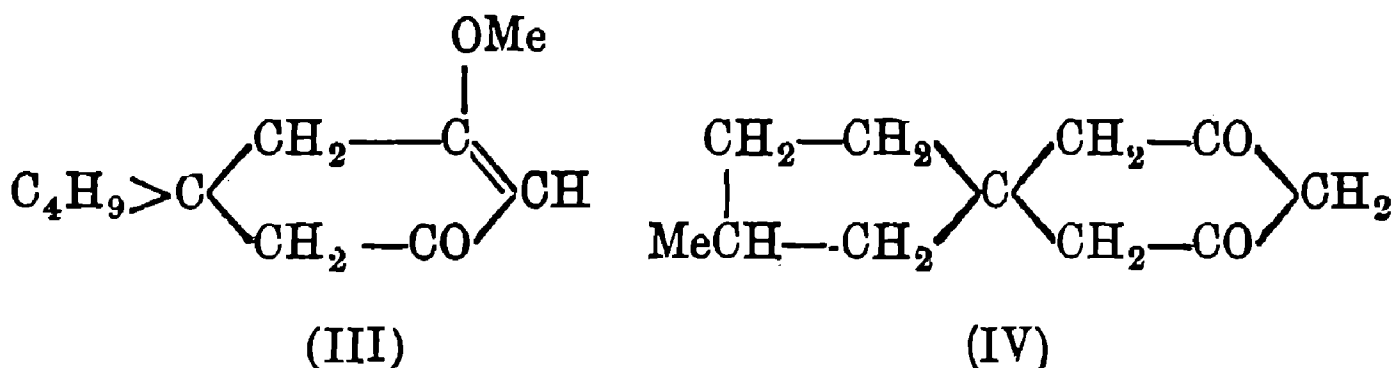
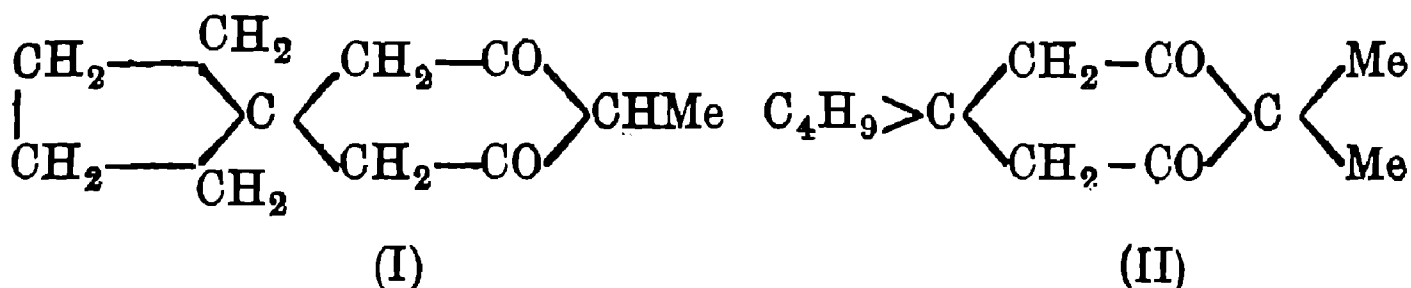


The Chemistry of Alkycyclopentanones. Part III.

The Synthesis of 3'-Methylcyclopentane-spiro-cyclohexane-3 : 5-dione.

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In a recent paper (*J. Chem. Soc.*, 1932, 1079) the author has shown that when *cyclopentane-spiro-cyclohexane-3:5-dione* is methylated in presence of alcoholic sodium ethoxide a mixture of *c*-methyl-(I), *C*-dimethyl-(II), and *O*-methyl-(III) derivatives are formed.

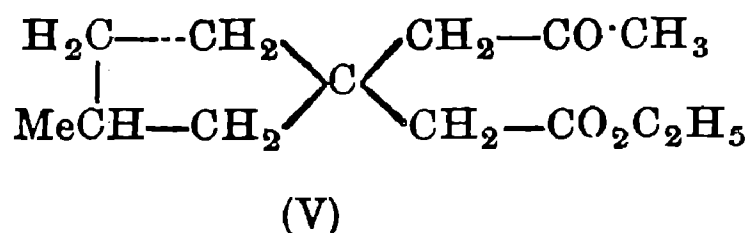


It appeared of interest to subject 3'-methylcyclopentane-spiro-cyclohexane-3:5-dione (IV) to this reaction in order to see how far the presence of a methyl group affected its course ; hence its synthesis was undertaken.

Two methods were tried. The condensation of 3-methylcyclopentenylacetone with ethyl sodiomalonate and hydrolysis of the resulting ester (*cf.* Vorländer, *Annalen*, 1897, 294, 253 ; also Norris and Thorpe, *J. Chem. Soc.*, 1921, 119, 1205). Though this condensation gave an excellent yield, the method proved unsatisfactory owing to the difficulties involved in the preparation of the requisite ketone in a good yield from 3-methylcyclopentenylacetic acid by Blaise-Maire reaction.

The second method was the ring-closure of the keto ester (V) which was prepared by the action of zinc methyl iodide on the acid chloride of ethyl hydrogen 3-methylcyclopentane-1:1-diacetate.

Though the method involved a number of stages, the yield of the dione (IV) was so good that it could be recommended for its preparation.



The alkylation of this, as well as of some other diones, under a variety of conditions will form the subject matter of another communication.

EXPERIMENTAL.

Dehydration of Ethyl 3-methylcyclopentane-1-ol-1-acetate.

(i) *Phosphorus oxychloride method.*—A mixture of phosphorus oxychloride (12 c.c.), the hydroxy ester (16.8 g.) (Desai, *J. Chem. Soc.*, 1932, 1074), and benzene (30 c.c.) was heated on the water-bath until the evolution of hydrogen chloride ceased. The oil obtained by pouring the mixture into water was extracted with ether, washed with dilute sodium carbonate solution, dried, recovered and distilled when most of it boiled at 94-97°/10 mm. On redistillation *ethyl 3-methylcyclopentenyl acetate* boiled at 94-95°/10 mm. and had $d_4^{21^\circ}$, 0.9526; $n_D^{21^\circ}$, 1.4502, whence $[R_L]_D$, 47.4. (Calc., 47.37). (Found: C, 71.2; H, 9.7. $\text{C}_{10}\text{H}_{16}\text{O}_2$ requires C, 71.4; H, 9.5 per cent).

(ii) *Thionyl chloride method.* (Darzens, *Compt. rend.*, 1911, 152, 1601).—Thionyl chloride (12 g.) was gradually added to an ice-cold solution of the hydroxy ester (16.6 g.) in pyridine (8 c.c.) and the mixture kept in ice for 2½ hours. The oil, precipitated on adding the mixture to dilute hydrochloric acid solution, was extracted with ether, washed alternately with dilute hydrochloric acid, sodium carbonate and water, dried, recovered and distilled when most of the liquid passed over at 96-99°/12 mm., leaving some undistillable residue. On redistillation the b.p. was 98-99°/12 mm., but the method was not found to be better than the phosphorus oxychloride method.

(iii) *Gaseous hydrogen chloride method.*—It was observed that partial dehydration of the hydroxy ester occurred when its alcoholic solution was saturated with gaseous HCl. But it did not offer any advantage over the first method.

3-Methylcyclopentenylacetic acid.—The unsaturated ester was hydrolysed with an excess of 10% aqueous alcoholic potassium hydroxide at room temperature and the acid isolated in the usual way. It boiled at 127-28°/12 mm., remained as a gum, and had $d_4^{20}, 1.015$; $n_D^{20}, 1.4722$, whence $[R_L]_D, 38.54$. (Calc., 38.01). (Found: C, 68.5; H, 8.7; Eq. wt., 139.0. $C_8H_{12}O_2$ requires C, 68.6; H, 8.5 per cent. Eq. wt., 140). Attempts to prepare a solid dibromide were unsuccessful. The high molecular refraction is due to some $\alpha\beta$ -isomer.

3-Methylcyclopentenylacetone.—3-Methylcyclopentenylacetic acid (14 g.) was heated with an excess of thionyl chloride for 1 hour and the acid chloride (b.p. 110-21°/21 mm.) was diluted with an equal volume of dry benzene. This was gradually added to a well-cooled solution of zinc methyl iodide [prepared by heating zinc-copper couple (16 g.), methyl iodide (8 c.c.), ethyl acetate (3 c.c.) and toluene (12 c.c.) for 12 hours] in toluene. The mixture was kept in ice for 4 hours and then decomposed with cold dilute sulphuric acid. The filtered toluene solution was extracted with ether, washed with water and ammonium sulphate, dried and distilled, when the ketone boiled at 93-94°/18 mm., yield 50%. (Found: C, 78.2; H, 10.3. $C_9H_{14}O$ requires C, 78.3; H, 10.1 per cent). The *semicarbazone* crystallised from dilute alcohol in needles, m.p. 185° (decomp.). (Found: C, 61.2; H, 8.7. $C_{10}H_{17}ON_3$ requires C, 61.5; H, 8.7 per cent).

Condensation of 3-methylcyclopentenylacetone with ethyl sodio-malonate: Synthesis of 3-methylcyclopentane-spiro-cyclohexane-3:5-dione (IV).—The above ketone (13.8 g.) was gradually added to a well-cooled suspension of ethyl sodiomalonate in absolute alcohol (2.3 g. Na, 16 g. ethyl malonate and 30 c.c. alcohol), and the reaction was completed by heating for 12 hours on the water-bath. The resulting dione-ester was hydrolysed directly by adding caustic potash (25%, 50 c.c.) and heating for 6 hours. Alcohol was evaporated off and the aqueous solution was extracted with ether to remove the neutral impurities. The slightly acidic solution was heated on a sand-bath till the evolution of carbon dioxide ceased and the dione crystallised from the strongly acid solution on cooling. This was recrystallised from dilute alcohol in plates or from benzene-petrol mixture in cubes, m.p. 127-28°. The aqueous solution gave red colour with alcoholic ferric chloride solution.

(Found: C, 73.2; H, 9.0. $C_{11}H_{16}O_2$ requires C, 73.3; H, 8.9 per cent).

The *methylene* derivative was immediately precipitated as an oil on adding formaldehyde to the saturated solution of the dione and solidified on standing and scratching. It crystallised from dilute alcohol in long slender needles, m.p. 161-62°. (Found: C, 74.0; H, 8.7. $C_{23}H_{32}O_4$ requires C, 74.2; H, 8.6 per cent).

The *anilide*, prepared by heating the dione with an excess of aniline on a free flame for 15 minutes, solidified on rubbing with dilute hydrochloric acid. It crystallised from dilute alcohol (charcoal) in needles, m.p. 156°. (Found: C, 80.1; H, 8.3. $C_{17}H_{21}ON$ requires C, 80.0; H, 8.2 per cent).

Synthesis of ethyl 3-methylcyclopentane-1-acetone-1-acetate.—Ethyl hydrogen 3-methylcyclopentane-1: 1-diacetate (Desai, *J. Chem. Soc.*, 1932, 1070) (23 g.) was heated with thionyl chloride (20 c.c.) for 2 hours and the excess of thionyl chloride removed. The crude acid chloride diluted with benzene (25 c.c.) was gradually added to a well-cooled toluene solution of zinc methyl iodide (1.2 mol.), and the mixture was decomposed with cold dilute sulphuric acid after 3 hours. The filtered toluene solution was extracted with ether, washed with water and ammonium sulphate solution, dried and distilled when most of it boiled at 152-55°/14 mm. (20 g.). This was hydrolysed with 50% caustic potash and the acid isolated in the usual manner. The keto-acid, which was admixed with the glutaric acid, was partially purified by extraction with light petrol (b.p. 40-60°), in which the keto-acid was freely soluble.

The *semicarbazone* of the acid crystallised from dilute alcohol in needles, m.p. 182° (decomp.). (Found: C, 56.4; H, 8.3. $C_{12}H_{21}O_3N_3$ requires C, 56.5; H, 8.2 per cent).

3-Methylcyclopentane-1-acetone-1-acetic acid, regenerated from semicarbazone, boiled at 181-82°/12 mm. and remained as a viscous gum. It had d_4^{20} , 1.056; n_D^{20} , 1.4713, whence $[R_L]_D$, 52.41. (Calc., 52.53). (Found: C, 66.5; H, 9.3; Eq. wt., 198.5. $C_{11}H_{18}O_3$ requires C, 66.6; H, 9.1 per cent. Eq. wt., 198).

The *ethyl ester*, prepared with alcoholic hydrogen chloride, boiled at 145°/14 mm. and had d_4^{21} , 0.9908; n_D^{21} , 1.4562, whence $[R_L]_D$, 62.0. (Calc., 61.7). (Found: C, 68.9; H, 9.8. $C_{13}H_{22}O_3$ requires C, 69.0; H, 9.7 per cent).

The *semicarbazone* crystallised from dilute alcohol in leafy plates, m.p. 87-88°. (Found: C, 59.5; H, 8.9. $C_{14}H_{23}O_3N_3$ requires C, 59.4; H, 8.8 per cent).

The ester (5 g.), dissolved in a solution of sodium (0.5 g.) in absolute alcohol (15 c.c.), was heated on the steam-bath for 6 hours, when it was quantitatively converted into 3'-methyl*cyclopentane-spiro-cyclohexane-3:5-dione* (IV).

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