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AN ALTERNATIVE FORMATION OF TRICARBONYLCYCLOHEXADIENYLIUM IRON SALTS BY ACID-CATALYSED DECARBONYLATION

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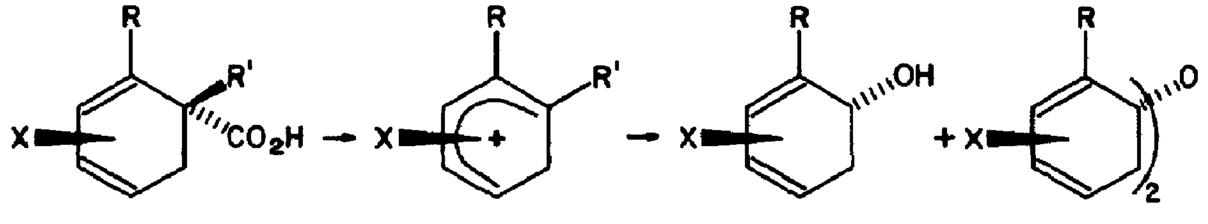
Abstract: The action of concentrated sulphuric acid on (1, R = H or CO_2Me, R' = H) generates the cation (2, R = H or CO_2Me, R' = H); the stereoisomer (5, R = H, R' = H) is unaffected. This is an alternative procedure of some utility for the preparation of some cation salts, notably of (2, R = CO_2Me, R' = H).

The potential synthetic importance[1] of the title cations makes desirable a range of methods for their preparation, particularly in view of limitations on the method of hydride abstractions by trityl cation from the diene complexes, due to steric effects and frequent lack of regiospecificity.

Concentrated sulphuric acid causes decarbonylation of a number of organic acids,[2] with loss of CO, notably of those such as pivalic acid derivatives which can yield a rather stable carbonium ion.[3] Because of the stabilities of the complexed cations, a similar reaction seemed possible, and the generation of a specifically substituted one would then depend on ability to prepare the required acid. In fact acids of type (1) (R = CO_2CH_3 or H, R' = H) in cold concentrated H_2SO_4 yield the cation (2).[†] The carboxyl-substituted cations are, as already noted,[4] more reactive than others towards nucleophilic reagents, including water. The cation (2) (R = CO_2Me, R' = H), for example, reacts almost

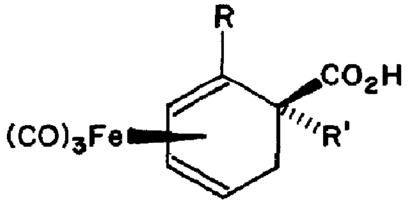


(1) (2) (3) (4)

X = $Fe(CO)_3$

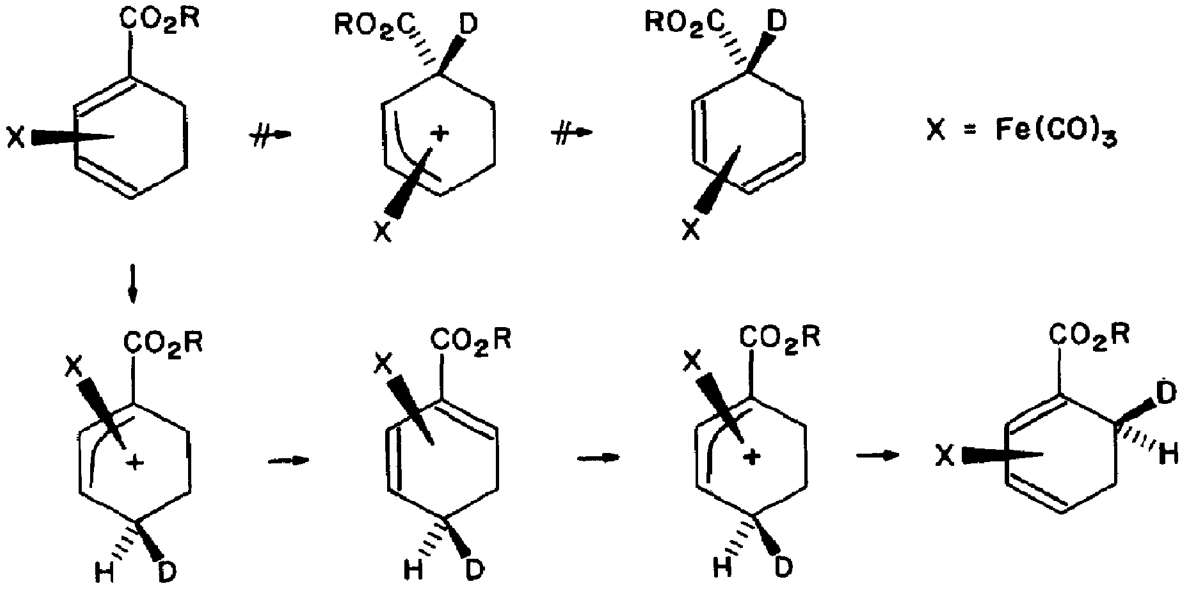
instantaneously with water to give (3) and (4). The hexafluorophosphate salt of (2, R' = H) can, however, be generated from a mixture of (3) and (4) by treatment with HPF_6-etherate.

There is evidence that in a stereoisomer with a 5β-CO_2H, as in (5, R' = H) this is not removed. A mixture of (1) (R,R' = H) and (5) (R,R' = H)[5] gives a cationic product corresponding only to the content of the former, and (5) (R = H, R' = CH_3) is largely recovered unchanged.



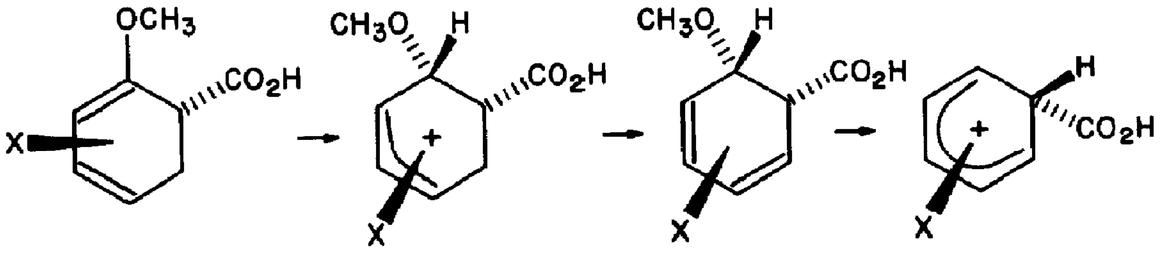
(5)

The 1-CO_2Me or 1-CO_2H does not react, which indicates that protonation by the acid does not occur at the 1-carbon, in line with arguments[4] which explain the introduction of only one D with deutero-acid.



Examination of the acid (1) (R = OCH_3, R' = H) is of particular interest, in view of the alternative formation of cations and acid-catalysed loss of OCH_3[6] and the possibility of competition. In fact, only OCH_3 is lost and the product is (6). The process is presumably as shown below.

The loss of CO_2H for cation generation has, therefore, considerable limitations but useful in some cases; there is, for example, no other method at present available for preparation of (2). The structures of products are supported by appropriate physical data, notably ^{1}H NMR spectra.[7]



(6)

X = Fe(CO)$_3$

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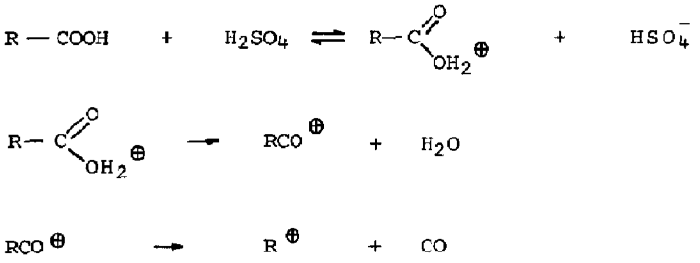
7. ^{1}H NMR: 2 (PF_6^- salt, CD_3CN, TMS); δ 7.7 (1H, d, $J_{3,4}$ = 5-6 Hz, 3-H), 5.83 (1H, t, $J_{4,5}$ = 5-6 Hz, 4-H), 4.63 (1H, d, $J_{1,6\beta}$ = 6 Hz, 1-H), 4.3 (1H, t, $J_{5,6\beta}$ = 6 Hz, 5-H), 3.73 (3H, s, CO_2CH_3), 3.3-2.8 (1H, m, 6β-H), 1.7 (1H, d, $J_{6\beta,6\alpha}$ = 16 Hz, 6α-H).
3 ($CDCl_3$, TMS); δ 6.18 (1H, d, $J_{2,3}$ = 4.5 Hz, 2-H), 5.67 (1H, dd, $J_{3,4}$ = 6 Hz, 3-H), 4.77 (1H, dd, $J_{6,5\beta}$ = 10-11 Hz, $J_{6,5\alpha}$ = 3.5-4.0 Hz, 6-H), 3.72 (3H, s, CO_2CH_3), 3.28

(1H, br s, CH), 3.04 (1H, m, 4-H), 2.48 (1H, m, $J_{4,5\beta}$ = 4 Hz, $J_{5\alpha,5\beta}$ = 15 Hz, 5β-H), 1.62 (1H, m, 5α-H), methylene protons at 5-position show splitting patterns characteristic[5] of an adjacent α-substituent.

4 ($CDCl_3$, TMS); δ 6.13 (2H, dd*, $J_{2,3} = J_{2',3'}$ = 4.5 Hz, 2- and 2'-H), 5.49 (2H, dd, $J_{3,4}$ = 6 Hz, 3- and 3'-H), 4.30 (2H, dd*, $J_{6',5'\beta}$ = 10-11 Hz, 6- and 6'-H), 3.71 (3H, s, CO_2CH_3), 3.65 (3H, s, $CO_2CH'_3$), 3.02 (2H, m, 4- and 4'-H), 2.26 (2H, m, 5β- and 5β'-H), 1.64 (2H, m, 5α- and 5α'-H), *the double doublets at δ 6.13 and 4.30 arise from the overlap of signals due to diastereometrically non-equivalent protons.

6 (PF_6^- salt, CD_3CN, TMS); δ 6.94 (1H, t, J = 6 Hz, 3-H), 5.95 (2H, t, J = 7 Hz, 2- and 4-H), 4.39 (2H, t, J = 7 Hz, 1- and 5-H), 3.83 (1H, t, J = 7 Hz, 6-H), I.R. (KBr) cm^{-1}, 3500-2500 (br, CO_2H), 2120, 2070, 1720.

† The formation of the cation (**2**) may proceed via a mechanism proposed by Hammet[8] for decarbonylation of classical carboxylic acids.



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