Mono- and Di-carbonium Ions from 1,3-Diketones

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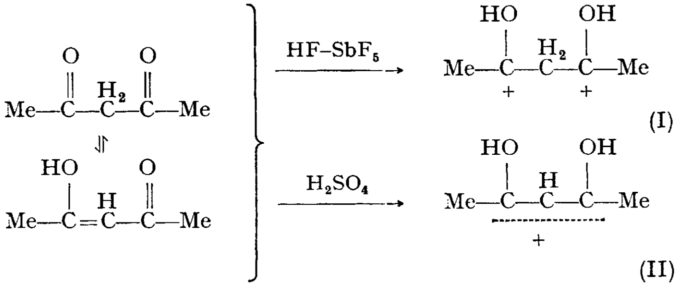
RECENTLY, Olah and Comisarov[1] reported the formation of dioxodicarbonium ions (acyl dications) from dicarboxylic fluorides and SbF_5. These ions proved to be formed only when the carbonyl groups are separated by at least three methylene groups and the positively charged parts do not interact directly.

Here, we report another class of dicarbonium ions, 1,3-dihydroxydicarbonium ions, in which the positively charged carbons are separated by only one methylene group and may interact *via* hyperconjugation with that group.



Dicarbonium ion (I) is formed when acetylacetone is dissolved in a very strong acid, *e.g.*, HF–SbF_5. Its ^1H n.m.r. spectrum consists of three single lines at −16·36, −5·47, and −3·41 p.p.m.† with intensity ratio 2 : 2 : 6. These peaks are assigned to the COH, CH_2, and CH_3, resonances, respectively. The very strong deshieldings—being far stronger than in, *e.g.*, protonated ethyl methyl ketone‡—are consistent with the dicationic nature of (I).

In less strongly acidic solutions, *e.g.*, 96% sulphuric acid or fluorosulphuric acid, monocation (II) is formed which can be regarded as the enol form of acetylacetone protonated at the C=O group. The spectrum of (II) consists of two sharp peaks at −6·19 and −2·58 p.p.m. (intensity ratio 1 : 6) which are characteristic of a hydrogen at C-2 and methyl groups at C-1 (C-3) of an allylic cation. The chemical shifts of (II) are in excellent agreement with those of the 1,3-dihydroxycyclopentenyl ion reported by Deno *et al.*[2]

In a similar way, benzoylacetone and dibenzoylmethane form dicarbonium ions in HF–SbF_5 and allylic ions in sulphuric acid. The spectrum of the dication of dibenzoylmethane has peaks at −6·03 (CH_2), between −7·9 and −8·75 (Ph), and at −14·2 p.p.m. (OH, greatly broadened) with intensity ratio 2 : 10 : 2. That of benzoylacetone has peaks at −3·52 (CH_3), −5·77 (CH_2), between −7·85 and −8·68 (Ph) (intensity ratio 3 : 2 : 5) and a broadened peak at about −13·9 p.p.m. for one OH group. No signal was found for the second OH group (presumably the one next to the methyl group), which we believe is due to too fast an exchange with solvent protons. The phenyl–H regions of the dications of dibenzoylmethane and benzoylacetone (peaks for three protons at −8·68, −8·58, −8·48 and −8·37, and for two protons at −8·10, −7·95 and −7·85 p.p.m. for benzoylacetone) are identical in shape.

The monocation of benzoylacetone gives resonance lines at −6·74 (CH), −2·70 (CH_3) and between −7·45 and −8·4 p.p.m. (C_6H_5) (intensity ratio 1 : 3 : 5), that of dibenzoylmethane at 7·01 (CH) and between −7·5 and −8·3 p.p.m. (Ph) with intensity ratio 1 : 10.

In HF containing approximately 1·5 moles of SbF_5 per mole of acetylacetone, the mono- and di-cations are present in equal amounts and still give sharp resonance lines for the CH_3, CH_2, and CH groups. This shows equilibration according to (II) + H^+ $\rightleftarrows$ (I) to be a slow process in relation to the n.m.r. time scale, in accord with the fact that proton transfer to and from a carbon atom is a

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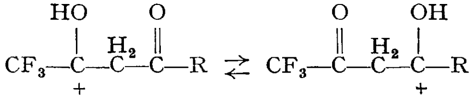
† The spectra were measured at temperatures between −20° and +30° with Me_4N^+ as internal reference, the chemical shift of which is taken as −3·20 p.p.m.

‡ Resonances at −14·7 (COH), −3·13 (methyl CH_3), −3·55 (CH_2), and −1·44 (ethyl CH_3) p.p.m.

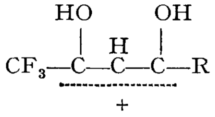
fairly highly activated process.[3] In HF–SbF_5, the OH resonance of (II) consists of two equally strong peaks at −12·22 and −11·30 p.p.m. at −60° which collapse into one peak at higher temperatures.

In a recent paper, Olah and Pittman[4] discussed the ^1H n.m.r. spectra of monoprotonated $CF_3 \cdot CO \cdot OH_2 \cdot COR$ (R=Me, CF_3, Ph) in terms of rapidly equilibrating structures (III) and (IV). In view of our results we believe that the single structure (V) should be assigned to those ions. The shifts of about −7 p.p.m. tabulated[4] for the protons at the central carbons of the ions would be much too far downfield for the CH_2 protons in (III) and (IV), and are fully compatible with the allylic hydrogen of (V).



$$\mathrm{CF_3{-}\underset{+}{\overset{HO}{\overset{|}{C}}}{-}\overset{H_2}{C}{-}\overset{O}{\overset{\|}{C}}{-}R \rightleftarrows CF_3{-}\overset{O}{\overset{\|}{C}}{-}\overset{H_2}{C}{-}\underset{+}{\overset{OH}{\overset{|}{C}}}{-}R}$$

(III) (IV)



$$\mathrm{CF_3{-}\overset{HO}{\overset{|}{C}}{-}\overset{H}{C}{-}\overset{OH}{\overset{|}{C}}{-}R}\quad +$$

(V)

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[1] G. A. Olah and M. B. Comisarov, *J. Amer. Chem. Soc.*, **1966**, **88**, 3313.

[2] N. C. Deno, H. G. Richey, N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, *J. Amer. Chem. Soc.*, **1963**, **85**, 2991.

[3] C. MacLean and E. L. Mackor, *Discuss. Faraday Soc.*, **1962**, **34**, 1656.

[4] G. A. Olah and C. U. Pittman, *J. Amer. Chem. Soc.*, **1966**, **88**, 3310.