529. *Sterculic Acid. The Synthesis of Some Related β-Diketones and* cyclo*Propanes.*

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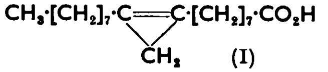
β-Diketones have been prepared, including 9 : 11-dioxononadecanoic acid, which has been shown to be identical with the ozonolysis product of sterculic acid. From the diketones, *via* the glycols and the dibromides, *cyclo*propanes have been made for comparison with dihydrosterculic acid.

The dioxo-acid obtained by catalytic reduction of the ozonide of sterculic acid (I) was shown[1,2] to be 9 : 11-dioxononadecanoic acid (II; $x = 7$, R = H). By Adams and Hauser's method[3] the β-diketones (II), (III), and (IV) have been prepared. In the presence of sodium amide and twice the theoretical amount of ethyl heptanoate, methyl undecyl ketone yielded 7 : 9-dioxoeicosane (IV; $m = 5$, $n = 10$). Ethyl nonanoate and methyl undecyl ketone similarly yielded 9 : 11-dioxodocosane (IV; $m = 7$, $n = 10$); ethyl heptanoate and hexyl methyl ketone gave 7 : 9-dioxopentadecane (IV; $m = n = 5$). The three diketones were isolated as their copper derivatives.

From equimolecular proportions of dimethyl azelaate and methyl octyl ketone the main product appeared to be 9 : 11 : 19 : 21-tetraoxononacosane (III; $x = 7$) with only a trace of the ester (II; $x = 7$, R = CH_3). When, however, two molecular proportions of dimethyl azelaate were employed the product was almost entirely methyl 9 : 11-dioxononadecanoate (II; $x = 7$, R = CH_3). Similarly hexyl methyl ketone gave 7 : 9 : 17 : 19-tetraoxopentacosane (III; $x = 5$) and methyl 9 : 11-dioxoheptadecanoate (II; $x = 5$, R = CH_3).



$CH_3\cdot[CH_2]_7\cdot C{=}C\cdot[CH_2]_7\cdot CO_2H$ with CH_2

(I)

$CH_3\cdot[CH_2]_x\cdot CO\cdot CH_2\cdot CO\cdot[CH_2]_7\cdot CO_2R$

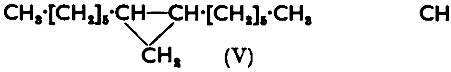
(II)

$CH_3\cdot[CH_2]_x\cdot CO\cdot CH_2\cdot CO\cdot[CH_2]_7\cdot CO\cdot CH_2\cdot CO\cdot[CH_2]_x\cdot CH_3$

(III)

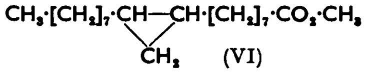
$CH_3\cdot[CH_2]_m\cdot CO\cdot CH_2\cdot CO\cdot[CH_2]_n\cdot CH_3$

(IV)



$CH_3\cdot[CH_2]_5\cdot CH{-}CH\cdot[CH_2]_5\cdot CH_3$ with CH_2

(V)



$CH_3\cdot[CH_2]_7\cdot CH{-}CH\cdot[CH_2]_7\cdot CO_2\cdot CH_3$ with CH_2

(VI)

The corresponding dioxononadecanoic acid (II; $x = 7$, R = H) was identical in m. p., mixed m. p., and infrared spectrum with the product obtained from sterculic acid by Faure and Smith.[2] 9 : 11-Dioxoheptadecanoic acid (II; $x = 5$, R = H) was obtained similarly. All these compounds, as β-diketones, gave intense red colours with alcoholic ferric chloride, and readily formed copper derivatives. That the Adams and Hauser condensation had, in these cases also, occurred at the methyl rather than at the methylene group of the ketones was shown by (i) the failure of the products to yield sodium hydrogen sulphite addition compounds and give the iodoform reaction, (ii) their ability to form urea complexes in high yield, and (iii) their alkaline hydrolysis to the expected products.

On reduction with potassium borohydride 7 : 9-dioxopentadecane gave pentadecane-7 : 9-diol. The corresponding dibromide gave, on treatment with sodium iodide and zinc in acetone,[4] a bromine-free product with the expected properties of 1 : 2-dihexyl*cyclo*propane (V). Similarly, but by the use of sodium borohydride, methyl 9 : 11-dioxoheptadecanoate and methyl 9 : 11-dioxononadecanoate were converted into *cyclo*propanes.

All these *cyclo*propane derivatives show infrared absorption at 3·27—3·30 μ and 9·83 μ.

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[1] Nunn, *J.*, 1952, 313.

[2] Faure and Smith, *J.*, 1956, 1818.

[3] Adams and Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1220.

[4] Hall, Lewis, and Polgar, *J.*, 1955, 3971; Hass, McBee, Hinds, and Gluesenkamp, *Ind. Eng. Chem.*, 1936, **28**, 1178; Shortridge, Craig, Greenlee, Derfer, and Boord, *J. Amer. Chem. Soc.*, 1948, **70**, 946.

Cole [5] attributes the absorption at 3040—3058 cm.$^{-1}$ (3·27—3·30 μ) to methylene in a *cyclo*propane ring, and states that the band at 1010 cm.$^{-1}$ (9·83 μ) is unreliable when oxygen functions are present. The medium band at 9·83 μ in 1 : 2-dihexyl*cyclo*propane strengthens the case for attributing the 9·8 μ band in the spectrum of dihydrosterculic acid itself to the presence of a *cyclo*propane ring.

EXPERIMENTAL

7 : 9-*Dioxoeicosane.*—Clean sodium (15·2 g.) was added in small portions with stirring to anhydrous liquid ammonia (300 c.c.), together with a small crystal of ferric nitrate to catalyse the conversion of the sodium into amide. When this conversion was complete ammonia was evaporated (steam-bath), sufficient anhydrous ether being added to keep the volume of liquid at approximately 300 c.c. After nearly all the ammonia had evaporated (indicated by the refluxing of the ether) the suspension of sodium amide was stirred and refluxed for a few minutes, then cooled to room temperature.

Methyl undecyl ketone (59·4 g., 0·3 mole; m. p. 29°) in dry ether (50 c.c.) was added to the stirred suspension of sodium amide during 5—10 min. After a further 5 min. ethyl heptanoate (94·8 g., 0·6 mole; b. p. 187°) in dry ether (50 c.c.) was added, and the stirring and refluxing continued for 2 hr. The mixture was poured into water (300 c.c.), neutralised with dilute hydrochloric acid, and extracted with ether, yielding a viscous liquid which was dissolved in an equal volume of methanol. A hot filtered solution of copper acetate (40 g.) in water (350 c.c.) was added to the methanol solution and the mixture allowed to cool to room temperature. The air-dried product was washed with light petroleum (b. p. 40—60°; 100 c.c.), and again dried. A small sample, recrystallised from methanol, gave the *copper salt* of 7 : 9-dioxoeicosane as pale blue crystals, m. p. 88° (Found: C, 70·5; H, 11·0. $C_{40}H_{74}O_4Cu$ requires C, 70·4; H, 10·9%).

The impure salt was shaken with sulphuric acid (10%; 500 c.c.) and ether (200 c.c.) until the ethereal layer was pale yellow. The aqueous acid layer was again extracted with ether and the combined ethereal solutions dried (Na_2SO_4). The solvent was distilled and the residue, fractionated *in vacuo* through a 20-cm. Vigreux column, yielded 7 : 9-*dioxoeicosane* (12 g.), b. p. 210°/12 mm., m. p. 27° (Found: C, 77·4; H, 12·2. $C_{20}H_{38}O_2$ requires C, 77·4; H, 12·2%).

9 : 11-*Dioxodocosane.*—In the same manner as above, the *copper salt* of 9 : 11-dioxodocosane was prepared as pale blue crystals, m. p. 85°, from sodium (10·2 g.), methyl undecyl ketone (39·6 g.), and ethyl nonanoate (74·4 g.; b. p. 227°) (Found: C, 72·0; H, 11·5. $C_{44}H_{82}O_4Cu$ requires C, 71·5; H, 11·2%).

This copper salt and cold hydrochloric acid (15%; 400 c.c.) ultimately gave a product, b. p. 230°/0·2 mm., which when crystallised from ethanol gave 9 : 11-*dioxodocosane* (30 g.), m. p. 45° (Found: C, 78·2; H, 12·6. $C_{22}H_{42}O_2$ requires C, 78·1; H, 12·4%).

Hydrolysis. 9 : 11-Dioxodocosane (2·2 g.) in sodium hydroxide (1%; 25 c.c.) was heated on the water-bath for 2 hr. and finally boiled for a few minutes. Extraction with ether yielded a solid (odour of methyl octyl ketone), but conversion into the 2 : 4-dinitrophenylhydrazone gave, on repeated recrystallisation, a product, m. p. 69° alone or when mixed with methyl undecyl ketone 2 : 4-dinitrophenylhydrazone, m. p. 69°. The absence of octyl undecyl ketone showed that the Adams and Hauser condensation had occurred on the methyl group of the methyl undecyl ketone. Moreover, concentration of the aqueous alkaline liquid, followed by acidification with concentrated hydrochloric acid, gave a soft solid which did not smell of acetic acid. Conversion into anilide, and several crystallisations, yielded a product, m. p. 74° alone or when mixed with the dodecananilide, m. p. 76°.

7 : 9-*Dioxopentadecane.*—From sodium (15·2 g.), hexyl methyl ketone (38·5 g.; b. p. 64°/18 mm.; n_D^{17} 1·4159), and ethyl heptanoate (95 g.), the *copper salt* of 7 : 9-dioxopentadecane was prepared as pale blue crystals, m. p. 115° (Found: C, 66·6; H, 10·0. $C_{30}H_{54}O_4Cu$ requires C, 66·5; H, 10·0%). Treatment with hydrochloric acid (20%; 500 c.c.) gave 7 : 9-*dioxopentadecane* (25 g.), b. p. 180—184°/17 mm., n_D^{22} 1·4640 (Found: C, 74·7; H, 11·5. $C_{15}H_{28}O_2$ requires C, 75·0; H, 11·7%).

9 : 11 : 19 : 21-*Tetraoxononacosane and Methyl* 9 : 11-*Dioxononadecanoate.*—From sodium (3·0 g., yielding 0·12 mole of $NaNH_2$), methyl octyl ketone (9·4 g., 0·06 mole; b. p. 90—94°/10

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[5] Cole, *J.*, 1954, 3807. Cf., Wibley and Bunce, *Analyt. Chem.*, 1952, **24**, 623.

mm., m. p. +2°), and dimethyl azelaate (13·4 g., 0·06 mole; n_D^{18} 1·4366; b. p. 143—150°/10 mm.) the *copper salt* of 9 : 11 : 19 : 21-tetraoxononacosane was prepared as pale blue crystals, m. p. 92° (Found : C, 66·0; H, 9·4. $C_{58}H_{100}O_8Cu_2$ requires C, 66·2; H, 9·5%).

Treatment of this salt with cold hydrochloric acid (20%; 120 c.c.) and crystallisation of the product from light petroleum (b. p. 40—60°) and from methanol, gave 9 : 11 : 19 : 21-*tetraoxononacosane* (4·5 g.) as plates, m. p. 66° (Found : C, 75·0; H, 11·3. $C_{29}H_{52}O_4$ requires C, 75·0; H, 11·2%).

A fraction, b. p. 178—182°/0·2 mm., was also obtained, which, after extraction with methanol, gave *methyl* 9 : 11-*dioxononadecanoate* (0·5 g.) as crystals, m. p. 40° (Found : C, 70·5; H, 10·6. $C_{20}H_{36}O_4$ requires C, 70·6; H, 10·6%). However, when sodium (8·7 g., 0·36 mole of $NaNH_2$), dimethyl azelaate (74 g., 0·34 mole), and methyl octyl ketone (26·6 g., 0·17 mole) were used, the *copper salt* of methyl 9 : 11-dioxononadecanoate (74 g.) was obtained as pale blue crystals, m. p. 94° (Found : C, 64·7; H, 9·3. $C_{40}H_{70}O_8Cu$ requires C, 64·7; H, 9·4%). Treatment of this with cold hydrochloric acid (10%; 300 c.c.), followed by distillation, and extraction with light petroleum (b. p. 40—60°) gave methyl 9 : 11-dioxononadecanoate (21 g.; m. p. 40°), identical with the specimen obtained above.

Methyl 9 : 11-*Dioxoheptadecanoate and* 7 : 9 : 17 : 19-*Tetraoxopentacosane*.—In the same manner the *copper salt* of methyl 9 : 11-dioxoheptadecanoate was prepared as pale blue crystals, m. p. 82°, from sodium (5·1 g., 0·22 mole of $NaNH_2$), hexyl methyl ketone (12·8 g., 0·1 mole), and dimethyl azelaate (44·5 g., 0·2 mole) (Found : C, 62·8; H, 9·0. $C_{36}H_{62}O_8Cu$ requires C, 63·0; H, 9·0%). From this salt there was obtained, in the usual way, *methyl* 9 : 11-*dioxoheptadecanoate* (9 g.), a pale yellow oil, m. p. 3°, n_D^{19} 4677 (Found : C, 69·2; H, 10·4. $C_{18}H_{32}O_4$ requires C, 69·2; H, 10·3%).

The residue from the distillation yielded 7 : 9 : 17 : 19-*tetraoxopentacosane* (0·6 g.) as crystals, m. p. 54° (from light petroleum) (Found : C, 73·6; H, 10·7. $C_{25}H_{44}O_4$ requires C, 73·5; H, 10·8%).

9 : 11-*Dioxononadecanoic Acid*.—Methyl 9 : 11-dioxononadecanoate (2 g.), dilute hydrochloric acid (40 c.c.), and methanol (4 c.c.) were boiled under reflux for 24 hr., and then cooled. A solid separated on the surface and was removed by two extractions with ether (2 × 50 c.c.), Sodium hydrogen carbonate solution (5%; 20 c.c.) and dilute sodium carbonate (1 drop) were added to the ethereal solution and the mixture shaken vigorously for ½ hr. Sodium 9 : 11-dioxononadecanoate separated and was washed with a little ether and warmed with dilute hydrochloric acid. Ether extraction of the aqueous acid mixture and crystallisation of the product from 2-methylpentane gave 9 : 11-dioxononadecanoic acid (0·1 g.), needles, m. p. 57·8—58·6° alone, or when mixed with the dioxo-acid isolated by Faure and Smith[3] (Found : C, 69·9; H, 10·3. Calc. for $C_{19}H_{34}O_4$: C, 69·9; H, 10·5%).

9 : 11-*Dioxoheptadecanoic Acid*.—Similarly, methyl 9 : 11-dioxoheptadecanoate (2 g.), dilute hydrochloric acid (40 c.c.), and methanol (4 c.c.), boiled under reflux for 24 hr., yielded 9 : 11-*dioxoheptadecanoic acid* (0·7 g.) as plates, m. p. 49·8—50·0° (Found : C, 68·2; H, 10·0. $C_{17}H_{30}O_4$ requires C, 68·4; H, 10·1%). Surprisingly, this acid did not form a sparingly soluble sodium salt.

Pentadecane-7 : 9-*diol*.—7 : 9-Dioxopentadecane (10 g.) in methanol (10 c.c.) was added to potassium borohydride (3·2 g.) in aqueous methanol[6] (32 c.c. of methanol + 8 c.c. of water), and the mixture kept at room temperature for 24 hr. Dilution with water, neutralisation with dilute hydrochloric acid, extraction with ether, and recrystallisation from light petroleum (b. p. 40—60°) gave *pentadecane*-7 : 9-*diol* (1·9 g.), as needles, m. p. 91° (Found : C, 73·5; H, 12·9. $C_{15}H_{32}O_2$ requires C, 73·8; H, 13·1%). Unsaturated alcohols are probably also formed in the reduction.[7]

1 : 2-*Dihexyl*cyclo*propane*.—Pentadecane-7 : 9-diol (1·8 g.) was refluxed with 50% w/v hydrogen bromide–acetic acid (50 c.c.) for 24 hr.; the mixture was then poured into water and extracted with ether, yielding a yellow liquid (2·6 g.) (Found : Br, 39·5. Calc. for $C_{15}H_{30}Br_2$: Br, 43·2%). The crude dibromide (2·5 g.) was refluxed with dry acetone (125 c.c.), sodium iodide (12·5 g.), and zinc dust (7·5 g.) for 6 hr.[4] The zinc dust was filtered off from the hot mixture and extracted with boiling chloroform (2 × 25 c.c.). The combined acetone and chloroform filtrates were poured into water and the whole was extracted with ether; the extract was

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[6] Chaiken and W. G. Brown, *J. Amer. Chem. Soc.*, 1949, **71**, 122; Schlesinger, H. C. Brown, Hoekstra, and Rapp, *ibid.*, 1953, **75**, 199.

[7] Dreiding and Hartman, *ibid.*, p. 939.

washed with water, dried ($MgSO_4$), and evaporated. Distillation gave a product, b. p. 100—110° (bath)/0·5 mm., which was dissolved in light petroleum (b. p. 40—60°; 5 c.c.) and the solution poured on a column of acid-washed alumina (8 g.); the column was eluted with light petroleum (b. p. 40—60°; 50 c.c.). Evaporation of the first fraction (20 c.c.), 1 : 2-*dihexyl*cyclo*propane* (0·8 g.), gave a liquid, free from bromine (Found: C, 85·2; H, 14·8. $C_{15}H_{30}$ requires C, 85·7; H, 14·3%). The infrared absorption showed bands at 3·27—3·30, and 9·83 μ (medium intensity).

Methyl 9 : 11-*Dihydroxyheptadecanoate.*—Methyl 9 : 11-dioxoheptadecanoate (7 g.) in methanol (10 c.c.) was added to sodium borohydride (1·8 g.) in methanol (20 c.c.). After a few minutes, a solution of sodium borohydride (1·8 g.) in water (10 c.c.) was added, and the whole kept at room temperature for 24 hr. The resulting solid yielded *methyl* 9 : 11-*dihydroxyheptadecanoate* (1·6 g.), m. p. 65° [from light petroleum (b. p. 60—80°)] (Found: C, 68·7; H, 11·6. $C_{18}H_{36}O_4$ requires C, 68·4; H, 11·4%). This ester (1·2 g.) was refluxed with 50% w/v hydrogen bromide–acetic acid (25 c.c.) for 24 hr. and the mixture worked up as above. The resulting liquid (1·4 g.) (Found: Br, 35·1. Calc. for $C_{18}H_{34}O_2Br_2$: Br, 36·2%), on debromination with zinc and sodium iodide in acetone as above, gave a colourless, bromine-free liquid (0·3 g.), b. p. 130° (bath temp.)/0·3 mm., showing in its infrared spectrum bands at 9·83 and 3·27—3·30 μ.

Methyl ω-(2-*Octyl*cyclo*propyl*)*octanoate.*—Methyl 9 : 11-dioxononadecanoate (6 g.) was reduced with sodium borohydride to *methyl* 9 : 11-*dihydroxynonadecanoate* (1 g.), m. p. 78° (Found: C, 70·3, 69·7; H, 12·1, 11·2. $C_{20}H_{40}O_4$ requires C, 69·8; H, 11·6%). This ester (0·9 g.) on treatment with hydrogen bromide–acetic acid as described above gave a brown wax (1 g.) (Found: Br, 32·2. $C_{20}H_{38}O_2Br_2$ requires Br, 34·0%). Debromination with zinc and sodium iodide in acetone, as before except that the alumina column was eluted with ether, gave *methyl* ω-(2-*octyl*cyclo*propyl*)*octanoate* (0·2 g.), as a liquid, b. p. 200° (bath temp.)/0·5 mm. (Found: C, 76·9; H, 12·5; Br, 0. $C_{20}H_{38}O_2$ requires C, 77·4; H, 12·3%). The infrared absorption spectrum showed a band at 3·27—3·30 μ and one of medium intensity at 9·8 μ.

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