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^{13}C N.M.R. SPECTRA OF CARBENIUM SALTS OBTAINED FROM DERIVATIVES OF PHTHALIC ACID

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Summary: o-Methoxycarbonylbenzoyl chloride reacts with Lewis acids in SO_2/CD_2Cl_2 to give solutions of carbenium salts which can be identified using ^{13}C nmr spectroscopy.

Acyl dialkyloxonium salts[1] and one example each of a diacyl alkyloxonium-[2] and a triacyloxonium-[3] salt have been reported but nmr data, especially ^{13}C data are sparse. Our interest in cationic alkylating and acylating agents and the divergence of published data[2] from our own findings prompt this report of some of our results. We were not able to repeat the published experiment,[2] in which methyl hydrogen phthalate was apparently treated with aluminium chloride. However, it is clear that $\delta_{c(Me)}$ = 53.72 ppm cannot correspond to the diacyl alkyloxonium salt (**1**) nor, as we shall demonstrate, to an acyloxy alkoxycarbenium salt because the value for $\Delta\delta_{c(Me)}$ = 0.8 ppm is too small.

An indication of the expected chemical shift difference on proceeding from a neutral methoxy-compound to a methoxonium salt follows from the chemical shifts of dimethyl ether (δ_c = 60.0 ppm in CD_2Cl_2 at 298 K) and trimethyloxonium fluoroborate (δ_c = 78.8 ppm in CD_2Cl_2/SO_2 at 253 K).† The protonation of dimethyl phthalate using $HF\text{-}SbF_5$ in CD_2Cl_2/SO_2 at 253 K also produced downfield shifts to the methyl and carbenium carbon atoms ($\Delta\delta_c$) of 14.1 and 14.4 ppm respectively.$ The chemical shift changes that occurred when phthalide (**2**) was protonated with $HF\text{-}SbF_5$ at 253 K (**3**) and methylated using trimethyloxonium fluoroborate in $CD_2Cl_2\text{-}SO_2$ at 253 K (**4**) are shown on the stuctural formulae.

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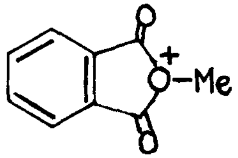
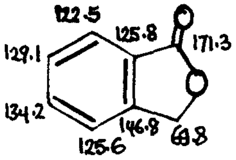
† Few ^{13}C nmr data are available for oxonium salts.
See, however, G.A. Olah, H. Doggweiler, and J.D. Felberg, J. Org. Chem., 1984, **49**, 2112.

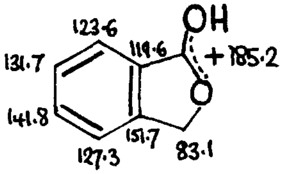
$ The ^{13}C nmr spectrum of dimethyl phthalate has been reported previously (P.E.Hanson, Org. Mag. Res., 1976, **8**, 591. Our values for dimethyl phthalate (a) and for dimethyl phthalate + $HF\text{-}SbF_5$ (b) are given. [(a) $\delta_c(CD_2Cl_2)$ at 298 K = 52.3(Me), 129.0(CH), 131.3(CH), 132.1 (C), and 168.1 (C): (b) $\delta_c(CD_2Cl_2/SO_2)$ at 253 K = 66.4(Me), 134.6(CH), 139.6(CH), 123.2(C), and 182.5(C) ppm.



(1)



(2)



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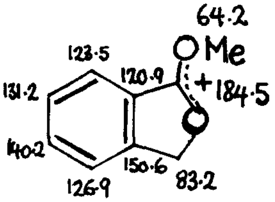
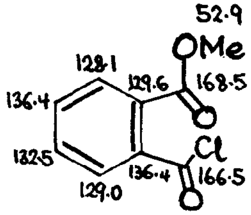
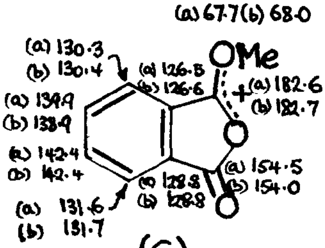


(4)

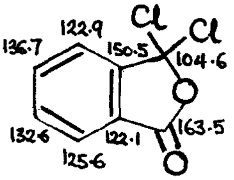
The rearrangement reactions that are known to occur when unsymmetrically substituted half ester - half acid chlorides derived from phthalic acid undergo Friedel - Crafts reactions[4] are most simply explained by invoking cations such as (1),[2] but no ion of this type has been positively identified by nmr spectroscopy at the present time. o-Methoxycarbonylbenzoyl chloride (5)[5] gave the chemical shifts shown when the spectrum was recorded in CD_2Cl_2/SO_2 at 253 K. The addition of one mol equivalent of SbF_5 (a) or $AlCl_3$ (b) to such a solution both resulted in the formation of the ion (6). We also include chemical shift data for ψ-phthaloyl chloride (7) and the corresponding ψ-ester (8).[6]



(5)



(6)



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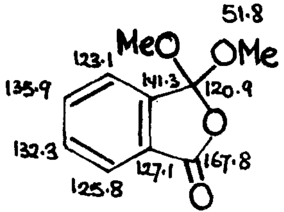

(8)

We presume that the small chemical shift differences that were recorded in different experiments result mainly from the fact that the ratio of $CD_2Cl_2:SO_2$ and the molarities were not constant. Our results clearly show that although the ion (1) is not formed from (5) under the conditions used by us, the ion (6) can be generated under stable ion conditions. The most important feature shown in the spectra of the ion (6) is the dramatic upfield shift for the residual carbonyl carbon: we presume that this is due to a shortening of the carbonyl carbon - oxygen bond. Upfield shifts of carbonyl carbons have been noted previously without comment.[7]

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References

1. F. Klages, E. Muhlbauer, and G. Lukasczyk, Chem. Ber., 1961, **94**, 1464.
2. M.V. Rao, S.H. El Ashry, and M.V. Bhatt, Tetrahedron Lett., 1981, **22**, 145.
3. H. Boekhoff and W. Heitz, Makromol. Chem., 1979, **180**, 1055.
4. see B.H. Chase and D.H. Hey, J. Chem. Soc., 1952, 553.
5. E.L. Eliel and A.W. Burgstahler, J. Am. Chem. Soc., 1949, **71**, 2251.
6. A. Kirpal, A. Galuschka, and E. Lassak, Chem. Ber., 1935, **68**, 1330.
7. A.C. Hopkinson, L.H. Dao, P. Duperrouzel, M. Maleki, and E. Lee-Ruff, J.C.S., Chem. Commun., 1983, 727.

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