Formation of Methylketenylacylium Ion in SbF_5–FSO_3H

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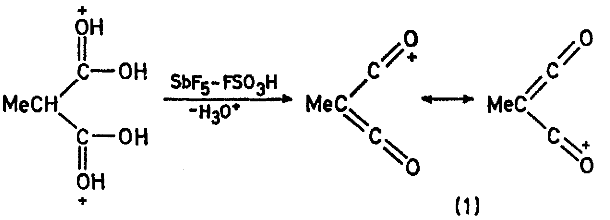
Summary Methylketenylacylium ion is formed on heating methylmalonic acid, methylmalonyl chloride, or dimethyl methylmalonate in SbF_5-SO_2.

WE recently reported[1] the formation of 6-bromoazulene-1,3-diacylium ion from the corresponding dicarboxylic acid and dimethyl ester in SbF_5–FSO_3H. This system contained a vinylogous ketenylacylium ion as a resonance-contributing structure which may impart stabilization to the positive charge that develops upon acylium ion formation. We now report the observation of a simple ketenylacylium ion resulting from treatment of methylmalonic acid and its derivatives with SbF_5–FSO_3H.

Methylmalonic acid (0·10 g) slowly dissolved in SbF_5–FSO_3H (2 ml) to give a colourless solution, δ 2·65 (d, 3H, broadened) and 5·50 (q, 1H, broadened) p.p.m.; the n.m.r. spectrum was unchanged over several hours at room temperature. This spectrum was presumably due to diprotonated methylmalonic acid, in analogy with the reported diprotonation of malonic acid in this medium.[2]



(1)

Warming the sample to 55° produced a gradual change in the spectrum which was 90% complete after 2 h. The resonances at δ 2·65 and 5·50 were no longer present but were replaced by a singlet at δ 3·05 p.p.m. assigned to the methyl group of (**1**).

The i.r. spectrum of the initial species present exhibited a strong band at 6·15 μm (no other carbonyl bands were present) which has been assigned to the protonated carboxylic acid functional group.[3] After 2 h at 55° the sample exhibited bands at 4·45m, 4·65s, and 6·18 μm. These bands have been assigned to the acylium ion,[4] keten,[5] and protonated carboxylic acid[3] functional groups respectively. The i.r. spectrum is similar to the reported spectrum of t-butylcyanoketen,[5] a compound with which it is isoelectronic. The band at 6·18 μm was of variable intensity suggesting that it may result from moisture contamination or that dehydration does not go to completion. The reversibility of acylium ion formation was shown by addition of water to (**1**), which caused the resonance at δ 3·05 p.p.m. to be replaced with resonances at δ 2·25 (t, 3H) and 5·52 (q 1H) p.p.m., so that the spectrum was identical to that of methylmalonic acid in D_2O.

To establish that a double dehydration to form (**1**) had occurred, the ester cleavage of dimethyl methylmalonate was observed under conditions similar to those employed for methylmalonic acid. Adding dimethyl methylmalonate (0·10 g), to SbF_5–FSO_3H (2 ml) produced a colourless solution, δ 2·62 (d, 3H), 5·40 (q, 1H), and 5·45 (s, 6H) p.p.m., ν 6·18 μm. Warming the sample to 55° produced a gradual change in the n.m.r. spectrum consistent with the loss of two equivalents of protonated methanol.[6] After 4 h at 55° the spectrum had resonances at δ 3·05 (s, 3H), 5·10 (s, 1·5H), and 5·20 (s, 4·5H). Additional heating produced no change in the singlet at δ 3·05 but the one at 5·10 decreased as the singlet at δ 5·20 increased in area until it appeared as 6H on integration. The peak at δ 5·20 was due to further reaction of the protonated methanol, produced in ester cleavage, with solvent.[1] The observation that both protonated methyl ester resonances were lost established that both methoxy-groups are lost by cleavage and hence both hydroxy-groups are cleaved in the dehydration of methylmalonic acid to form (**1**).

Methylmalonyl chloride (0·10 g), was also added to SbF_5–FSO_3H (2 ml) to produce a brown solution, δ 2·82 (s, 3H), 2·78 (s, 2H), and 3·05 (s, 1H) p.p.m. The spectrum changed rapidly at 55°, exhibiting only a singlet at δ 3·05 after 1 h. The i.r. spectrum of the initial solution showed bands at 4·60m, 4·68s, 5·40w, and 6·20s μm; after heating for 1 h it had bands at 4·45m, 4·65s, and 6·18m μm and was thus almost identical to the spectrum obtained from methylmalonic acid in SbF_5–FSO_3H. Addition of lithium chloride to the solution showing the single resonance at δ 3·05 p.p.m. produced a new resonance at δ 2·80 p.p.m. which was probably due to an equilibrium mixture of protonated methylmalonyl chloride and (**1**). The complexity of the initial n.m.r. spectrum of methylmalonyl chloride in the acid medium suggests that partial cleavage to an acylium ion occurs rapidly on contact with solvent and that an intermediate resulting from loss of one equivalent of H_2Cl^+ was present. However, the same singlet at δ 3·05 p.p.m. was formed at 55°, establishing that (**1**) was formed.

The above observations strongly indicate the formation of a methylketenylacylium ion by a novel cleavage of malonic acids, esters, or acid chlorides in strong acid media. Ions of this type have previously been postulated in the mass spectral fragmentation patterns of dimethyl 2-methylcyclobutane-1,1-dicarboxylate,[7] 4-pyrone,[8] pyridones,[9] and β-ketoenolates,[10] but this is the first direct chemical formation of this unusual resonance-stabilized acylium ion.

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