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Studies on 5—8 Fused Ring Compounds. III. Hydrogenolysis of 4,4-Dimethyltricyclo[6.3.0.$0^{1,7}$]undecane-2,6-dione

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Synopsis. Hydrogenolysis of 4,4-dimethyltricyclo[6.3.0.$0^{1,7}$]undecane-2,6-dione with a Pd–C catalyst gave *cis*-4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione and 8,8-dimethylspiro[4.6]undecane-6,10-dione. The *cis* isomer has been shown to isomerize almost completely to the *trans* isomer under acidic and basic conditions.

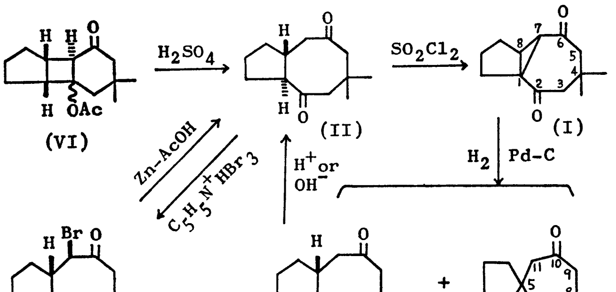
Previously it has been reported that 4,4-dimethyltricyclo[6.3.0.$0^{1,7}$]undecane-2,6-dione (I) has been formed as the main product in the chlorination by sulfuryl chloride of 4,4-dimethylbicyclo[6.3.0]undecane(II).[1]

Hydrogenolysis of I in ethanol with a palladium-charcoal catalyst at ordinary room temperature and pressure cleaved the three-membered ring with ease to give *cis*-4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione (III), mp 116—117 °C, as the main product together with a small amount of an isomer (IV), mp 62—63 °C. The ratio of III to IV was approximately 10: 1.

A molecular peak appeared at 208 in the mass spectrum of III as in the case of II.[2] The fragmentation of III was identical with that of II, differing only in relative intensity. Furthermore, III isomerized readily to II when left to stand at room temperature in acidic or alkaline methanol. This shows that II and III are the *cis* and *trans* isomers concerning the ring fusion of the 5—8 fused ring and that II is more stable than III. When a solution of either II or III in 0.4 mol/dm^3 KOH–methanol solution was left to stand at 25 °C, NMR and IR spectroscopy showed that only II was present; III was undetectable even after 45 h. It was not possible to separate II and III by gas chromatography, and hence the equilibrium constant for the reaction *cis*⇌*trans* could not determined.

X-Ray analysis of the 7-bromo derivative (V; mp 111—113 °C[1]†) of II showed that the 5—8 ring fusion of V was *trans*.[3] V was synthesised from II, the more stable isomer, by bromination with pyridinium bromide perbromide. The debromination of V by zinc dust[4] in acetic acid at room temperature yielded the starting dione (II). Hence the ring fusion of II was *trans*, the same as that of V. II resulted from the retro-aldol cleavage of a photoadduct VI,[2] and since the 5—4 ring fusion of VI was *cis*,[2] it is likely that the isomerization from an unstable *cis* configuration to a more stable *trans* configuration, occured in the retro-aldol cleavage to give II. The carbonyl group at position 2 in II and III undergoes enolization in an acidic or alkaline solution, facilitating the *cis-trans* isomerization.

IV arising from the hydrogenolysis of I over Pd–C showed the same molecular peak as that of II and III in its mass spectrum. However, the fragmentation of IV differs considerably from that of II or III. In the NMR spectrum of IV, hydrogen atoms other than those in the five-membered ring appear as singlets and there is an absence of coupling. The *gem*-dimethyl groups show a single peak at 1.05 δ(6H) and the three methylene groups at positions 7, 9, and 11 appear as singlets at 2.73 δ (2H), 2.69 δ(2H), and 2.42 δ(2H), respectively. These results suggest that the protons in the carbonyl-containing ring do not assume a fixed conformation and IV has been estimated to be a spiro compound, 8,8-dimethylspiro[4.6]undecane-6,10-dione. Consequently, in the hydrogenolysis of I over Pd–C, the C(1)–C(7) linkage is cleaved preferentially to give III, accompanied by a slight cleavage of the C(7)–C(8) linkage to give IV. However, the cleavage of the C(1)–C(8) linkage did not occur.



Experimental

Hydrogenolysis of I. A suspension of I (0.5 g) and 5% Pd–C (0.5 g) in a solution of ethanol (40 ml) was stirred at room temperature with hydrogen at 1 atm until absorption was complete (3 h). The filtered solution was concentrated under reduced pressure to give a crystalline residue. Crystallization from hexane gave III (0.24 g); mp 114—116 °C. Recrystallization from hexane gave pure III; mp 116—117 °C. IR (Nujol) 1700 cm^{-1}; (CCl_4) 1705 cm^{-1}. NMR ($CDCl_3$): δ 1.10 (3H, CH_3) and 1.20 (3H, CH_3). Found: C, 75.08; H, 9.55%. Calcd for $C_{13}H_{20}O_2$: C, 75.00; H, 9.62%. MS: *m/e* 208 (M^+, 7%), 193 (8), 190 (1), 180 (2), 152 (11), 141 (56), 124 (20), 112 (29), 95 (17), 83 (base, 100), 81 (5), 67 (32), 55 (23), and 41 (27).

The mother liquor afforded III (0.12 g), and IV (36 mg) as needles. IV; mp 60—62 °C, which was recrystallized from hexane; mp 62—63 °C. IR (Nujol) 1700 cm^{-1}; (CCl_4) 1700

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† This compound was assumed to be the 5-bromo-derivative in a previous paper,[1] but X-ray analysis[3] showed it to be the 7-bromo derivative.

cm^{-1}. NMR ($CDCl_3$) δ 1.05 (s, 6H, *gem*-$(CH_3)_2$), 1.4—2.2 (broad, 8H, 5-membered ring H), 2.42 (s, 2H, CH_2), 2.69 (s, 2H, CH_2), and 2.73 (s, 2H, CH_2). Found: C, 75.12; H, 9.67%. Calcd for $C_{13}H_{20}O_2$: C, 75.00; H, 9.62%. MS: *m/e* 208 (M^+, 41%), 193 (2), 180 (2), 167 (5), 152 (6), 148 (5), 141 (13), 128 (16), 124 (15), 111 (23), 98 (6), 95 (8), 83 (base, 100), 81 (25), 70 (30), 67 (31), 56 (37), and 41 (39).

Epimerization of III to II. A solution of III (20 mg) in 5% H_2SO_4–methanol was left to stand at room temperature for 2 weeks, and extracted with ether. The extract was washed with aqueous sodium hydrogencarbonate and water, and then dried over sodium sulfate. After the removal of ether, a crystalline residue was obtained (mp 60—62 °C); the IR spectrum was identical with that of II.[2)]

Equilibrium for the Reactions $II \rightleftharpoons III$. Equilibrium was approached from both sides by allowing each compound (II and III, 40 mg) to stand for 45 h in 0.4 mol/dm^3 KOH–methanol solution (5 ml) at 25 °C. The solution was extracted with ether and washed with water, dried and evaporated. In each case the products were identical to II on the basis of their IR and NMR spectra, and III was not detected. In GPC analysis II and III showed the same retention time.

Debromination of V. The bromination of II with pyridinium bromide perbromide in ethanol gave V.[1)] To a solution of V (50 mg) in ether (4 ml) and acetic acid (1 ml), zinc dust (90 mg) was added. The reaction mixture was stirred at room temperature for 50 min and diluted with ether (10 ml). The ethereal solution was filtered and the zinc washed with ether. The combined ethereal solution was washed twice with aqueous sodium hydrogencarbonate and finally with water, and then dried over sodium sulfate. After the removal of ether, a crystalline residue was obtained (31 mg), mp 62—63 °C, and identified as II by IR spectroscopy. Recrystallization from hexane afforded pure II; mp 64—65 °C.

References

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