# Direct Observation and Reactivities of Benzoyl- and Methoxycarbonyldiphenylmethyl Cations

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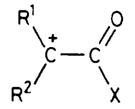
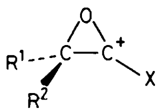
$^{13}$C N.m.r. spectra, rates of decomposition, and reaction products are reported for the methoxycarbonyldiphenylmethyl and benzoyldiphenylmethyl cations in $ClSO_3H-CHCl_3$.

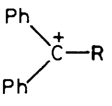
Several recent studies[1–4] have described the generation and stability of carbocations with strongly electron-withdrawing substituents in the α-position. There is direct n.m.r. spectral evidence for the α-cyanodiphenylmethyl cation[2] and a study of the solvolysis of $PhCH(O_3SMe)CO_2Me$ and of $PhCH(O_3SMe)COPh$ has been interpreted in terms of discrete secondary benzylic cations[4] (**1**, $R^1$ = Ph, $R^2$ = H, X = OMe and Ph) rather than a cyclic ion (**2**). However, minimal basis set *ab initio* studies[5,6] suggested that primary α-ketocarbonium ions are stabilized by donation from the oxygen lone pair to the vacant p-orbital on the carbon (**2**, $R^1$ = $R^2$ = H). This has



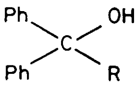
(**1**)



(**2**)



(**3**)



(**4**)

**Table 1.** $^{13}$C N.m.r. data for (**3**) and (**4**)[a]

| Carbon atom | δ/p.p.m. | | | |
|---|---|---|---|---|
| | (**4**, R = $CO_2Me$) | (**3**, R = $CO_2Me$) | (**4**, R = COPh) | (**3**, R = COPh) |
| >C=O | 175.0 | 168.8 | 200.6 | 195.6 |
| $\overset{+}{>C}-$ | — | 191.2 | — | 202.8 |
| ⩾C–OH | 80.7 | — | 85.0 | — |
| Aromatic | 141.1<br>128.0<br>127.2 | 151.1<br>134.5<br>132.9 | 141.8<br>134.9<br>132.7<br>130.7<br>128.2<br>128.0<br>127.9 | 150.5<br>145.0(w)<br>144.0(w)<br>139.7<br>135.3<br>133.2<br>130.4<br>130.1 |
| $-OCH_3$ | 54.0 | 58.2 | — | — |

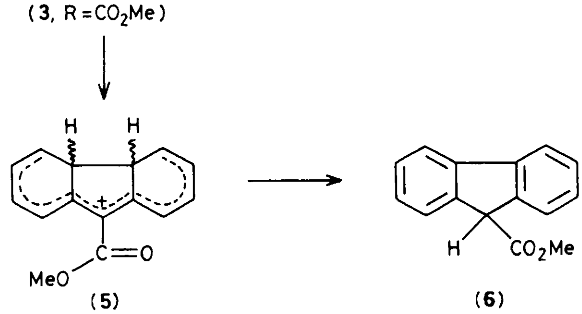
[a] Chemical shifts are in p.p.m. from $Me_4Si$. Spectra were recorded on a Bruker WH400 MHz spectrometer.

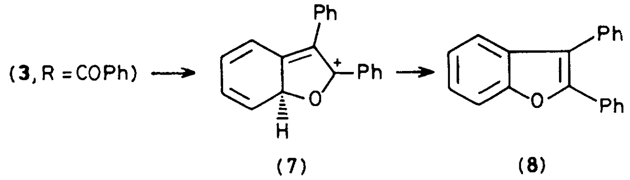
recently been confirmed by large basis set post-Hartree–Fock calculations[7] which show the formylmethyl cation (**1**, $R^1 = R^2 = X = H$) to collapse without a barrier to the oxiranyl cation (**2**, $R^1 = R^2 = X = H$). To summarise, then, theory shows α-ketocarbonium ions to adopt structure (**2**), and experimental results show that when one R group is phenyl, structure (**1**) is preferred.

We now report the preparation and $^{13}C$ n.m.r. spectral data for the α-ketocarbonium ions, (**3**), where R is $CO_2Me$ or COPh. These ions were generated by addition of $ClSO_3H$ to a frozen solution of the trisubstituted methanol (**4**) in $CDCl_3$ at −78 °C. The solution was slowly warmed with careful mixing and the $^{13}C$ n.m.r. spectra were recorded at −55 °C. Details of the $^{13}C$ n.m.r. spectra of the carbonium ions and their parent alcohols are given in Table 1. In order to assign signals associated with the carbonyl and cationic carbons, the starting alcohols (**4**) were synthesised with $^{13}C$ enrichment at the carbonyl carbon position (50% for the ester, 90% for the ketone). The cationic carbons absorbed at δ 191.2 and 202.8 p.p.m. in the methoxy-carbonyl- and benzoyl-substituted ions respectively; these values are close to the chemical shift of δ 199.4 p.p.m. for the related ion with R = H[8] but less than for the α-methyl substituted ion (R = Me, δ 229.3 p.p.m.[8]) and larger than that for the α-cyanodiphenylmethyl cation (**3**, R = CN, δ 168.8 p.p.m.[2]). The hazards in using $^{13}C$ n.m.r. chemical shifts as a measure of electron densities in carbonium ions have been well documented[8] and these α-substituted diphenylmethyl cations provide another example of an apparent inverse relationship between the electron-donating ability of the substituent R in (**3**) and the electron density on the cationic carbon as measured by the chemical shift. However, these chemical shifts do, as expected, change in parallel with the calculated charges on the cationic carbon [CNDO-2, for (**3**), R = Me, 0.248; COMe, 0.203; $CO_2H$, 0.201].[9]

The aromatic carbons in (**3**) are deshielded relative to those in (**4**), indicating that the positive charge is delocalised onto the phenyl rings. By analogy with previous work[2,8] the signals at δ 151.1 (**3**, R = $CO_2Me$) and 150.5 p.p.m. (**3**, R = COPh) were assigned to the *para*-carbons of the diphenyl groups (which compare with δ 148.2 for R = Me[8] and 153.3 p.p.m. for R = CN[2]), and here also there is a trend in the chemical shifts, although over a smaller range, which in this case follows the usual electron-donating properties of these groups. The combined charges for the two diphenyl groups from the CNDO-2 calculations (+0.588 e for R = Me, +0.635 e for R = COMe, and +0.688 e for R = $CO_2H$) also follow the same order.

Neutralisation of the orange coloured $ClSO_3H$–$CHCl_3$ solutions of both carbonium ions at −40 °C gave only the ether dimers, formed by removal of one water molecule from two molecules of (**4**). Subsequent dissolution of the ethers in $ClSO_3H$–$CHCl_3$ resulted in the immediate formation of the same carbonium ions as those produced from (**4**). At higher temperatures the rate of disappearance of the carbonium ions was monitored using $\lambda_{max}$ in the visible spectrum. Kinetic runs were performed at high dilution (*ca.* $10^{-5}$ M) and both ions were found to decay with first order kinetics. At 0 °C the α-methoxycarbonyldiphenylmethyl cation has $t_{1/2} = 4.6$ min and at 1 °C the α-benzoyldiphenylmethyl cation has $t_{1/2} = 4.4$ min. Product analysis from $ClSO_3H$–$CHCl_3$ at 0 °C gave low yields (10–15%) of the ether dimer from the α-carbonyldiphenylmethyl cation and of diphenylacetophenone from the α-benzoyldiphenylmethyl cation. However extraction work from 96% $H_2SO_4$ at 0 °C resulted in almost quantitative recovery. Product analysis of the ester (**3**, R = $CO_2Me$) gave methyl fluorene-9-carboxylate (**6**) and a dimer resulting from subsequent electrophilic attack by the α-methoxycarbonyldiphenylmethyl cation on the fluorene at higher concentrations (*ca.* $10^{-2}$ M) than that required for product studies. Fluorene formation is postulated to occur by an initial 1,5-electrocyclisation to (**5**), followed by a rapid 1,3-hydride shift and proton loss.





Neutralization of a solution of the α-benzoyldiphenylmethyl cation in 96% $H_2SO_4$ yielded 2,3-diphenylbenzofuran,[10] (**8**), and a dimer resulting from electrophilic attack by the α-benzoyldiphenylmethyl cation on the 2,3-diphenylbenzofuran. Formation of the benzofuran is postulated to occur *via* the intermediate (**7**) which is formed by nucleophilic attack of oxygen on one of the phenyl groups. Proton loss from (**7**) is expected to be rapid and yields (**8**).

In separate experiments it was found that both methyl fluorene-9-carboxylate and 2,3-diphenylbenzofuran when dissolved in $ClSO_3H$–$CHCl_3$ at 0 °C produced only water-soluble products. It therefore seems probable that the ions react similarly in both aqueous $H_2SO_4$ and $ClSO_3H$–$CHCl_3$ but with accompanying sulphonation in the latter solvent system.

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