Cyclisations in Anhydrous Hydrogen Fluoride—a Novel Tricyclic Compound

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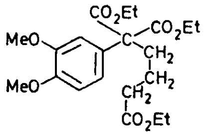
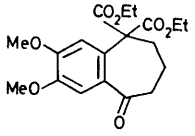
Summary A derivative of diethyl phenylmalonate (**1**) gave, on treatment with anhydrous hydrogen fluoride, a tricyclic compound (**3**) and not the expected benzocycloheptane derivative (**2**).

There are few methods reported for the direct synthesis of bridged β-diketones.[1] We have attempted to cyclise the triester (**1**) to the cycloheptane derivative (**2**) but treatment with anhydrous hydrogen fluoride over five days at room temperature gave directly the β-diketone (**3**). The n.m.r. spectrum of compound (**3**) showed two aromatic protons and only one CO_2Et group. The loss of a molecule of ethanol in addition to that lost in the expected cyclisation could only reasonably occur by an acid-catalysed Claisen condensation adjacent to the carbonyl group in compound (**2**) giving 4,8-dioxo-1-ethoxycarbonyl-4,5-dimethoxybenzo[1,2-*b*]bicyclo[3,2,1]octane (**3**), m.p. 150—151° (colourless prisms from ethanol)† [i.r. (Nujol) ν 1785, 1755 (CO at C-8) 1721 (ester CO) 1662 (ArCO) cm^{-1}, τ ($CDCl_3$) 2·49 and 3·21 (2H, s, Ar), 5·62 (2H, two overlapping quartets, CO_2CH_2Me), 6·09 (6H, s, OMe), 8·63 (3H, t, CO_2CH_2Me). The methine proton appeared as a broad doublet centred at τ 6·37 and the four methylene protons as a multiplet extending from τ 6·85—8·5].

The compound (**3**) being a β-diketone and a β-keto ester, was easily cleaved by alkali. It rapidly dissolved in warm 10% sodium hydroxide solution; the solution when refluxed and acidified gave 2,3-dimethoxy-5-oxo-6,7,8,9-tetrahydrobenzocycloheptene-9-carboxylic acid (**4**), m.p. 164—165° [(a) chloroform–60—80° light petroleum, (b) benzene].† In the i.r. spectrum the peaks at 1785 and 1755 cm^{-1} were absent.



(1)



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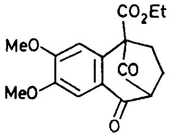

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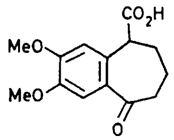

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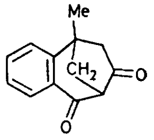

(5)

In a comparable acid-catalysed Claisen condensation, Herz and Caple[1a] heated 3-methyl-3-phenyladipic acid with polyphosphoric acid to give compound (**5**).

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† Satisfactory elemental analyses have been obtained for these compounds.

[1] (a) W. Herz and G. Caple, *J. Amer. Chem. Soc.*, 1962, **84**, 3517; (b) H. J. E. Loewanthal and Z. Neuwirth, *J. Org. Chem.*, 1967, **32**, 517; (c) P. W. Hickmott and J. R. Hargreaves, *Tetrahedron*, 1967, **23**, 3151.