

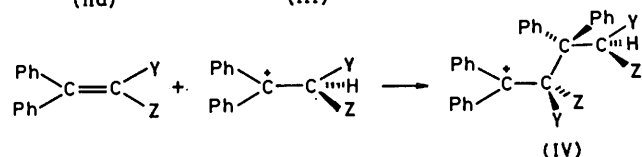
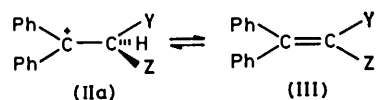
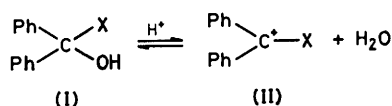
## Substituted Diphenylmethyl Cations. Part 2.† Modes of Decomposition of Ions and a Reinvestigation of the Electronic Absorption Spectra

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The various modes of decomposition of diphenylmethyl cations,  $\text{Ph}_2\text{C}^+-\text{X}$ , with different substituents X, have been examined. Substituents containing carbonyl groups cause the ions to cyclise rapidly to 9-substituted fluorenes. Trapping experiments have established the carboxy-, methoxycarbonyl-, and acetyl-substituted diphenylmethyl cations to be present in solution sufficiently long for reliable u.v. spectra to be recorded. The diphenyl(styryl)methyl cation immediately rearranges at room temperature to give the 1,3-diphenylindanyl cation. The diphenyl(phenylacetylenyl)methyl cation rapidly hydrates to form 1,3,3-triphenylprop-2-en-1-one in sulphuric acid solutions of intermediate strength, but in 96%  $\text{H}_2\text{SO}_4$  the 1,1,3-triphenylprop-2-ynyl cation is stable at room temperature. The energy of the absorption maximum of the first band in the electronic spectra of the diphenylmethyl cations correlate with the Taft substituent constants,  $\sigma^+$ .

THE equilibria between triarylmethanols and the triarylmethyl carbonium ions have been studied extensively and used to construct one of the most widely used acidity functions,  $H_R$ .<sup>1</sup> The parent triphenylmethyl cation is remarkably stable in aqueous sulphuric acid at room temperature but undergoes slow photochemical decomposition to dimers or fluorene derivatives, the amount of each product depending on the acid strength and the amount of molecular oxygen present.<sup>2,3</sup>

The diphenylmethanols (I) undergo the same type of ionisation but are less suitable indicators since the carbonium ions (II) are much less stable and decompose

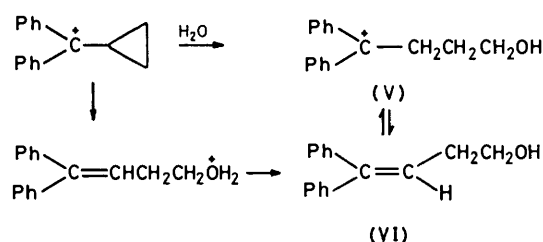


by a variety of pathways. Diphenylmethyl cations in which X is a saturated hydrocarbon group with a hydrogen atom on the carbon atom adjacent to the carbonium ion centre are in equilibrium with the olefins (III) formed by deprotonation, and in this instance diphenylmethanols although conceivably present in small amounts are not detectable spectroscopically or by extraction. At high acidities this type of ion is stable but at lower acidities, when considerable amounts of free olefin are present, the cation reacts with a neutral molecule to form a dimeric carbonium ion (IV). This in turn can react further with another molecule of olefin and slow polymerisation occurs. Most 1,1-diphenylethylenes polymerise by this mechanism with a maximum rate occurring where the acidity permits equal concentrations of olefin and carbonium ion.<sup>4,5,6</sup>

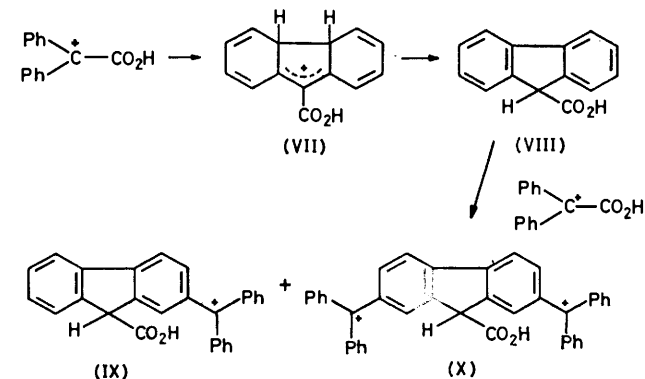
† Part 1, T. W. Toone, E. Lee-Ruff, P. G. Khazanie, and A. C. Hopkinson, *J.C.S. Perkin II*, 1975, 607.

The cyclopropyldiphenylmethyl cation (II; X = cyclopropyl) is stable at low temperatures in the non-nucleophilic 'magic acid' solutions,<sup>7</sup> but rapidly ring opens in aqueous sulphuric acid to yield the 3-hydroxybutyldiphenylmethyl cation (V).<sup>6</sup> This ion behaves similarly to the alkyl substituted ions described previously and is in equilibrium with the olefin 4,4-diphenylbut-3-en-1-ol (VI).

Benzilic acid (I; X =  $\text{CO}_2\text{H}$ ) undergoes a rapid



decomposition in dilute sulphuric acid to form the fluorene derivatives (IX) and (X).<sup>8</sup> It is probable that the carboxydiphenylmethyl cation is formed initially and that this cyclises to form the 9-carboxyindanyl cation (VII).



is indicative of a ground state reaction and as such it differs from the cyclisation of the triphenylmethyl cation in strong acid<sup>3</sup> and from the cyclisation of the diphenylmethyl cation in the mass spectrometer.<sup>9</sup> This electrocyclic reaction should occur in a conrotatory manner<sup>10</sup> but the subsequent rapid deprotonation and 1,3-hydride shift to form fluorene-9-carboxylic acid prevent elucidation of the stereochemistry of the re-

action. Finally the cations (IX) and (X) are formed by electrophilic attack on fluorene-9-carboxylic acid followed by decarbonylation. Many examples of the electrocyclic transformation of pentadienyl cations into cyclopentenyl cations are available in the literature<sup>11,12</sup> and in most instances the pentadienyl cations are sufficiently transient only to be observable at very low temperatures. In this respect then, the diphenylmethyl cations can be considered to be a particularly stable class of pentadienyl cations and the cyclisation of the benzilate cations to form fluorenes is similarly a reaction characteristic of pentadienyl cations.

Electronic absorption spectra have been reported for diphenylmethyl cations in both superacids<sup>8</sup> at low temperatures and also in 96% sulphuric acid at room temperature.<sup>13</sup> In both studies the existence of the cations was established purely on spectral evidence and subsequent extraction work to regenerate the diphenylmethanols was not attempted. In the light of the rapid decomposition of some diphenylmethyl cations to form other coloured ions and the oligomerisation of many alkyl-substituted cations to form structurally similar dimers and trimers, it seemed possible that some of the electronic spectra had been incorrectly assigned. We therefore decided to re-examine critically the spectra of the diphenylmethyl cations in aqueous sulphuric acid to attempt to further clarify the structure of the cations in solution both by trapping the carbonium ion with 2,6-dimethylphenol and by extraction of the indicator from the acid solutions by quenching with water.

#### EXPERIMENTAL

Benzilic acid, methyl benzilate, diphenylmethanol, and cyclopropyldiphenylmethanol were obtained commercially. 1-Hydroxy-1,1-diphenylpropan-2-one was prepared from acetonitrile and benzophenone in liquid ammonia, followed by hydrolysis of the imine,<sup>14</sup> needles from hexane, m.p. 62–63° (lit.,<sup>15</sup> 58–59°). 1,1,3-Triphenylprop-2-en-1-ol was prepared by addition of 2-phenylethylenmagnesium bromide to benzophenone, needles from ethanol, m.p. 106–108° (lit.,<sup>16</sup> 106–108°). 1,1,3-Triphenylprop-2-yn-1-ol was pre-

pared from phenylethylenmagnesium bromide and benzophenone, needles from ethanol-water, m.p. 78–80° (lit.,<sup>17</sup> 79°).

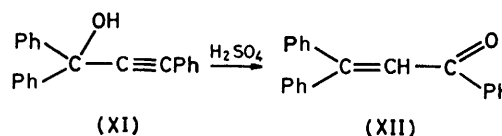
The alkyldiphenylmethanols were all prepared by addition of the required Grignard reagent to benzophenone and purified until m.p.s were in agreement with literature values.<sup>6</sup> Several compounds not previously reported were extracted from sulphuric acid solutions and for these compounds the analytical data and physical constants are reported in Table 1.

Electronic spectra were recorded on a Unicam SP 1800 spectrophotometer using stoppered 1 cm quartz cells. All the sulphuric acid solutions were made from reagent grade acid. The acids used in the  $pK_{R^+}$  determinations were analysed both by titration with base and by density measurements. Accurate dilution was effected by adding weighed amounts of water to the sulphuric acid solutions.

#### RESULTS AND DISCUSSION

(a) *Product Analysis*.—The stabilities of the diphenylmethyl cations and the various products formed on their decomposition are given in Table 2. The alkyl-substituted cations are all stable over a period of hours, the carboxy, methoxycarbonyl, and acetyl compounds decompose within a minute and the cyclopropyl, styryl, and phenylacetylenyl groups are destroyed immediately on dissolving in sulphuric acid. The ring opening of the cyclopropyl group has been studied extensively<sup>6</sup> and was not re-examined in the present work.

(1) 1,1,3-Triphenyl-2-yn-1-ol. 1,1,3-Triphenyl-2-yn-1-ol (XI) rearranged and was recovered from concentrated sulphuric acid as the chalcone 1,3,3-triphenylprop-



2-en-1-one (XII).<sup>18,19</sup> In 25%  $\text{H}_2\text{SO}_4$  (XI) initially had an identical u.v. spectrum to that in methanol (see Table 3) but this slowly changed to one similar to that of

TABLE 1  
Analytical data for compounds extracted from aqueous sulphuric acid

Compound	M.p. (°C)	Analysis (%)	<i>m/e</i> (70 eV)	Chemical shift $\delta(\text{CDCl}_3)$
(XXVI; X = COMe)	Needles from ethanol, 160–161°	Found: C, 83.65; H, 6.65 Calc.: C, 83.4; H, 6.7		2.10 (3 H, s) 2.17 (6 H, s) 4.80 (1 H, s) 6.9–7.4 (12 H, m)
(XXVI; X = CO <sub>2</sub> Me)	Prisms from ethanol, 138–139°	Found: C, 79.6; H, 6.3 Calc.: C, 79.75; H, 6.4		
(XXVI; X = CO <sub>2</sub> H)	Rhomboheda from ethanol, 228–230° (decomp.)	Found: C, 79.45; H, 6.1 Calc.: C, 79.5; H, 6.05		
(XXV)	Needles from methanol, 174–175° (decomp.)	Found: C, 70.35; H, 5.3 Calc.: C, 70.3; H, 4.8	470 ( $M^+$ ) 390 ( $M^+ - \text{SO}_3$ ) 208 182 167	1.90 (3 H, s) 3.50 (1 H, s) 6.80–7.20 (6 H, m) 7.32 (10 H, m)
(XX)	Oil	Found: C, 87.5; H, 6.9 Calc.: C, 87.9; H, 7.0	314 ( $M^+$ ) 268 ( $M^+ - \text{EtOH}$ ) 220 206 190 182	1.14 (3 H, t, <i>J</i> 7 Hz) 3.38 (2 H, q, <i>J</i> 7 Hz) 4.86 (1 H, d, <i>J</i> 9 Hz) 6.30 (1 H, d, <i>J</i> 9 Hz) 7.00–7.50 (15 H, m)

TABLE 2

Stability and decomposition products of diphenylmethyl cations (II) in concentrated sulphuric acid

X	Stability of initially formed diphenylmethyl cation in 80–96% H <sub>2</sub> SO <sub>4</sub>	Mode of decomposition	Compound extracted on dilution of sulphuric acid
Me	Stable for hours	Slow polymerisation <sup>a,b</sup>	(III; X = Y = H)
H	Stable for hours		(I; X = H)
Et	Stable for hours	Slow polymerisation <sup>a</sup>	(III; X = H, Y = Me)
Pr <sup>i</sup>	Stable for hours	Slow polymerisation <sup>a</sup>	(III; X = Y = Me)
Bu <sup>t</sup>	Stable for hours	Slow charring	(I; X = Bu <sup>t</sup> )
CH <sub>2</sub> Ph	Stable for hours	Slow polymerisation <sup>b</sup>	(III; X = H, Y = Ph)
CH <sub>2</sub> OPh	Stable for hours	Slow polymerisation	(III; X = H, Y = OPh)
C≡C-Ph	Immediately hydrates at acid strengths below 70% H <sub>2</sub> SO <sub>4</sub> ; in 96% H <sub>2</sub> SO <sub>4</sub> acetylenic group is intact	Hydration to chalcone in intermediate strength acid	(XII)
Cyclopropyl	Immediately hydrates	Ring opening of cyclopropane <sup>b</sup>	(III; X = H, Y = CH <sub>2</sub> CH <sub>2</sub> OH)
CO <sub>2</sub> H	Decomposes within 30 s at 3° in 85% H <sub>2</sub> SO <sub>4</sub>	Ring closure to fluorenyl derivatives <sup>c</sup>	(IX; OH for +) and (X; OH for +)
CO <sub>2</sub> Me	Decomposes within 30 s at 3° in 85% H <sub>2</sub> SO <sub>4</sub>	From spectral behaviour appears to be similar to benzoic acid	
COMe	Decomposes within 30 s at 3° in 85% H <sub>2</sub> SO <sub>4</sub>	Ring closure to fluorenyl derivatives	(XXV) and (XXIV)
CH=CHPh	Decomposes immediately in 96% H <sub>2</sub> SO <sub>4</sub>	Ring closure to indenyl derivative	(XVIII) and (XIX)

<sup>a</sup> Ref. 5. <sup>b</sup> Ref. 6. <sup>c</sup> Ref. 8.

an authentic sample of (XII) in methanol,  $\lambda_{\max}$  208, 233, 260sh, and 308 nm. In 50% H<sub>2</sub>SO<sub>4</sub> (XI) immediately formed a colourless solution with a u.v. spectrum like the one formed slowly in 25% H<sub>2</sub>SO<sub>4</sub>. Solutions of (XI) developed a yellow colour in the range 60–69% H<sub>2</sub>SO<sub>4</sub>. This reaction was easily reversed by addition of water and was attributed to a simple protonation equilibrium. The spectral shift on protonation was very large, characteristic of those previously reported for chalcones,<sup>20</sup> and there was also a smaller bathochromic

70–86% H<sub>2</sub>SO<sub>4</sub> showed a further small bathochromic shift as the acid strength was increased, but above 86% H<sub>2</sub>SO<sub>4</sub> the spectrum underwent another major change and in 96% H<sub>2</sub>SO<sub>4</sub> the spectrum was similar to that previously reported for the compound in SbF<sub>5</sub>-FSO<sub>3</sub>H at -65° (76). Furthermore the <sup>13</sup>C spectrum generated by dissociation of 1,1,3-triphenylprop-2-yn-1-ol in 98% D<sub>2</sub>SO<sub>4</sub> at 33° had chemical shifts very similar to those reported for ion (XIII) in FSO<sub>3</sub>H-SO<sub>2</sub>-SbF<sub>5</sub> at -60°. <sup>23</sup> In particular the non-aromatic carbons had peaks at  $\delta$  188.27 (186.8) for  $\alpha$ -C, 106.9 (105.9) for  $\beta$ -C, and 161.3 (159.1) for  $\gamma$ -C, where the assignment and values in parentheses are from the literature.<sup>23</sup> The small difference in chemical shifts may be attributed to solvent effects.

The <sup>13</sup>C n.m.r. spectrum of 1,3,3-triphenylprop-2-en-1-one in D<sub>2</sub>SO<sub>4</sub> had peaks at  $\delta$  193.7 ( $\gamma$ -C) and 183.3 ( $\alpha$ -C) and nine peaks in the aromatic region ( $\delta$  129–141). Both ions (XIII) and (XIV) were sufficiently stable at room temperature over a period of hours to reproduce the same n.m.r. spectra and, at u.v. concentrations (ca. 10<sup>-4</sup>M), to produce identical u.v. spectra over 24 h. Clearly ions (XIII) and (XIV) do not readily interconvert in 96–98% H<sub>2</sub>SO<sub>4</sub> but on dilution (XIII)

TABLE 3

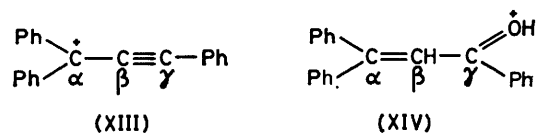
U.v. and visible spectra of 1,1,3-triphenylprop-2-yn-1-ol in different solvents

Solvent	$\lambda_{\max.}/\text{nm}$
Methanol	208, 233sh, 243, 252
50% H <sub>2</sub> SO <sub>4</sub>	208, 260br, 335br
86% H <sub>2</sub> SO <sub>4</sub>	208, 397, 460
96% H <sub>2</sub> SO <sub>4</sub>	455, 515
SbF <sub>5</sub> -FSO <sub>3</sub> H <sup>a</sup>	449, 504

<sup>a</sup> Ref. 7b.

solvent shift. A plot of  $\log I$  versus  $-H_R$ <sup>21</sup> gave a slope of 0.49, showing that the compound behaved very differently from the ionisation behaviour of a carbinol indicator. A plot of  $\log I$  against  $-H_0$ <sup>22</sup> had a slope of 0.964 ( $r$  0.994) and these data yielded a  $pK_{\text{BH}^+}$  value of -4.86 (i.e.  $H_0$  value at  $\log I$  0). The indicator slope is much closer to ideal behaviour and, as ketones usually have indicator slopes of less than unity (commonly in the range 0.7–0.9) the data are again more consistent with a simple protonation on the hydrated compound (XII). Noyce and Jorgenson<sup>20</sup> obtained a  $pK_{\text{BH}^+}$  value of -5.65 for 1,3,3-triphenylprop-2-en-1-one in 5% dioxan-sulphuric acid mixtures. The difference in solvent systems and also in the  $H_0$  functions used to treat their protonation data can easily account for the differing  $pK_{\text{BH}^+}$  values.

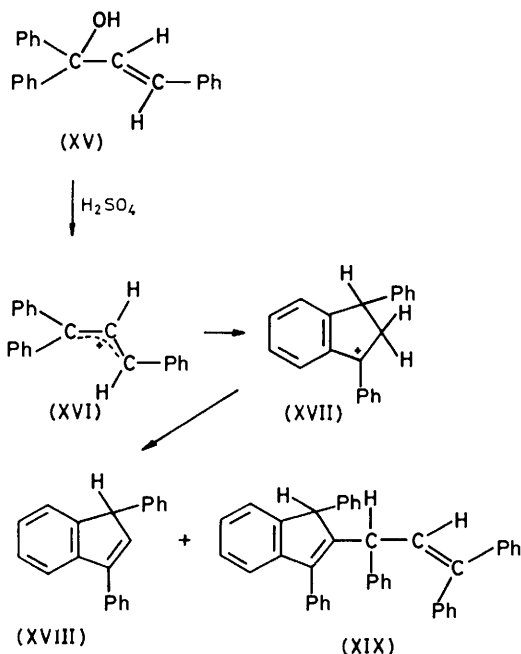
Solutions of 1,1,3-triphenylprop-2-yn-1-ol in the range



hydrates to form (XIV) and 1,1,3-triphenylprop-2-en-1-one is extracted on dilution of the acid solution with water. Similar behaviour has been noted previously for other carbinols containing  $\alpha$ -alkynyl groups.<sup>24,25</sup>

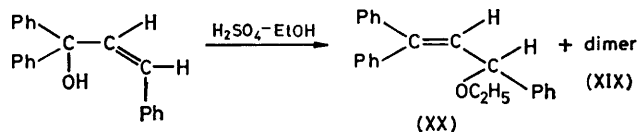
(2) 1,1,3-Triphenylprop-2-en-1-ol. Dissolution of 1,1,3-triphenylprop-2-en-1-ol (XV) in 96% H<sub>2</sub>SO<sub>4</sub> at room temperature immediately produced a yellow

solution,  $\lambda_{\text{max}}$  418 ( $\log \epsilon$  4.14) and 308 nm (3.74), which did not change noticeably over several hours. The n.m.r. spectrum of this coloured solution [a multiplet in the aromatic region,  $\delta$  4.87br (1 H) and 4.46 (2 H, q)] was very similar to that reported for the 1,3-diphenylindanyl cation (XVII).<sup>26</sup> In  $\text{D}_2\text{SO}_4$  the peak at  $\delta$  4.46



was absent and the peak at  $\delta$  4.87 slowly diminished over a period of several hours. These observations are consistent with the 1,3-diphenylindanyl cation being in equilibrium with 1,3-diphenylindene (XVIII). The electronic spectrum of the ion in 96%  $\text{H}_2\text{SO}_4$  was almost identical to those reported for the 1-phenylindanyl and the 3-methyl-1-phenylindanyl cations,<sup>27</sup> further supporting the assignment of structure (XVII).

The 1,1,3-triphenylpropenyl cation (XVI), presumably an intermediate in the formation of the 1,3-diphenylindanyl cation, was not detected by spectroscopy and,



as there were no visible rapid colour changes during the mixing of the 1,1,3-triphenylprop-2-en-1-ol in sulphuric acid, it appears that the 1,1,3-triphenylpropenyl cation must cyclise very rapidly. These observations are in agreement with those of Pittman and Miller,<sup>26</sup> who found that 1,1,3-triphenylprop-2-en-1-ol in  $\text{FSO}_3\text{H-SO}_2$  at  $-60^\circ$  formed the 1,1,3-triphenylpropenyl cation but at  $-30^\circ$  cyclisation to the 1,3-diphenylindanyl cation occurred rapidly.

In 20%  $\text{H}_2\text{SO}_4$ -80% ethanol (v/v) 1,1,3-triphenylprop-2-en-1-ol was converted into the dimer (XIX) (29%) and the ether (XX) (71%). Formation of the ether provides good evidence for the intermediacy of the 1,1,3-triphenyl-

propenyl cation in sulphuric acid solutions, but here also the products were formed immediately and the intermediate cation was not detected. Clearly in this solution bimolecular trapping of the carbonium ion by ethanol competes favourably with unimolecular cyclisation.

The ether (XX) when dissolved in 96%  $\text{H}_2\text{SO}_4$  immediately gave the 1,3-diphenylindanyl cation. In boiling acetic acid or in trifluoroacetic acid at room temperature the ether gave a mixture of the dimer (XIX) (ca. 80%) and 1,3-diphenylindene (XVIII) (ca. 20%).<sup>28</sup> This contrasts sharply with extraction from 96%  $\text{H}_2\text{SO}_4$  where the yield of the monomeric 1,3-diphenylindene was  $>95\%$  and little dimer was produced.

(3) *1-Hydroxy-1,1-diphenylpropan-2-one*. In 96%  $\text{H}_2\text{SO}_4$  1-hydroxy-1,1-diphenylpropan-2-one formed a yellow solution which rapidly went colourless and then turned red. In 60%  $\text{H}_2\text{SO}_4$  at  $-10^\circ$  followed by dilution with ice and extraction after three minutes the only products were starting material and 9-acetylfluorene (XXIV).<sup>29</sup> In more concentrated acid at room temperature the reaction is considerably more complicated and (XXIV) and the sulphonic acid (XXV) were isolated. The presence of the diphenylcarbinol and sulphonic acid groups in (XXV) were assigned to the fluorenyl ring system on the basis of mass spectral results but their exact positions were not established. [The sharp m.p. of (XXV) suggested that only one compound was isolated.] Also the mechanism of the removal of an acetyl group to form the carbinol was not investigated further.

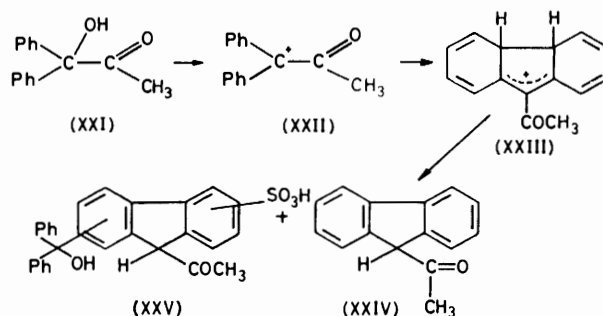
(b) *Trapping of Transient Diphenylmethyl Cations*.—Diphenylmethanols with the electron-withdrawing groups  $\text{CO}_2\text{H}$ ,  $\text{CO}_2\text{Me}$ , and  $\text{COMe}$  in 96%  $\text{H}_2\text{SO}_4$  initially formed yellow solutions but within a few seconds these were transformed into stable red solutions. These latter solutions were mistakenly reported as the diphenylmethyl cations previously.<sup>13</sup> In 86%  $\text{H}_2\text{SO}_4$  the same sequence of colour changes occurs but much more slowly and, by using rapid mixing and a fast scan over a limited

range (usually 20 nm) both from high wavelength and from low wavelength on ice-cold solutions, estimates of the absorption maximum (but not of the extinction coefficients) of the initial decomposing yellow-coloured ions for the ketone and ester were obtained. Subsequently these ions were found to be much longer lived in chlorosulphonic acid-methylene chloride solutions at  $-40^\circ$  and the more reliable spectral data from that study were used in the spectral correlation section.

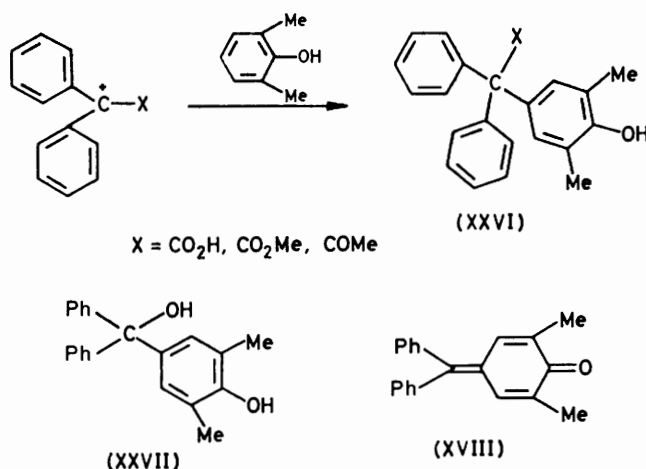
Trapping experiments using at least a ten-fold excess of 2,6-dimethylphenol on the initially formed yellow solutions resulted in immediate and permanent loss of colour from the solution. Dilution of these solutions

followed by ether extraction provided only the triarylmethane derivatives (XXVI), the products of electrophilic addition. Work-up procedures were simplified by allowing the sulphuric acid solution to stand for several minutes before dilution thereby eliminating the excess of 2,6-dimethylphenol through sulphonation. Under these conditions, however, the triphenylmethanes with the carboxylic acid and, to a lesser extent, the methoxy-

Finally, the  $\text{ClSO}_3\text{H}-\text{CH}_2\text{Cl}_2$  solutions of both methyl benzilate and 1-hydroxy-1,1-diphenylpropan-2-one at  $-40^\circ$  were rapidly neutralised by addition of a small amount of a slurry of sodium hydrogencarbonate in water and the only extraction products were found to be starting materials. Clearly then both these carbinols are in equilibrium with the carbonium ions. Previously stable  $\alpha$ -carboxycarbonium ions have been generated



carbonyl side chains began to decarbonylate and in addition to compounds (XXVI), the carbinol (XXVII) and 3,5-dimethylfuchstone<sup>30,31</sup> (XXVIII) were obtained on dilution. Separation and purification of (XXVII) was difficult as it dehydrated to (XXVIII) in solution



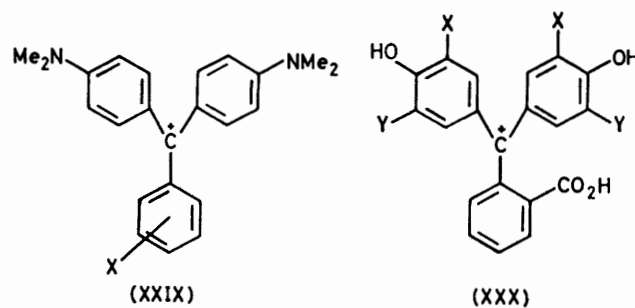
and on silica gel. Similar trapping experiments on the final red solutions resulted in little apparent reaction, and on dilution and extraction no triarylmethanes or fuchstones were obtained.

In the absence of direct spectral evidence for ions (II) with electron-withdrawing groups  $\text{CO}_2\text{H}$ ,  $\text{CO}_2\text{Me}$ , and COMe in sulphuric acid solutions these trapping experiments provide good evidence that either the carbonium ions (II), or some isomeric ions which can rapidly revert to (II), must be responsible for the initially formed yellow coloured solutions. Formation of the initial coloured solutions requires more acidic conditions (above 80%  $\text{H}_2\text{SO}_4$ ) than for the alkyl-substituted diphenylmethyl cations and this is also consistent with the formation of ions (II) in which there are deactivating groups.

from the structurally similar 3,3'-thienylic acid and its methyl ester in  $\text{ClSO}_3\text{H}-\text{CH}_2\text{Cl}_2$  solutions.<sup>32</sup>

The alkyldiphenylmethyl cations and the parent cation did not react noticeably with 2,6-dimethylphenol in the short length of time used in the trapping experiments. No attempt was made to persuade these more stable cations to undergo condensation reactions but the condensation of triarylmethyl carbonium ions with phenol in strong acid conditions has been studied extensively.<sup>33-37</sup>

(c) Correlation of  $\lambda_{\text{max}}$  with Substituent Constants.—The Hammett substituent constants are usually considered to represent the influence of a substituent on the electron density at a reacting site of a molecule in a ground state reaction. However there are several examples of the correlation of the energy of an electronic transition with the appropriate substituent constants.<sup>38-40</sup>



For example, the energy of the first electronic transition of the Malachite Green ions (XXIX)<sup>38</sup> and the second electronic energy transition of the phenolphthalein cations (XXX)<sup>39</sup> both correlate with Hammett substituent constants. For both these classes of ions the results have been interpreted as movement of electrons from the ring (or rings) not bearing the substituents X and Y towards the central carbon atom. In both these groups of ions electron-withdrawing substituents in the

TABLE 4  
Spectral data for diphenylmethyl carbonium ions (I)

Substituent X	$\lambda_{\max}$ , for first electronic transition (nm)	$\log \epsilon$	$10^4$ Energy of transition ( $\text{cm}^{-1}$ )	$\sigma^*$
Me	428	4.51	2.336	0.00
H	443	4.63	2.257	0.49
Et	430	4.49	2.326	-0.10
Pr <sup>i</sup>	432	4.22	2.314	-0.19
Bu <sup>t</sup>	434	4.12	2.304	-0.30
CH <sub>2</sub> Ph	430	4.32	2.326	0.22
CH <sub>2</sub> OPh	447	3.23	2.237	0.85
CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	437	4.53	2.288	
CO <sub>2</sub> H	452 <sup>a</sup>		2.213	
CO <sub>2</sub> Me	476 <sup>a</sup>		2.101	2.00
COMe	464 <sup>a</sup>		2.155	1.65

<sup>a</sup> Recorded in chlorosulphonic acid-methylene chloride solutions at  $-40^\circ$ .

ring (or rings), although not formally involved in the transition, do in fact lower the energy of the transition.

The diphenylmethyl cations have only the possibility of electron migration from the two identical phenyl groups, and this produces one electronic transition in the visible spectrum. In principle, then, the spectra of these ions should be simpler to analyse than those of the previously examined triarylmethyl cations. The first electronic transition of the parent diphenylmethyl cation is  $\pi \rightarrow \pi^*$  and has been analysed at the simplest level of sophistication using simple Huckel theory.<sup>41,42</sup> In the ground state the diphenylmethyl cation has a large amount of charge (+0.35) on the exocyclic carbon atom and in the first excited state the charge on this atom is zero. There is therefore a large migration of electron density from the phenyl groups to the exocyclic carbon atom. Substituents on the exocyclic carbon atom will therefore, to a first approximation, affect only the ground state and not the first excited state. Electron-donating substituents should stabilise the ground state and produce a blue shift and this prediction is borne out by the alkyl substituents as shown by the data in Table 4. Electron-withdrawing substituents have the opposite effect, producing a red shift in the spectrum, presumably by destabilising the ground state.

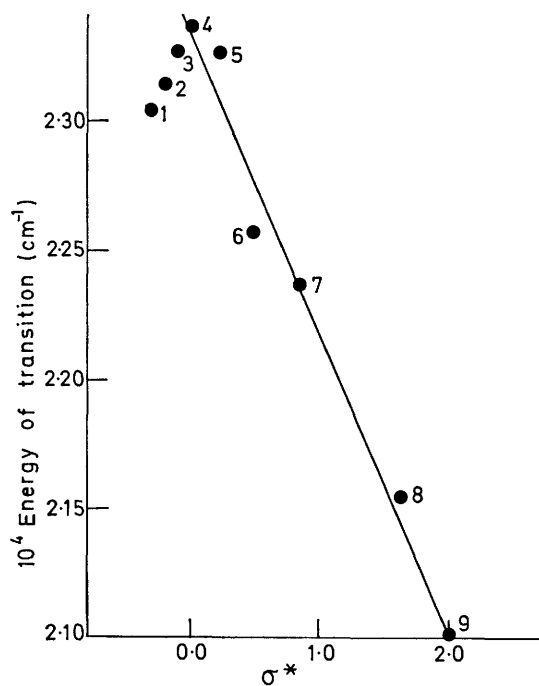
Previously, a rough correlation was established between the first electronic energy transition of the diphenylmethyl cations and the Taft  $\sigma^*$  substituent constants.<sup>13,43</sup> However, several of the previously reported spectra were, as established above, those of the decomposition products. It is, therefore, now necessary to re-examine this relationship.

The spectral data in Table 4 are for the ions in aqueous sulphuric acid solutions, except for cations with the strongly electron-withdrawing carboxy, methoxycarbonyl, and acetyl groups, which were too unstable to produce reproducible spectra in aqueous sulphuric acid and were therefore examined in chlorosulphuric acid-methylene chloride solutions at  $-40^\circ$ . The electronic spectra of alkyl-substituted diphenylmethyl cations have been examined in a wide variety of aqueous sulphuric acid solutions<sup>21,44</sup> and in 'magic acid'<sup>7b</sup> and they exhibit negligible solvent effects. This lack of spectral shifts

for the stable diphenylmethyl cations coupled with reasonably good agreement between the spectra for the methoxycarbonyl and acetyl-substituted ions in aqueous sulphuric acid (using the crude rapid scan method on the rapidly decomposing ion) and in chlorosulphuric acid-methylene chloride solutions suggest that use of data from different solvents is valid when studying spectral correlations for these ions.

The plot of the energy of the first transition of the diphenylmethyl cations against  $\sigma^*$  is given in the Figure. A least squares treatment on these data gave a slope,  $\rho^*$ , of  $-9.75 \times 10^2 \text{ cm}^{-1}$  and this compares with  $\rho$  values of  $-1.27 \times 10^3 \text{ cm}^{-1}$  for the phenolphthaleins,<sup>39</sup>  $-1.36 \times 10^3 \text{ cm}^{-1}$  for the phenolsulphonphthaleins,<sup>39</sup> and  $-6.5 \times 10^2 \text{ cm}^{-1}$  for the Malachite Greens.<sup>38</sup> The correlation coefficient for the diphenylmethyl cations was 0.965.

The graph in the Figure shows considerable scatter at low  $\sigma^*$  values and this is attributed to an increase in the angle of twist of the phenyl groups when the bulky isopropyl and t-butyl groups are present. The arguments using the Huckel calculations to account for the ability of a substituent to remove positive charge from the exocyclic carbon atom assume the *same* geometry for the two phenyl groups. If the substituent is bulky and causes an increase in the out-of-plane angle of the phenyl groups then less positive charge can be delocalised onto the phenyl groups and the ground state of the ion is destabilised,<sup>42,45</sup> but the first excited state is unchanged. This produces a red shift in the first band in the electronic spectrum. Furthermore, since this electronic transition involves movement of electron density largely from the  $\pi$ -orbitals of the phenyl



Plot of the energy of the first electronic transition against Taft substituent constant  $\sigma^*$ : 1, Bu<sup>t</sup>; 2, Pr<sup>i</sup>; 3, Et; 4, Me; 5, CH<sub>2</sub>Ph; 6, H; 7, CH<sub>2</sub>OPh; 8, COMe; 9, CO<sub>2</sub>Me

groups into an orbital located mainly on the exocyclic carbon, then as the angle between these orbitals increases the probability of this first transition occurring will decrease and will be reflected in a decrease in the extinction coefficient. Examination of the data in Table 4 reveals small red shifts and decreases in extinction coefficients for the series  $\text{Me} > \text{Et} > \text{Pr}^i > \text{Bu}^t$ . Clearly then the steric effect of these substituents is dominating over the weak electron-donating properties of these substituents. A similar red shift and decrease in intensity occur when *ortho*-methyl groups are introduced into the cation formed from ionisation of Michler's ketone.<sup>45</sup>

Removal of the two bulkiest substituents, *t*-butyl and isopropyl, from the data leaves a group of ions which are not, from models, sterically much more hindered than the parent cation. A least squares treatment on these remaining seven points has  $\rho^* = -10.17 \times 10^2 \text{ cm}^{-1}$  and a correlation coefficient of 0.989.

The spectrum of one diphenylmethyl cation, 1,1,3-triphenylprop-2-ynyl (XIII), was not included in the correlation in the Figure. Comparison of the spectra of alkynyl carbenium ions (Table 5) showed that the first

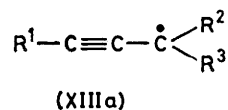
TABLE 5

Electronic absorption spectra of alkynylcarbenium ions (XIIIa)<sup>a</sup>

Substituents	$\lambda_{\text{max.}}/\text{nm}$
$\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Ph}$	504, 449
$\text{R}^1 = \text{R}^2 = \text{Ph}, \text{R}^3 = \text{CH}_3$	493, 406
$\text{R}^1 = \text{CH}_3, \text{R}^2 = \text{R}^3 = \text{Ph}$	452, 420

<sup>a</sup> Data taken from ref. 7b.

band in the spectrum is at *ca.* 500 nm only when there is a phenyl group ( $\text{R}^1 = \text{Ph}$ ) attached to the acetylene and this band was therefore assigned to a  $\pi \rightarrow \pi^*$  transition involving a shift of electron density from the phenyl-acetylenyl group towards the carbenium centre. The second band in the spectrum is at *ca.* 450 nm only when



$\text{R}^2 = \text{R}^3 = \text{Ph}$  and assignment of this band to the diphenyl fragment and using a  $\sigma^*$  value of 1.35 for the phenylacetylene group would place this point on the energy- $\sigma^*$  plot.

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