405. 5 : 6 : 7 : 8-*Tetrahydro*-8-*methylindane*-1 : 5-*dione*.

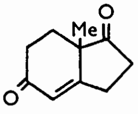
By C. B. C. Boyce and J. S. Whitehurst.

5 : 6 : 7 : 8-Tetrahydro-8-methylindane-1 : 5-dione has been synthesised in good yield. The naphthalene analogue could not be prepared by using the same conditions, and differences between the two ring systems are discussed.

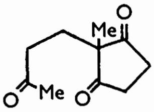
Acklin, Prelog, and Prieto [1] have recently prepared the indane (I); we had also obtained this substance, by a less tedious method.

2-Methyl*cyclo*pentane-1 : 3-dione was prepared from 2-methyl*cyclo*pentane-1 : 3 : 4-trione [2] (*a*) by vigorous acid-catalysed hydrogenolysis and (*b*) by Wolff–Kishner [3] reduction of its semicarbazone. For the latter, the slow addition of semicarbazide to the trione proved vital to the success of the subsequent decomposition. The alkali-catalysed addition of methyl vinyl ketone to the dione was almost quantitative in hot methanol yielding the crystalline trione [4] (II) and this was smoothly cyclised by toluene-*p*-sulphonic acid in refluxing benzene. The overall yield from the dione was about 70% and the entire operation could be completed within a day.

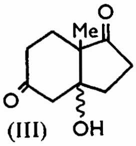
Heating the trione (II) with oxalic acid [5] or boric acid gave only a small yield of the indane (I). When passed through alumina the trione (II) gave some ketol [5] (III) but the separation of the two was difficult. The ketol (III), which from its constitution might have been expected to undergo ready dehydration with thionyl chloride–pyridine,[6] in practice yielded some required product (I) and much 2-methyl*cyclo*pentane-1 : 3-dione. Clearly the formation of the latter involves a reverse Michael reaction. However, with toluene-*p*-sulphonic acid in hot benzene the ketol (III) readily gave the indane (I).



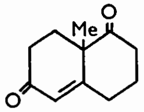
(I)



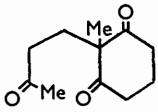
(II)



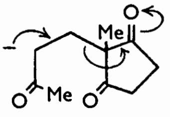
(III)



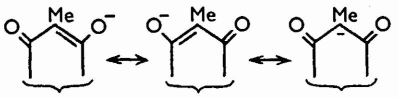
(IV)



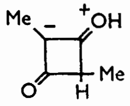
(V)



(VI)



(VIIa) (VIIb) (VIIc)



(VIII)

Similar experiments designed to provide the octalin (IV) gave different results. This compound is readily made from 2-methyl*cyclo*hexane-1 : 3-dione and 4-diethylaminobutan-2-one.[7,8] Under similar conditions 2-methyl*cyclo*pentane-1 : 3-dione gave a dark product from which the indane (I) could only be obtained in low yield. Moreover, the trione (V), prepared from methyl vinyl ketone and 2-methyl*cyclo*hexane-1 : 3-dione,[9] did not lose water when treated with toluene-*p*-sulphonic acid in benzene. Further, whereas diethylamine–pyridine is known to cyclise the trione (V) to the octalin (IV),[7] a similar experiment with the trione (II) gave principally the product, 2-methyl*cyclo*pentane-1 : 3-dione, of retro-Michael reaction.

[1] Acklin, Prelog, and Prieto, *Helv. Chim. Acta*, 1958, **41**, 1416.
[2] Butz and Orchin, *J. Amer. Chem. Soc.*, 1943, **65**, 2296.
[3] Panouse and Sanniè, *Bull. Soc. chim. France*, 1955, 1036.
[4] Cf. ref. 1.
[5] Wieland and Miescher, *Helv. Chim. Acta*, 1950, **33**, 2215.
[6] Darzens, *Compt. rend.*, 1911, **152**, 1601.
[7] Swaminanthan and Newman, *Tetrahedron*, 1958, **2**, 65; U.S.P. 2,714,615/1955.
[8] Unpublished work of Robinson, quoted by Cocker and Halsall, *J.*, 1957, 3441.
[9] Nazarov, Zav'yalov, Burmistrova, Gurvich, and Shmonina, *Zhur. obshchei Khim.*, 1956, **26**, 1441.

The explanation for these reverse Michael reactions (*i.e.*, VI) is probably to be found in the stability of the anion from 2-methyl*cyclo*pentane-1 : 3-dione. Fully developed mesomerism in the system (VIIa—VIIb) requires the structures to be planar. Both ring systems satisfy this requirement but in addition (leaving aside the nature of carbanions themselves [10]) the *cyclo*pentane system is also planar in the mesomeric anion (VIIc), and this will make a greater contribution to the ground state than in the corresponding *cyclo*hexane case. The published values of the dissociation constants of *cyclo*hexane-1 : 3-dione [11] (5·26) and *cyclo*pentane-1 : 3-dione [12] (4·5) support this contention. Tetronic acid [13] (pK 3·76) possesses a similar cyclic system and 2 : 4-dimethyl*cyclo*butane-1 : 3-dione [14] is a surprisingly strong acid (pK 2·8) and behaves as a typical monoenol. To account for its acidity (VIII) has been invoked as an effective contributor to the ground state. The anion of (VIII) is clearly analogous to (VIIc).

EXPERIMENTAL

Ethyl 4-methyl-2 : 3 : 5-trioxo*cyclo*pentylglyoxylate [2] was hydrolysed by 2N-aqueous hydrochloric acid to the trione, m. p. 77—79° (overall yield from butan-2-one, 26%).

2-*Methyl*cyclo*pentane*-1 : 3-*dione*.—(*a*) A solution of semicarbazide hydrochloride (112 g.) and sodium acetate (150 g.) was added at 20° during 30 min. to well-stirred 2-methyl*cyclo*pentane-1 : 3 : 4-trione monohydrate (144 g.) in ethanol (1000 ml.) and water (500 ml.). After stirring for a further hour the pale yellow semicarbazone was collected, washed with aqueous ethanol, and dried in a vacuum oven (yield 178 g., 97%). The semicarbazone (80 g.) was added to potassium hydroxide (80 g.), dissolved in ethylene glycol (800 ml.), at 130°. The solution was heated at 150° for 30 min. and at 180° for 1 hr., and then all solvent was removed (0·05 mm.). The residue in water (400 ml.) was acidified to pH 3 with hydrochloric acid, and the precipitate crystallised from water; the dione had m. p. 208—209°. The average yield from 20 such runs involving variations of the above procedure was 51% (Panouse and Sannié [3] claim 86%).

(*b*) The trione monohydrate (1·44 g.) was hydrogenated (20°; 760 mm.) with reduced Adams's catalyst (100 mg.) in acetic acid (25 ml.) containing perchloric acid (0·5 ml.). Absorption, rapid at first, ceased after 6 hr. Treatment with 50% potassium hydroxide (to remove perchloric acid) and subsequent concentration gave a pale brown oil which crystallised from water (0·35 g., 31%; m. p. 205—207°).

5 : 6 : 7 : 8-*Tetrahydro*-8-*methylindane*-1 : 5-*dione*.—(*a*) The dione (40 g.), 4-diethylaminobutan-2-one (62·4 g.), pyridine (30 ml.), and benzene (500 ml.) were refluxed for 18 hr. After being cooled and washed with 2N-hydrochloric acid the organic layer was dried ($MgSO_4$) and distilled. The liquid product was crystallised from ether–light petroleum (b. p. 40—60°) (2 : 1), yielding the pure compound (10·3 g., 17%), m. p. 73°. The mother liquors darkened rapidly in air and extensive chromatography on alumina did not furnish any more material. (A nitrogen atmosphere had no appreciable effect on the yield or quality of the product.)

(*b*) A mixture of 2-methyl*cyclo*pentane-1 : 3-dione (65 g.), anhydrous methanol (250 ml.), freshly distilled methyl vinyl ketone (61·5 g.), and potassium hydroxide (3 pellets) was refluxed for 5 hr. The solvent was removed *in vacuo*, and the solid residue treated with water and chloroform. The organic layer, after being dried ($MgSO_4$), was distilled. 2-Methyl-2-3′-oxobutyl*cyclo*pentane-1 : 3-dione was collected at 108—112°/0·1 mm. and solidified on cooling (88 g., 83%). An analytical specimen had m. p. 117—118° (ethyl acetate) (Found: C, 65·9: H, 8·1. Calc. for $C_{10}H_{14}O_3$: C, 65·9; H, 7·7%). Infrared absorption (cm.$^{-1}$): 1762 (*cyclo*pentanone); 1732 (carbonyl); no hydroxyl absorption.

The compound (45 g.) in benzene (250 ml.) was refluxed with toluene-*p*-sulphonic acid (2 g.), a modified Dean–Stark water separator being used. After 2 hr. more toluene-*p*-sulphonic acid (2 g.) was added, the theoretical amount of water being collected after 5 hr. The solvent was

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[10] Leffler, " The Reactive Intermediates of Organic Chemistry," Interscience Publishers, New York, 1956; Ziegler and Wenz, *Chem. Ber.*, 1950, **83**, 354.

[11] Schwarzenbach and Lutz, *Helv. Chim. Acta*, 1940, **23**, 1147.

[12] Waller, Wolf, Hutchings, Williams, Broschard, and Goldman, *J. Amer. Chem. Soc.*, 1952, **74**, 4978.

[13] Kumler, *J. Amer. Chem. Soc.*, 1935, **57**, 1929; 1938, **60**, 859; Schwarzenbach and Lutz, *Helv. Chim. Acta*, 1940, **23**, 1162.

[14] Woodward and Small, *J. Amer. Chem. Soc.*, 1950, **72**, 1297.

removed *in vacuo*, and crystallisation of the oily residue from 2 : 1 ether–light petroleum deposited large crystals of 5 : 6 : 7 : 8-tetrahydro-8-methylindane-1 : 5-dione (33·5 g., 83%), m. p. 72—73°.

2-Methyl-2-3′-oxobutyl*cyclo*hexane-1 : 3-dione was made similarly in 85% yield. It was an oil, b. p. 114—118°/0·01 mm., n_D^{18} 1·5110, and had the expected infrared absorption. Newman[7] gives b. p. 114—116°/0·1 mm.

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