

**888.** *The Self-condensation of cycloDecane-1 : 2-dione.*

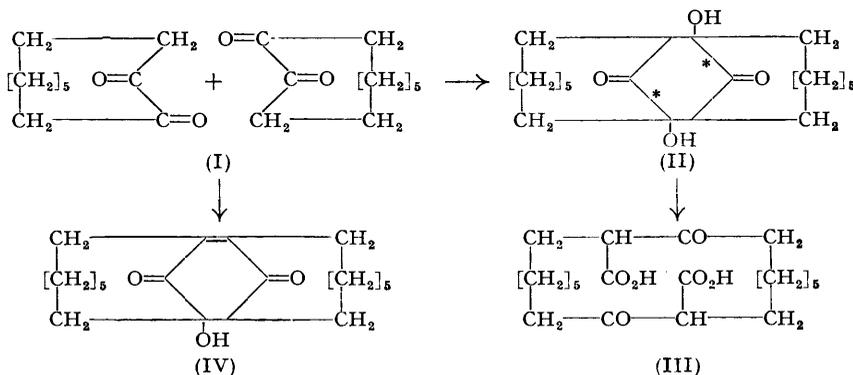
By R. A. RAPHAEL and A. I. SCOTT.

With methanolic sodium methoxide *cyclodecane-1 : 2-dione* gives 2 : 5-dihydroxy-2 : 6-3 : 5-bisheptamethylenecyclohexane-1 : 4-dione and 2-hydroxy-2 : 6-3 : 5-bisheptamethylenecyclohex-5-ene-1 : 4-dione. The steric configuration of these compounds is discussed.

DURING another investigation, a condensation was attempted between *cyclodecane-1 : 2-dione* and sodionitromalondialdehyde in aqueous alcoholic sodium hydroxide. The main product was sebacic acid but a small amount of a neutral non-nitrogenous, high-melting material was obtained. The same compound, a dimer of *cyclodecane-1 : 2-dione*, was formed in much better yield by treatment of the dione alone with methanolic sodium methoxide, the product crystallising from the reaction mixture. The compound exhibited no carbonyl reactivity, but infra-red absorption measurements (Nujol mull) showed the presence of strong bands at  $1682\text{ cm.}^{-1}$  ( $\text{C}=\text{O}$ -stretching frequency) and  $3426\text{ cm.}^{-1}$  (OH-stretching frequency).

The most stable configuration of *cyclodecanone* is that in which the oxygen of the carbonyl group is enclosed as far as possible by the polymethylene chain, the so-called

"O-inside" configuration (Prelog, Centenary Lecture, *J.*, 1950, 420). It follows therefore that the most favourable conformation of *cyclodecane-1 : 2-dione* is the "O-inside, O-outside" structure, as in (I), a concept deriving support from ultra-violet absorption measurements on alicyclic  $\alpha$ -diketones (Leonard and Mader, *J. Amer. Chem. Soc.*, 1950, **72**, 5388). This structure is very favourable for a double aldol-type condensation, and the postulated constitution (II) for the dimer produced was confirmed by oxidative degradation with



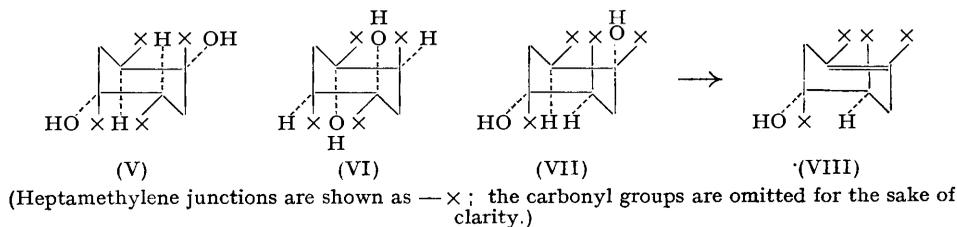
sodium bismuthate (Rigby, *J.*, 1950, 1907), whereby *cyclooctadecane-1 : 10-dione* was produced. This product is readily derived from (II) by fission of the bonds marked \* and decarboxylation of the resulting acid (III); the latter was isolated from a milder reaction procedure. The formulation (II) also accounts for the lack of carbonyl properties (cf. Prelog, Barman, and Zimmerman, *Helv. Chim. Acta*, 1949, **32**, 1284) and for the resistance to acylation.

Attempted conversions of the dimer into the corresponding substituted benzoquinone by use of dehydrating agents gave, in nearly every case, only unchanged material. However, fusion with toluene-*p*-sulphonic acid gave an intense purplish-blue melt, now being investigated.

A more soluble second product,  $\text{C}_{20}\text{H}_{30}\text{O}_3$ , from the preparation of the dimer also showed no carbonyl or hydroxylic reactions although its infra-red spectrum (in  $\text{CCl}_4$ ) exhibited the stretching frequencies of these groups at  $1712 \text{ cm.}^{-1}$  and  $3565 \text{ cm.}^{-1}$ , respectively; in addition a weak  $\text{C}=\text{C}$ -stretching frequency was observable at  $1621 \text{ cm.}^{-1}$ . This indication of one double bond was confirmed by quantitative micro-hydrogenation. The ultra-violet absorption of this compound [ $\lambda_{\text{max}}$ ,  $2450 \text{ \AA}$  ( $\epsilon = 75,000$ ),  $\lambda_{\text{inf}}$ ,  $2520 \text{ \AA}$  ( $\epsilon = 72,500$ ); in EtOH] is in accord with the chromophoric properties expected from a dialkylated *cyclohex-2-ene-1 : 4-dione* (cf. Bastron, Davis, and Butz, *J. Org. Chem.*, 1943, **8**, 515). All these properties point clearly to (IV) for this second product. The resistance of (II) to drastic dehydrating agents shows that it cannot be an intermediate in the formation of (IV) and it is thus highly probable that the stereochemistry of the two molecules is different.

The production of the dimer (II) from *cyclodecane-1 : 2-dione* involves the creation of four asymmetric centres and the resulting six-membered ring probably adopts the more stable, chair conformation. There are then three possible modes of attachment of a heptamethylene chain to the six-membered ring, namely, equatorial-equatorial (*e-e*), polar-polar (*p-p*), and equatorial-polar (*e-p*) (cf. Barton, *Experientia*, 1950, **6**, 312). The relative stability of the chain in these three configurations may be assessed by using the known relationship between the constellation of a polymethylene chain and its energy content (Prelog, *J.*, 1950, 424). "Catalin" molecular models of the three configurations show that in the *e-e* and the *p-p* mode of attachment the heptamethylene chain has six energetically unfavourable *c* constellations while the *e-p* linking has only five *c* constellations and one favourable *b* constellation; this latter configuration represents an enhanced stability of *ca.* 3 kcal. The most stable structures are therefore those in which both heptamethylene chains possess the energetically favourable *e-p* junction; these are only three (V, VI, and VII).

Structure (VII) possesses adjacent hydrogen and hydroxyl groups which are opposed and stereochemically polar. These are the optimum conditions for ready dehydration by an *E2* reaction (Ingold *et al.*, *J.*, 1948, 2903; Barton, *loc. cit.*; Barton *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 370, 1066; *J.*, 1951, 1048, 2598; Shoppee and Summers, *J.*, 1952, 1786). The dehydration is further favoured by the fact that each chain in (VIII) is made



up of four favourable *b* constellations, one very favourable *d* constellation, and only one unfavourable *c* constellation, a gain in stability of *ca.* 12 kcal. for each chain. The remaining hydrogen and hydroxyl groups in (VIII) are both equatorial and would therefore resist ionic dehydration. It is thus highly likely that (VIII) represents the steric structure of the unsaturated product. This leaves a choice between the two closely related conformations (V) and (VI) for the structure of the dimer. Neither has an adjacent polar hydrogen and polar hydroxyl and thus both would explain the resistance to dehydration. Structure (V), is however, far more probable as the bulky hydroxyl groups occupy the less sterically hindered and thermodynamically more stable equatorial positions. That this conformational analysis predicts only two products of optimum stability is in good accord with the practical findings; the combined yields of the products (II) and (IV) represent an almost quantitative conversion of the *cyclodecane-1 : 2-dione*.

#### EXPERIMENTAL

Melting points were determined on a Kofler block.

*2-Hydroxycyclodecanone*.—This was prepared from diethyl sebacate by the method of Prelog, Frenkiel, Kobelt, and Barman (*Helv. Chim. Acta*, 1947, **30**, 1741), in comparable yield. A higher-boiling by-product, b. p. 200—230°/0.1 mm., formed needles (from methanol), m. p. 125—126°, of 2 : 12-dihydroxycycloeoicosane-1 : 11-dione [Found : C, 70.45; H, 10.25%; *M* (ebullioscopic in benzene), 351.  $C_{20}H_{36}O_4$  requires C, 70.55; H, 10.65%; *M*, 340].

*cycloDecane-1 : 2-dione*.—A mixture of crude 2-hydroxycyclodecanone (35 g.), bismuth oxide (35 g.), and acetic acid (150 c.c.) was stirred in a boiling-water bath for 45 minutes (cf. Rigby, *J.*, 1951, 793). Bismuth compounds were then filtered off, the filtrate diluted with water, and the dione extracted with light petroleum (b. p. 40—60°). One crystallisation from a small volume of light petroleum (b. p. 40—60°) of the solid so obtained gave nearly pure *cyclodecane-1 : 2-dione* (22 g.) as yellow prisms, m. p. 41—43° (Prelog *et al.*, *loc. cit.*, give m. p. 44°).

*Self-condensation of cycloDecane-1 : 2-dione*.—*cycloDecane-1 : 2-dione* (5.28 g.) in methanol (20 c.c.) was added to methanolic sodium methoxide [from methanol (50 c.c.) and sodium (2 g.)], in a 100-c.c. flask, which was then filled to the stopper with methanol. The crystals (2.8 g.; m. p. 242—248°), obtained after 16 hours at room temperature, gave 2 : 5-dihydroxy-2 : 6 : 3 : 5-bisheptamethylenecyclohexane-1 : 4-dione (1 : 9-10 : 18-bisoxomethylenecyclooctadecane-1 : 10-diol) (II) as fine needles (from toluene), m. p. 255° [Found : C, 71.2; H, 9.4%; *M* (ebullioscopic in benzene), 304.  $C_{20}H_{32}O_4$  requires C, 71.4; H, 9.55%; *M*, 336], which were sparingly soluble in cold common organic solvents but slowly dissolved in hot dioxan, chloroform, toluene, pyridine, and acetic acid. Potassium hydrogen sulphate at 200°, phosphoric oxide in hot triethylamine-benzene, phosphorus tribromide in hot toluene, phthalic anhydride at 200°, boiling acetic anhydride, and benzoyl chloride-pyridine produced no change. The compound was recovered unchanged on dilution of a solution in concentrated sulphuric acid.

The methanolic filtrate was diluted with water (2 vols.) and set aside. The second product (IV) (1.8 g.; m. p. 150—158°) crystallised from light petroleum (b. p. 100—120°), giving 2-hydroxy-2 : 6 : 3 : 5-bisheptamethylenecyclohex-5-ene-1 : 4-dione (1 : 9-10 : 18-bisoxomethylene-cyclooctadec-9-en-1-ol) as prismatic clusters, m. p. 169—171° [Found : C, 75.7; H, 9.7%;

microhydrogenation (Pd in acetic acid), 1.1 $\bar{F}$ .  $C_{20}H_{30}O_3$  requires C, 75.45; H, 9.5%. Treatment with the dehydrating agents mentioned above left the compound unchanged.

*Sodium Bismuthate Oxidation of (II).*—The dimer (1 g.), in warm acetic acid (100 c.c.), phosphoric acid (8 c.c.; 3.3M) and sodium bismuthate (4 g.; 4 mols.) were stirred at 70–75° for 6 hours. The cooled mixture was diluted with water (50 c.c.) and then shaken with ether (3 × 250 c.c.), and a flocculent suspension of unchanged dimer (0.35 g.) in the ether was filtered off. The sticky solid from the washed, dried, extract was extracted with boiling light petroleum (b. p. 40–60°); this gave a pale yellow oil which quickly solidified. The solid was pressed on porous tile and was then crystallised from a small volume of light petroleum (b. p. 40–60°) at 0°, furnishing prismatic plates (80 mg.), m. p. 94–96° alone and mixed with authentic *cyclooctadecane-1:10-dione* (m. p. 96°).

Oxidation of (II) at 50° with only 2 mols. of bismuthate gave a small yield of 1:10-*dioxo-cyclooctadecane-2:11-dicarboxylic acid* (III), needles (from benzene), m. p. 128° (Found: C, 65.2; H, 8.6.  $C_{20}H_{32}O_6$  requires C, 65.2; H, 8.75%).

Oxidation of the dimer with chromium trioxide in acetic acid at 80° gave azelaic acid.

We are indebted to Professor Prelog for providing a specimen of *cyclooctadecane-1:10-dione*. We also thank Dr. G. D. Meakins of the University of Manchester for determining the infra-red spectra. A maintenance award to one of us (A. I. S.) from the Department of Scientific and Industrial Research is gratefully acknowledged.

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