146. *Decalin*-1 : 5-*dione and* 2 : 2′-*Diketodi*cyclo*pentyl.*

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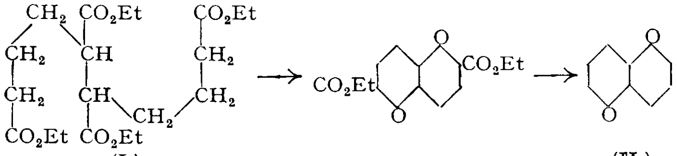
The double Dieckmann-type of cyclisation of *ethyl octane*-1 : 4 : 5 : 8-*tetracarboxylate* might give a naphthalene or a di*cyclo*pentyl derivative. We were interested in the former possibility, but the reaction takes the latter course. The *diketodi*cyclo*pentyl* which was obtained on hydrolysis of the product was independently synthesised.

Decalin-1 : 5-*dione* has been obtained by catalytic reduction of 1 : 5-dihydroxynaphthalene, followed by oxidation of the decalin-1 : 5-diol produced, but the yields were unsatisfactory.

So far as we are aware the only decalindiones that have been described are two in which both keto-groups are situated in one *cyclo*hexane ring (cf. Ganapathi, *Current Sci.*, 1938, **6**, 448; Chuang and Tien, *Ber.*, 1936, **69**, 25). Diketones which are fused *cyclo*hexanones are of interest in view of the possibility of building on two more rings and in the first instance we have examined methods for the synthesis of decalin-1 : 5-dione because of its symmetry.

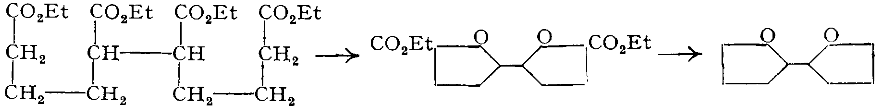
Ethyl octane-1 : 4 : 5 : 8-*tetracarboxylate* (I) was obtained by the action of silver powder on ethyl α-bromoadipate. Its cyclisation might proceed according to (A) or (B); analogy for (A) is found in the formation of chrysene derivatives from ββ′-diaryladipic acids, and for (B) in the synthesis of indigotin from dianilinomaleic acid.

(A)



(I.) (II.)

(B)



(I.) (III.)

The cyclisation with sodium was unsuccessful, but with potassium a keto-ester was obtained which on hydrolysis afforded diketones, $C_{10}H_{14}O_2$. The product melted over a range of temperature and may have contained some of the desired decalindione (II), but it consisted essentially of (III). This 2 : 2′-*diketodi*cyclo*pentyl* was prepared in a purer condition by hydrolysis of the product of oxidation of ethyl sodio*cyclo*pentanone-2-carboxylate with iodine. Catalytic hydrogenation of 1 : 5-dihydroxynaphthalene at 120—180°/10—20 atms. over a nickel–kieselguhr catalyst affords 5-hydroxy-1-tetralone (Schroeter and Tetralin G.m.b.H., G.P. 352,720) but the yield was not stated. At higher pressures (120 atms.) with Raney nickel at 100—150°, the chief products are α-decalols but 5—8% of x-*decalin*-1 : 5-*diol* could be isolated. The substance is apparently a stereoisomeride of the decalin-1 : 5-diol reported by Campbell and Harris (*J. Amer. Chem. Soc.*, 1941, **63**, 2721). These authors oxidised $\Delta^{9:10}$-octalin by means of selenium dioxide in acetic anhydride solution at 30°, thereby introducing two acetoxyl groups. The product was hydrolysed and oxidised to an octalindione. The latter (0·3 g.) on dehydrogenation and acetylation of the product afforded a few mg. of 1 : 5-diacetoxynaphthalene. Although the yield was small, this is not unusual in such dehydrogenations, and the experiment seems to be conclusive in view of the sharp m. p. of the octalindione. Our *x*-decalin-1 : 5-diol could be oxidised by chromic acid to the diketone (II), which was obtained in two stereoisomeric forms, of which that of higher melting point is regarded as derived from *trans*-decalin. In view of other interests the work has been temporarily abandoned.

EXPERIMENTAL.

Ethyl Octane-1 : 4 : 5 : 8-*tetracarboxylate* (I).—Silver powder prepared by either of the following methods was used : (1) Freshly precipitated silver chloride was mixed with an excess of aqueous sodium hydroxide (10%), and formalin (33%) added very gradually. The reduction was completed by heating on the steam-bath, and the silver collected, washed, and dried. (2) A dilute solution of silver nitrate was stirred with an equivalent of copper bronze until reduction appeared complete. The presence of traces of copper in the product was an advantage.

A mixture of ethyl α-bromoadipate (100 g.) (Ingold, J., 1921, **119**, 316) and silver powder (50 g.) was vigorously stirred and heated to 140—160°. After 2 hours the mixture was cooled and filtered, and the silver bromide washed with ether. The dry solid (80 g., indicating complete removal of bromine) was triturated with aqueous sodium hydroxide and formalin, and the silver used again. On distillation of the residue after removal of ether, 40—50% of ethyl adipate was first obtained, b. p. 90—174°/0·2—0·3 mm. and largely b. p. 90—110°; redistilled, b. p. 245°/760 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4300. The second fraction, b. p. 180—200°/0·2—0·3 mm., was redistilled, b. p. 192—195°/0·2—0·3 mm. (21·9 g.; 31%), $n_{\mathrm{D}}^{20^\circ}$ 1·4518 (Found : C, 59·5; H, 8·2. $C_{20}H_{34}O_8$ requires C, 59·7; H, 8·5%).

2 : 2′-*Diketodi*cyclo*pentyl* (III).—(A) Ethyl *cyclo*pentanone-2-carboxylate (14·4 g.) was added slowly to a suspension of sodium powder (2·4 g.) in dry ether (150 c.c.). After subsidence of the initial reaction the mixture was refluxed for 3 hours, cooled, and stirred while iodine (9·6 g.) in ether (150 c.c.) was introduced during 2 hours. After being stirred for 1 hour more, the liquid was filtered and evaporated, leaving an orange-red oil that decomposed on attempted distillation. The crude product was refluxed with a solution of sodium hydroxide (3 g.) in water (70 c.c.) and alcohol (30 c.c.) for 3 hours. The neutral product was isolated by means of ether and distilled. After removal of a considerable amount of *cyclo*pentanone, a fraction, b. p. 124—128°/15 mm., was obtained as a light yellow oil which partly solidified at 0°. The drained solid crystallised from light petroleum (b. p. 40—60°) in colourless needles, m. p. 67—69° (Found : C, 72·0; H, 8·6. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·4%). The overall yield was only 2—4%.

(B) Reaction occurred when a mixture of ethyl octane-1 : 4 : 5 : 8-tetracarboxylate (16·0 g.), potassium powder (4·1 g.), and toluene (20 c.c.) at 0° was allowed to reach the room temperature. The orange-coloured oily product (31 g.) from three such experiments, worked up in the known manner, was hydrolysed by refluxing for 5 hours with hydrochloric acid (30 c.c., *d* 1·16), alcohol (45 c.c.), and water (85 c.c.). The neutral product was isolated by means of ether and distilled, b. p. 100—120°/0·2—0·3 mm. (3·9 g.; 20%) (Found : C, 71·6; H, 8·6%), $n_{\mathrm{D}}^{20^\circ}$ 1·4880. This material slowly solidified and on recrystallisation from light petroleum (b. p. 40—60°) had m. p. 48—54° (Found : C, 72·1; H, 8·5%). A mixture with the product from (A) had m. p. 55—65°. Further crystallisation raised the m. p. to 51—65° and this, mixed with the product from (A), had m. p. 62—68°. These results indicate admixture with some other substance, possibly decalin-1 : 5-dione, but it is clear that the material is essentially diketodi*cyclo*pentyl.

The *bis*-2 : 4-*dinitrophenylhydrazone* crystallised from acetic anhydride in reddish-orange needles, m. p. 230—240° (decomp.) (Found : N, 21·2. $C_{22}H_{22}O_8N_8$ requires N, 21·3%). The semicarbazone was anomalous (N, 25·9%), but the same substance, m. p. 230—240° (decomp.) (N, 25·5%), was obtained from the product of the action of sodium on the tetracarboxylic ester and subsequent hydrolysis.

The diketone (1·6 g.) was methylated by means of sodamide (1·6 g.) and methyl iodide (6 g.) in ethereal solution under the usual conditions. The fraction of the product, b. p. 175—185°/14 mm., was converted into a *dioxime*, which formed white crystals, m. p. 207—211° (decomp.), from methyl alcohol (Found : N, 13·3. $C_{11}H_{12}O_2N_2$ requires N, 13·3%). From this result it appears that one methyl group was introduced ($C_{10}H_{16}O_2N_2$ requires N, 14·4 and $C_{12}H_{20}O_2N_2$ requires N, 12·5%).

x-*Decalin*-1 : 5-*diol*.—1 : 5-Dihydroxynaphthalene (32 g.) in ethanol (60 c.c.) along with a catalyst (2 g. of Raney nickel or copper chromite) was heated at 150—200° with hydrogen (120 atms.) for 8 hours. The phenolic and the neutral products were separated, and the latter distilled. The fraction, b. p. 115—150°/15 mm., consisted chiefly of mixed α-decalols. On keeping, crystals were deposited and recrystallisation from aqueous methanol, light petroleum (b. p. 60—80°), and acetone afforded *cis*-1-decalol, long needles, m. p. 92—94°. The second fraction, a viscous oil, b. p. 175—180°/15 mm., solidified and then crystallised from benzene in colourless prisms, m. p. 137—147° (Found : C, 70·5; H, 10·7. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6%). The m. p. of different specimens was variable in the range 130—150°. By repeated crystallisation from ethyl acetate a product, m. p. 159—161°, was obtained and this is possibly an individual stereoisomeride. The following results were obtained :

Catalyst.	Temp.	Time, hrs.	Pressure.	Crystalline 1 : 5-diol, g.	Other non-phenolic, g.	Phenolic, g.
Ni	150—200°	8	to 120 atms.	2·5	28	—
Ni	100—150	3	,, 120 ,,	2·6	26	3
Ni	150	5	,, 110 ,,	2·5	22	trace
Ni	100	4	,, 100 ,,	2·1	23	2—3
CuCrO	220—250	36	,, 150 ,,	none	2	*ca.* 25

The phenolic product from the last-mentioned experiment constituted 90% of the whole. On distillation it gave 12 g. (b. p. 125—130°/15 mm.) of 5 : 6 : 7 : 8-tetrahydro-1-naphthol. The substance crystallised from light petroleum (b. p. 60—80°) in colourless plates, m. p. 65° (Found : C, 80·7; H, 8·3. Calc. for $C_{10}H_{12}O$: C, 81·0. H, 8·2%). Crystallisation of the residue from alcohol and from benzene afforded greenish-grey needles, m. p. 165—170° (Found : C, 77·7; H, 7·5%). The acetate had m. p. 129—131° (Found : C, 72·2; H, 6·9%). This substance has not been identified.

Decalin-1 : 5-*dione* (II).—(A) A solution of chromic anhydride (6·4 g., four times the theoretical amount) in water (5 c.c.) and acetic acid (40 c.c.) was added dropwise to one of decalin-1 : 5-diol (2 g., crystallised from ethyl acetate) in acetic acid (10 c.c.) at 0° with good stirring. The mixture was allowed to reach the room temperature and kept for 18 hours. The solvent was removed by vacuum distillation through a column, the residue mixed with water, and the product isolated by means of ether. The yellow oil solidified and crystallisation from benzene afforded colourless needles, m. p. 165—167° (0·2 g.; 10%) (Found : C, 72·4; H, 8·2. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·5%).

(B) When decalin-1 : 5-diol (2·3 g.) in acetic acid (10 c.c.) was similarly treated with chromic anhydride (3·7 g., twice the theoretical amount) in water (3 c.c.) and acetic acid (20 c.c.), and the product worked up as before, evidence was obtained of the formation of a mixture of stereoisomerides. Crystallisation from light petroleum (b. p. 60—80°) furnished 0·6 g., m. p. 70—140°, and from the mother-liquor 0·4 g., prisms, m. p. 72—79° (total yield, 25%). Recrystallisation of the first crop from benzene–light petroleum gave 0·5 g. of a mixture of prisms and needles, m. p. 85—100° (Found : C, 72·1; H, 8·4%).

(C) Reduction of the quantity of chromic anhydride to 1·25 times the theoretical amount increased the yield to 60%. The product was separated into two fractions, the less soluble having m. p. 85—115° and closely resembling the mixture of similar m. p. obtained in (B). The more soluble fraction, prisms, m. p. 68—72° (about 1/4 of the whole product), is probably the nearly pure stereoisomeride of the former, m. p. 164—167° (A, above) (Found : C, 72·2; H, 8·6%).

This substance and also the mixtures, m. p. 85—100° and the like, may be converted into the isomeride, m. p. 164—167°, by heating with acetic acid for 6 hours at 100°.

All analogy points to the allocation of the *trans*-decalin configuration to the form of the higher m. p.

In the first place the hydrogenation of α-naphthol yields *cis*-1-decalol (cf. Hückel, *Annalen*, 1925, **441**, 1) and we have obtained this substance in considerable amount as a by-product of the hydrogenation of 1 : 5-dihydroxynaphthalene. Hence it is probable that the mixed decalindiols obtained by us are predominantly derived from *cis*-decalin; four such isomerides are possible, but these should yield only one diketone. Oxidation under the milder conditions affords the more fusible, more soluble diketone (cf. *cis*-1-decalone, m. p. 2°; *trans*-1-decalone, m. p. 33°). Finally *cis*-1-decalone is labile and may be transformed into *trans*-1-decalone in the presence of basic or acidic catalysts.

When *cis*- or *trans*-decalin-1 : 5-dione, or a mixture of these, was heated with methanolic potassium hydroxide, a series of colour changes occurred and eventually the solution became yellowish-brown. On the addition of water a neutral substance (m. p. *ca.* 143°) was precipitated. Acidification of the filtrate afforded 5-hydroxy-1-tetralone (Schroeter, *loc. cit.*). The substance, from mixed diketones, crystallised from ether–light petroleum (b. p. 40—60°) in prismatic needles, m. p. 154—156° (pure, m. p. 157°) and gave a 2 : 4-dinitrophenylhydrazone. The orange-yellow *p*-nitrobenzeneazo-derivative dissolved in alcoholic sodium hydroxide to a permanganate-coloured solution.

Diphenylhydrazone of trans-*Decalin*-1 : 5-*dione*.—This *derivative* separated immediately when phenylhydrazine (excess) was added to a cold solution of the diketone in acetic acid; pale yellow, short, prismatic needles, m. p. 230° (Found in material dried at 100° : C, 76·0; H, 7·3. $C_{22}H_{26}N_4$ requires C, 76·3; H, 7·5; N, 16·2%). The corresponding derivative from *cis*-decalin-1 : 5-dione, m. p. 68—72°, crystallised more slowly from the reaction mixture in pale yellow, prismatic needles, m. p. 172—173° to a gum which cleared at 208—210° (Found : N, 15·8%). This behaviour suggests that the substance contains some of the *trans*-compound or that conversion into the latter occurs in the process of heating.

3 : 4 : 7 : 8 : 9 : 10-*Hexahydronaphtha*(1 : 2 : 5 : 6)-*bis*-(2 : 3)-*indole*.—The diphenylhydrazone of the *cis*-diketone is converted into this substance by boiling acetic acid or more readily by hot alcoholic or aqueous alcoholic hydrochloric acid. Hydrogen chloride was passed rapidly into an alcoholic suspension until the liquid boiled and for a minute longer. The orange solution gave an ochreous precipitate on dilution with water; this was collected and crystallised from alcohol, in which it was moderately sparingly soluble, forming colourless, short needles, m. p. 312—316° (decomp.) (Found in material dried at 100° : C, 84·2; H, 6·5; N, 8·8. $C_{22}H_{20}N_2$ requires C, 84·6; H, 6·4; N, 9·0%). No coloration was developed with *p*-dimethylaminobenzaldehyde and aqueous alcoholic hydrochloric acid in the cold; on boiling, the liquid gradually became dichroic, brownish-green and red, and, on cooling, yellowish-brown; these effects can be alternated.

When similarly treated, the diphenylhydrazone of the *trans*-diketone afforded a substance that crystallised from alcohol, in which it was very sparingly soluble, in short microscopic needles showing a pronounced tendency to form X-shaped twins, m. p. 292—296° (decomp.) (Found : C, 74·3; H, 6·5; N, 8·1%). The substance apparently contains $C_{22}N_2$ and oxygen. Whereas the true bis-indole may be rapidly distilled up a tube, this compound suffers complete decomposition.

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