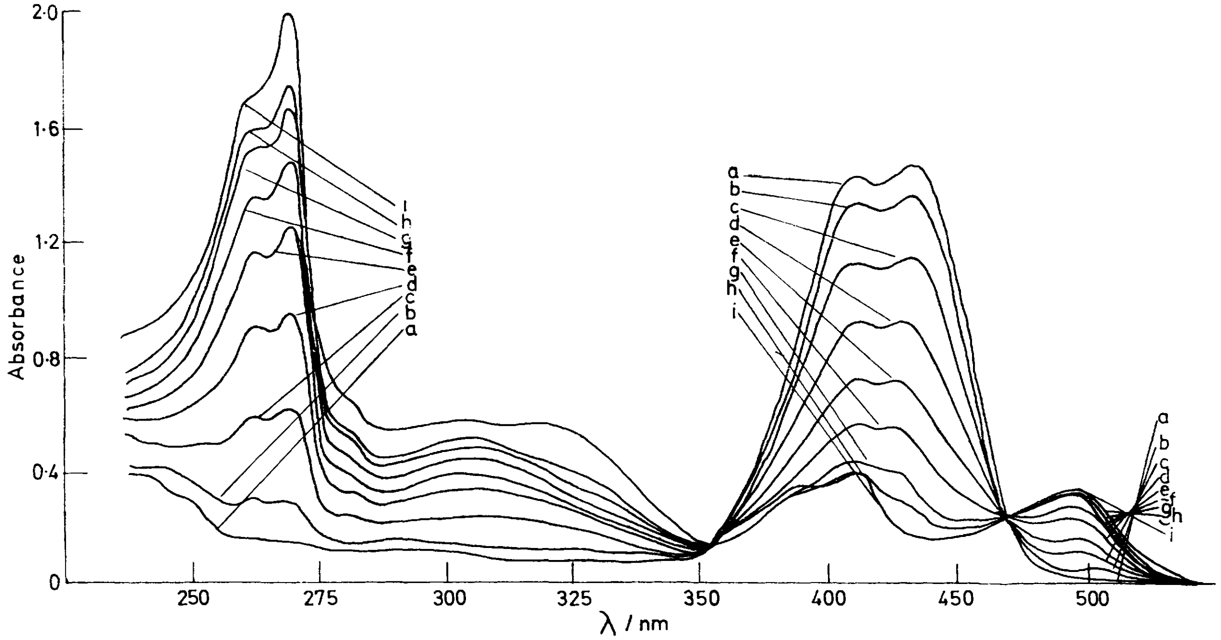


FIGURE 4 Absorption spectra of solutions of triphenylcarbonium ion in 99% sulphuric acid open to the atmosphere after various times of photolysis, a, 0; b, 19; c, 59; d, 100; e, 141; f, 187; g, 269; h, 388; i, 697 min

1183, 1143, 1090, 910, 663, and 643 cm^{-1}), u.v. in cyclohexane (Maxima at 256·5 and 248 nm) and mass spectrum (*m/e* 194, 180, 152, and 76) showed that the substance was a mixture of (IV) and its 3-methyl derivative. Analysis of the breakdown pattern in the mass spectrometer and comparison with authentic samples of the pure compounds prepared by non-photochemical methods indicated that (IV) was the major component and that the 3-methylfluoren-9-one represented a very small percentage of the total fluorenone. A colourless product ($R_F = 0{\cdot}30$) detected on the t.l.c. plate by its fluorescence when excited by light of 360 nm was eluted and evaporated to yield a gum which proved difficult to crystallise. A u.v. spectrum in cyclohexane (maxima at 311, 300, 282, 275, and 233 nm) and mass spectrum (*m/e* = 272, 257, 255, 195, 181, 165, 152, 91 and 77) showed that the substance was a mixture of predominantly 9-*p*-tolylfluoren-9-ol with a small amount of 3-methyl-9-phenylfluoren-9-ol.

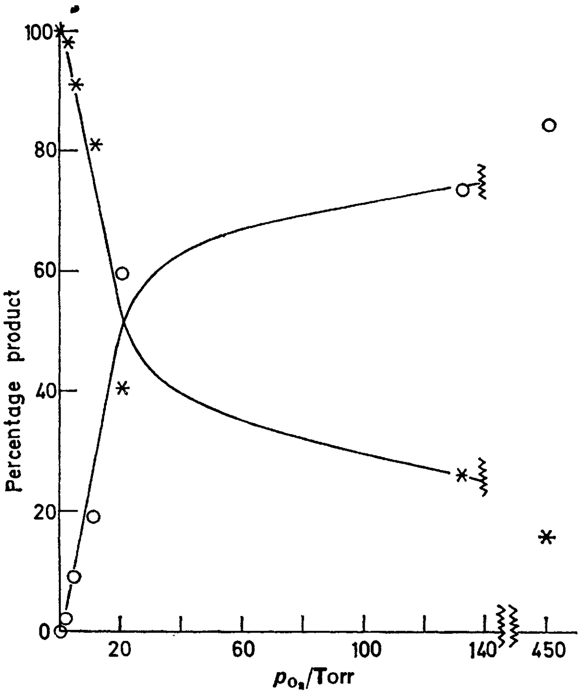


FIGURE 5 Variation of the percentage of 9-phenylfluoren-9-yl cation (✱) and 9-hydroxyfluoren-9-yl cation (○) in the product after photolysis with various partial pressures of oxygen.

(b) 4-*Chlorophenyldiphenylmethanol.* When aerated solutions of diphenyl-4-chlorophenylmethanol in 99% sulphuric acid were photolysed, the characteristic absorption of the carbonium ion ($\lambda_{\max}$ 444 nm, log ε 4·70) decreased in intensity and was replaced by an absorption which had maxima at 508, 405, 385, 280, 265, and 275 nm with isosbestic points at 473 and 360 nm. Methods of separation of the products were those previously described. The u.v. spectrum in cyclohexane (maxima at 257 and 248 nm) and mass spectrum with major peaks at *m/e* of 214, 180, 152, and 76 showed that the product was a mixture of predominantly (IV) with a small amount of the 3-chloro-derivative. Cyclohexane solutions of the colourless compound had maxima at 310, 298, 282, 276, 271, 231, and 225 nm and major mass spectrum peaks occurred at *m/e* of 292, 275, 257, 181, and 152. It was a mixture of predominantly 9-(4-chlorophenyl)fluoren-9-ol with a small amount of 3-chloro-9-phenylfluoren-9-ol.

(c) *Tri*-p-*tolylmethanol.* When aerated solutions of tri-*p*-tolylmethanol in 99% sulphuric acid were photolysed the characteristic absorption of the carbonium ion ($\lambda_{\max}$ 452 nm, log ε 5·03) decreased in intensity and was replaced by an absorption with maxima at 505, 465, 287, and 276 nm with isosbestic points at 466 and 365 nm. The methods of separation and analysis of the products were the same as for the previous compounds and the products were identified as 3,6-dimethylfluoren-9-one (u.v. in ether had maxima 262 and 253 nm and major mass spectrum peaks at *m/e* of 208, 180, and 165), and 3,6-dimethyl-9-*p*-tolylfluoren-9-ol (u.v. in cyclohexane had maxima at 317, 310, 300, 282, 275, 271, 239, and 232 nm, and major mass spectrum peaks at *m/e* of 300, 285, 283, 209, 149, and 91).

(d) *Tris-*(4-*chlorophenyl*)*methanol.* When aerated solutions of tris-(4-chlorophenyl)methanol in 99% sulphuric acid were irradiated, absorption characteristic of the carbonium ion ($\lambda_{\max}$ 465, log ε 5·01) decreased in intensity and was replaced by an absorption with maxima at 523, 420, 294, and 281 nm. The products were shown to be 3,6-dichlorofluoren-9-one (u.v. in ether showed maxima at 264 and 255 nm with major mass spectrum peaks at *m/e* of 252, 250, 248, 224, 222, 220, 187, 185, 150, 111, 110, 75 and 74), and 3,6-dichloro-9-(4-chlorophenyl)fluoren-9-ol (u.v. in cyclohexane had maxima at 320, 307, 276, 243, 235, 230, and 225 nm and major mass spectrum peaks at *m/e* of 366, 364, 362, 360, 349, 347, 345, 343, 329, 327, 325, 253, 251, 249, and 149).

Effect of Substituents on the Quantum Yield of Photolysis.—Radiation of 432 nm, which lay in the long wavelength absorption band of all the ions studied, was isolated by means of a metal interference filter; the quantum yield for disappearance of the carbonium ion was then measured by following the decreases in absorption. The intensity of the incident radiation was determined by potassium ferrioxalate actinometry using the method of Hatchard and Parker. The results are shown in Table 1.

TABLE 1

Quantum yields of disappearance of substituted carbonium ions

Carbonium ion	10^4 Quantum yield
Ph_3C^+	2·54
$(p\text{-}MeC_6H_4)Ph_2C^+$	0·53
$(p\text{-}MeC_6H_4)_3C^+$	0·34
$(p\text{-}ClC_6H_4)Ph_2C^+$	1·51
$(p\text{-}ClC_6H_4)_3C^+$	1·15

Effect of Oxygen on the Rate of Reaction of Substituted Ions and on the Product Distribution.—The rates of photolysis of the substituted ions were quenched by dissolved oxygen as was the case for Ph_3C^+. Solutions of the substituted methanols (*ca.* 10^{-5}M) in 99% sulphuric acid were thoroughly outgassed and the rates of photolysis measured (R_0) and compared with the rates for solutions open to the atmosphere (R), when the concentration of dissolved oxygen is *ca.* $2{\cdot}6 \times 10^{4}$M. The results together with the product distributions corresponding to the rates R are given in Table 2.

Effect of Water on the Rate of Photolysis.—When aerated solutions of Ph_3C^+ containing small amounts of added water were photolysed the products were unchanged and good isosbestic points were obtained in each case. The effect of added water was to increase the rate of disappearance of Ph_3C^+ (Table 3). When the percentage of water was increased to a value corresponding to 87·9% sulphuric acid a new product with an absorption around 460 nm began to be apparent, and at 78·1% sulphuric acid this was the predominant product. The photolysed solution was poured onto ice and extracted with benzene; the product was then separated into two fractions by t.l.c. using 10% methanol in chloroform as solvent. The least-polar component (R_F 0·9) was bright yellow and was eluted and evaporated to give an orange oil. The u.v. spectrum in ether (maxima at 361 and 260 nm) and mass spectrum (major peaks at *m/e* of 258, 229, 105, and 77) and i.r. in CCl_4 (carbonyl absorption at 1690 cm^{-1}) of the compound showed that it was diphenylquinomethane (VI).

TABLE 2

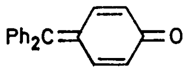
Relative rates of photolysis in the absence (R_0) and presence (R) of oxygen with the corresponding product distributions corresponding to R.

Carbonium ion	R_0/R	% Fluorenone	% 9-Aryl-fluoren-9-ol
Ph_3C^+	15·0	75	25
(p-MeC_6H_4)Ph_2C^+	3·7	46	54
(p-MeC_6H_4)$_3C^+$	6·8	28	72
(p-ClC_6H_4)Ph_2C^+	1·7	71	29
(p-ClC_6H_4)$_3C^+$	4·5	30	70

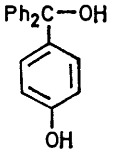
TABLE 3

Effect of sulphuric acid concentration on the rate of reaction of Ph_3C^+

% H_2SO_4	10^8 Rate (mol l^{-1} min^{-1})
99·1	4·55
97·8	5·13
93·4	8·31
88·6	9·00



(VI)



(VII)

The more-polar compound was colourless immediately after separation but upon exposure to air it become yellow. The compound was isolated as a pale yellow oil whose u.v. spectrum in ether (maxima at 361, 284, and 277 nm) i.r. in CCl_4 (OH absorption at 3605 and 3300 cm^{-1}), and mass spectrum (peaks at *m/e* of 276, 258, 229, 215, 199, 101, and 77) showed it to be diphenyl-4-hydroxyphenylmethanol (VII). The identities of both products were confirmed by comparison with samples of authentic materials prepared by non-photochemical methods. A sample of (VII) set aside on a t.l.c. plate in daylight was rapidly converted into (VI).

Photolysis in Phosphoric Acid.—Photolysis of solutions of Ph_3C^+ in phosphoric acid resulted in a decrease of the characteristic absorption of the ion and the appearance of a new absorption with maxima at 527 nm and isosbestic points at 454 and 360 nm (Figure 6). The product was isolated in the way previously described and was shown by its u.v. spectrum in cyclohexane ($\lambda_{max.}$ at 265 nm) and in AnalaR sulphuric acid ($\lambda_{max.}$ at 523, 442 and 410 nm) to be 4,4′-bis(diphenylhydroxymethyl)biphenyl. Neither the rate of photolysis nor the nature of the products were affected when the solution was outgassed.

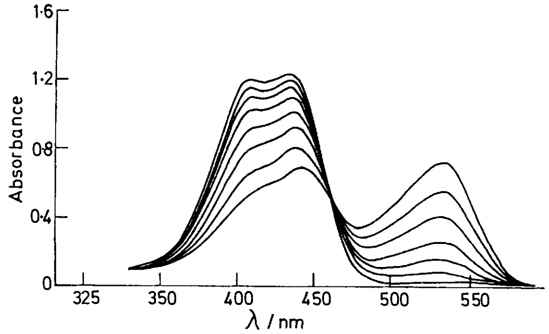


FIGURE 6 Absorption spectra of thoroughly outgassed solutions of triphenylcarbonium ion in phosphoric acid after various times of photolysis

DISCUSSION

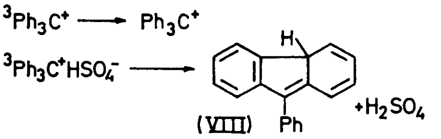
The structural similarity between the two kinds of carbonium ions (9-arylfluorenyl and 9-hydroxyfluoren-9-yl cations) formed by a cyclization reaction when aerated solutions of (I) in 99% sulphuric acid were irradiated and also the way in which the relative amounts of these products varied and the total amounts decreased as the concentrations of dissolved oxygen was increased, suggested that they may be formed from a common intermediate. The cryoscopy and spectroscopy of (I) in sulphuric acid dictates that the formation of Ph_3C^+ is represented by reaction (1) and the triplet state ($^3Ph_3C^+$) is formed by population of the singlet state ($\lambda_{max.}$ 430 nm) followed by intersystem crossing. The cyclization reaction in the absence of oxygen is described by reaction (5) and carbonium ion (III) would then be formed by removal of the allylic hydride ion, a well-known process in sulphuric acid [reaction (6)].

$$Ph_3COH + 2H_2SO_4 \longrightarrow Ph_3C^+ + 2HSO_4^- + H_3O^+ \quad (1)$$

$$Ph_3C^+ + h\nu\,(430\,nm) \longrightarrow {}^1Ph_3C^+ \longrightarrow {}^3Ph_3C^+ \quad (2)$$

$${}^1Ph_3C^+ \longrightarrow Ph_3C^+ \quad (3)$$

$${}^3Ph_3C^+ \longrightarrow Ph_3C^+ \quad (4)$$



$$(VIII) + 2H_2SO_4 \longrightarrow (III) + HSO_4^- + SO_2 + 2H_2O \quad (6)$$

The addition of oxygen appears to intercept one of the intermediates involved in this sequence of reactions. This may be (VIII) but is more likely to be $^3Ph_3C^+$ since Barton[10] and his co-workers have recently suggested that $^3Ph_3C^+$ reacts with molecular oxygen to form $^3Ph_3CO_2{}^+$, a Schenck-type adduct which is able

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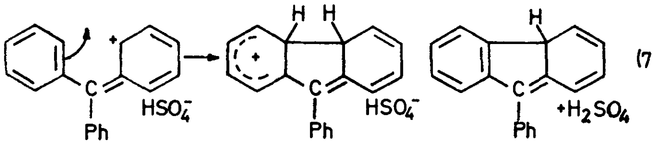
[10] D. H. R. Barton, G. Leclerc, P. D. Magnus, and I. D. Menzies, *J.C.S. Chem. Comm.*, 1972, 447.

to transfer triplet oxygen to a variety of substrates including ergosterol acetate, α-terpinene and tetraphenylfuran. This triarylmethylhydroperoxide is probably the precursor of the products in the presence of oxygen since Bissing[11] and his co-workers have shown that triarylmethyl hydroperoxides are in equilibrium with Ph_3C^+ in acid media before rearranging to ketone and phenol.

The excited state of Ph_3C^+ involved was probably the triplet state since the addition of oxygen to the outgassed systems reduced the quantum yield for the formation of (III) *ca.* 20 times more than it affected the rate of formation of (V). This suggested that oxygen had a strong quenching effect as well as reacting with $^3Ph_3C^+$ to form $^3Ph_3CO_2^+$. This quenching was not accompanied by any change in the already small ($8{\cdot}2 \times 10^{-4}$) quantum yield of fluorescence of Ph_3C^+. Many other substances which are normally efficient quenchers of triplet states were tried but were unsuitable because they were insufficiently soluble or reacted with the solvent. Paramagnetic nitric oxide (*ca.* 200 Torr) was added to an outgassed solution of sulphuric acid but instead of the expected quenching effect the reaction proceeded cleanly to (III) at a rate which was 2·5 times that of the outgassed system. No attempt was made to pursue this point.

The cyclization step may be regarded as a process which involves the electrophilic attack by one phenyl group on the other followed by elimination of a proton [see equation (7)].

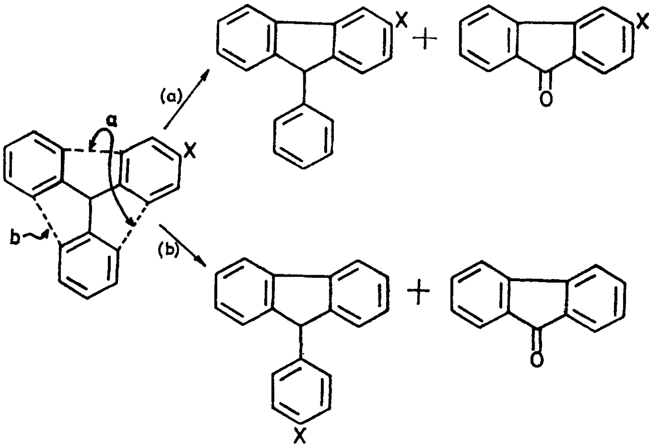


(7)

A second possibility is that the two hydrogen atoms are eliminated in one step as molecular hydrogen. Johnston and Ward[12] have concluded, after investigating the mass spectrum of the diphenylmethyl ion, that it loses hydrogen in a cyclization process which leads to the fluorenyl ion and that the reaction proceeds *via* an intermediate in which the hydrogen atoms have a *cis*-configuration. Replacement of the central carbon by nitrogen which contributes two electrons to the π system results in loss of hydrogen in two steps and therefore suggests an intermediate with a *trans*-configuration. Although the conclusion drawn from this work have been contradicted by Bishop and Fleming[13] it is probably true that, as a general rule, radical-cations lose radicals and even-electron species lose molecules. Obviously great care must be taken in extrapolating from results obtained in a mass spectrometer to a system with such a high degree of solvent participation.

Introduction of a methyl or chloro-substituent into one of the *para*-positions had the effect of reducing the quantum yield of disappearance of the carbonium ion, the methyl substituent being more effective than the chloro. Substituents in all three *para*-positions of the ions caused a further but relatively smaller reduction in the quantum yield. The effect of the substituents could be on ϕ_T (the quantum yield of intersystem crossing) or on the reactivity of the triplet ion. The latter possibility seems to be the most likely since these particular substituents do not normally have a very large effect on ϕ_T.[14] The positive inductive effect of the methyl group and the positive mesomeric effect of the chloro-group would tend to stabilise the carbonium ion and thereby increase the activation energy of the cyclization process. This assumes, of course, that the effect of substituents is the same in the triplet state as in the ground state which need not necessarily be the case.

When only one *para*-substituent, X, is present, the cyclization can be effected in two ways thus:



Completely random cyclization would result in a 2 : 1 ratio of products corresponding to routes (a) and (b) respectively. Our results, both from a consideration of fluoren-9-one and 9-arylfluoren-9-ol type products show conclusively that cyclization is predominantly *via* path (b) showing that the *meta*-position in the ring which carries the substituent is deactivated. One reason for this may be that since the effect of either substituent would be to localise the charge on that ring it may also tend to localise the gegenion (HSO_4^-) in a position which would cause steric hindrance towards ring closure by route (a). Alternatively it may be that the mechanism is not as ionic in character as equation (7) suggests and that the direction of cyclization is dictated by the spin densities on the *meta*-positions of the triplet-state carbonium ions. There are no general rules for predicting what effects substituents would have on the spin densities and a calculation which was

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[11] D. E. Bissing, C. A. Matuszak, and W. E. McEwen, *J. Amer. Chem. Soc.*, 1964, **86**, 3824.

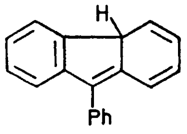
[12] R. A. W. Johnstone and S. D. Ward, *Chem. Comm.*, 1968, 1805.

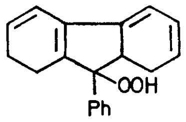
[13] M. J. Bishop and I. Fleming, *J. Chem. Soc.* (*C*), 1969, 1712.

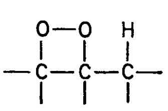
[14] S. P. McGlynn, T. Azumi, and M. Kinoshita, 'Molecular Spectroscopy of the Triplet State,' Prentice-Hall, New Jersey, 1969.

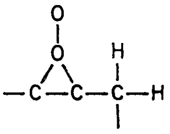
sufficiently detailed to be meaningful would not be straightforward for structures of this type.

We have considered the possibility that singlet oxygen, formed by energy transfer from $^3Ph_3C^+$, is involved in the oxygenation reaction mainly on the grounds that (VIII) is typical of compounds towards which singlet oxygen is extremely reactive and the hydroperoxide which would result from such a reaction (IX) could well be the precursor of the products formed. In addition, Kearns[15] has provided convincing evidence that dioxetans (X) are intermediates in the formation of carbonyl products and that perepoxides (XI) are intermediates in the formation of rearranged allylic hydroperoxides. Barton's[10] results however appear to preclude the possibility that singlet oxygen is involved at least in their solvent system even though the triplet energy of $^3Ph_3C^+$ ($E_T = 52$ kcal mol^{-1} from phosphorescence measurements in 99% H_2SO_4 glass) is sufficient to make the formation of singlet oxygen exothermic.

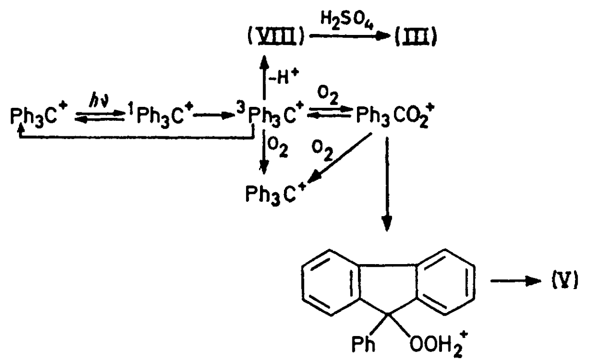

(VIII)


(IX)

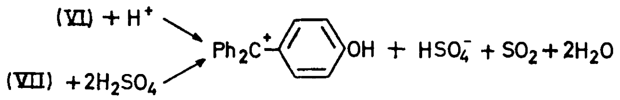

(X)


(XI)

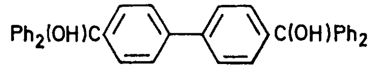
It is possible that the early stage of Figure 2 (*i.e.* low O_2 pressure) represents the well known paramagnetic quenching of $^3Ph_3C^+$ and the later linear portion (20—400 Torr) may be due to quenching of some other intermediate, *e.g.* the reversible adduct $^3Ph_3CO_2^+$. If this adduct is able to dissociate to Ph_3C^+ and O_2 as well as in the way suggested by Barton this would be an effective quenching mechanism which might also explain the low quantum yield for the overall reaction. The quenching of $^1Ph_3C^+$ is also a possibility since Brewer[16] has shown that the quenching of excited aromatic singlet states by oxygen is exceedingly efficient but that as the ionisation potential increases the rate of quenching decreases. Results in 99% sulphuric acid are summarized in the scheme below.



The two products isolated from photolyses carried out in 78% sulphuric acid clearly arise from the same carbonium ion since both products would give rise to the same ion thus:



Further work is necessary before the mechanism of formation of diphenyl-(4-hydroxyphenyl)methyl cation (XII) can be formulated but present indications are that it may be formed by attack by solvent water on the excited carbonium ion by a process which is analogous to that proposed by van Tamelen[3a] in a related system. Further work is also required on the phosphoric acid system where the only product found, 4,4'-bis(diphenylhydroxymethyl)biphenyl (XIII), was one of three products obtained by van Tamelen[3] on irradiation of (I) in 72% sulphuric acid. The fact that oxygen has no effect on the reaction supports the suggestion made initially by van Tamelen that the dimer results from an electrophilic attack by the carbonium ion in an excited singlet state on a carbonium ion in the ground state. However, the nature of the product suggests that it may be derived from an alternate intermediate suggested by the same authors. Phosphoric acid is a strong oxidising agent and may remove a hydride ion to produce the ion from which (XIII) would result.



(XIII)

We thank the S.R.C. for the award of a Research Studentship to D. M. A.

[2/1652 *Received*, 12*th July*, 1972]

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[15] D. R. Kearns, W. Fenical, and P. Radlick, *Ann. New York Acad. Sci.*, 1970, **171**, 34.

[16] T. Brewer, *J. Amer. Chem. Soc.*, 1971, **93**, 775.