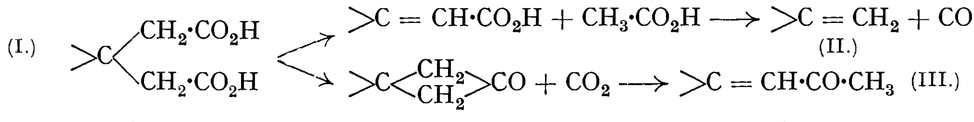
269. *Syntheses of Cyclic Compounds. Part XI. The Thermal Decomposition of* trans-*Hexahydrohydrindene- and of* trans-*Decahydronaphthalene-2 : 2-diacetic Acids.*

By Richard J. Tudor and Arthur I. Vogel.

The Sachse–Mohr hypothesis of multiplanar strainless ring systems for carbon rings of six or more atoms appears to be now generally accepted, but there is considerable purely chemical evidence that the simple unsubstituted *cyclo*hexane ring behaves differently from the strainless uniplanar *cyclo*pentane ring and from the multiplanar and strainless *cyclo*heptane ring. This is interpreted as arising from a rapid interconversion of the *cis*- and *trans*-forms of the 6-ring, so that the effective configuration is an average of the intermediate forms involving strain (cf. Ingold and Thorpe, J., 1928, 1318).

*cyclo*Hexane derivatives substituted in the *o*-positions, either by alkyl groups or by another *cyclo*hexane ring (decalin), are now accepted as strain-free compounds. The fusion of a *cyclo*hexane ring with a *cyclo*pentane ring in the *o*-position leads, according to the Sachse–Mohr theory, to two forms of hexahydrohydrindene (for diagrams, see Hückel and Friedrich, *Annalen*, 1927, **451**, 134; Kandiah, J., 1931, 923). Here no oscillation is possible owing to the locking of the *o*-carbon atoms. Models show that with one multiplanar form of the 6-ring, the five carbon atoms of the 5-ring lie in one plane for the *cis*-compound, which is therefore strainless, whereas for the *trans*-compound one of the carbon atoms of the 5-ring is not in the plane of the ring, thus conferring strain on the whole molecule. A possible but less probable alternative for the *trans*-system is a planar 5-ring and a planar (and therefore strained) 6-ring (see Hückel, *Fortschr. Chem., Physik, u. physikal. Chem.*, 1927, **19**, Heft 4, p. 31). Both alternatives require that the *trans*-hexahydrohydrindene system be strained.

The object of this investigation was to procure experimental evidence for the presence of strain in the *trans*-hexahydrohydrindene ring, or at least, evidence to show that this ring system behaved differently from the strainless *trans*-decahydronaphthalene ring, which was chosen for reference and comparison. The reaction employed was the thermal decomposition of the 2 : 2-diacetic acids, which has been shown (Part X, J., 1933, 1029) to proceed according to the mechanism

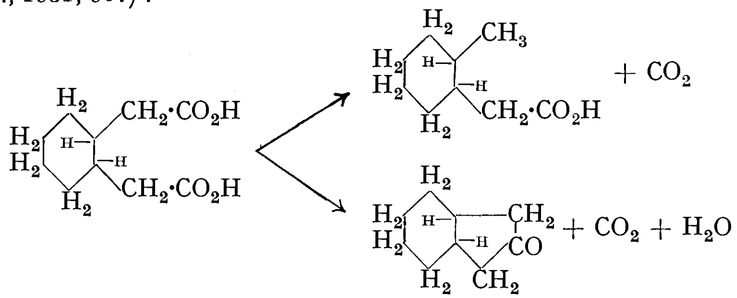


$$\text{(I.)}\ >C<\begin{matrix}CH_2{\cdot}CO_2H\\CH_2{\cdot}CO_2H\end{matrix}\ \begin{matrix}\nearrow\ >C=CH{\cdot}CO_2H+CH_3{\cdot}CO_2H\longrightarrow\ \underset{\text{(II.)}}{>C=CH_2}+CO_2\\ \searrow\ >C<\begin{matrix}CH_2\\CH_2\end{matrix}>CO+CO_2\longrightarrow\ >C=CH{\cdot}CO{\cdot}CH_3\ \text{(III.)}\end{matrix}$$

and in which the yield of the methylene compound (II) is employed for reference purposes owing to its stability and small tendency to polymerisation. It would be expected that any essential difference in the character of the two fused ring systems would be reflected in the difference in the angles between the two acetic acid residues directly attached to the rings, and hence in the yield of (II). The thermal decomposition of *trans*-decahydronaphthalene- and -hexahydrohydrindene-2 : 2-diacetic acids afforded 48% and 35·5% of the corresponding methylene compounds (cf. 33% and 15% for the *cyclo*hexane and *cyclo*pentane acids, J., 1933, 1029), and it is concluded that there is some real difference in the two parent systems. Physicochemical experiments, including the determination of the dissociation constants, with the object of providing further tests of this view, are in progress, as it is considered that conclusions from pyrogenic reactions require confirmation by other means, less open to criticism. This conclusion, which is in accord with the Sachse–Mohr theory, differs from that of Thorpe (J., 1931, 1023; see also Rao, J., 1929, 1960; 1930, 1171; Kandiah, J., 1931, 963), who regards both ring systems as strainless. A possible interpretation of this difference is that the methods employed by Rao and by Kandiah, involving a study of the stability of the corresponding *spirocyclo*propane derivatives and of the equilibrium in the presence of 64% potassium hydroxide between the keto- (open-chain) and cyclic acids (*locc. cit.*), are not sufficiently sensitive to detect the small differences present (cf. Desai, J., 1932, 1047; Ives, Linstead, and Riley, J., 1932, 1093).

It should be pointed out that the comparative method used by one of us, involving the reduction of the corresponding unsaturated cyano-ester with moist aluminium amalgam in ether and the isolation of the bimolecular compounds (Parts III, VI, and IX, J., 1928, 2010; 1930, 768; 1931, 1795), had indicated a difference for *trans*-decahydronaphthalene (6%) and *trans*-hexahydrohydrindene (15%; Kandiah, J., 1931, 930), and this led to the present investigation; further, *all* the results obtained by that comparative method are in accord with existing physical evidence, such as the so-called dissociation constants (cf. Ives, Riley, and Linstead, *loc. cit.*).

The thermal decomposition of *trans-cyclo*hexane-1 : 2-diacetic acid has been shown to proceed in accordance with the general scheme previously described (Part V, J., 1929, 721; Part VIII, J., 1931, 907):



the yield of ketone being 83% (contrast adipic acid, 80%). The facile formation of what is probably a somewhat strained ring system is remarkable.

EXPERIMENTAL.

In view of the high cost of the materials, details are given of improved methods of preparation.

trans-β-*Decalone* (cf. Huckel, *Annalen*, 1925, **444**, 1; Vogel, J., 1928, 2026; Rao, J., 1929, 1961; Thakur, J., 1932, 2128).—This was prepared in 97% yield by the oxidation of *trans*-β-decalol in glacial acetic acid solution with chromic acid, and isolated by benzene extraction after dilution with water; b. p. 117°/16 mm. (semicarbazone, m. p. 192—193°).

trans-cyclo*Hexane*-1 : 2-*diacetic Acid* (cf. Huckel and Friedrich, *Annalen*, 1927, **451**, 134; Kandiah, J., 1931, 924; Thakur, J., 1932, 2151).—100 C.c. of concentrated nitric acid were heated almost to the b. p. in a 1 l. Pyrex flask provided with a 12" air-condenser, 1" in diameter. 50 G. of *trans*-β-decalol, m. p. 73°, were added in small quantities during one hour; the reaction, once started, was self-maintaining, and the gas was extinguished after the first few g. of decalol had been introduced. When the addition was complete, copious brown fumes still being evolved, a further 50 c.c. of concentrated nitric acid were added, and the mixture was gently refluxed for 30 minutes, a water-condenser being attached to the top of the air-condenser. The product was cooled in ice for 2 hours, and the almost pure *trans-cyclo*hexane-1 : 2-diacetic acid, m. p. 161—162° (30·5 g.; 47%) filtered off, and washed with a little ice-cold water. The mother-liquor after standing for 1 hour deposited an acid, m. p. 137—138° (4·4 g.; 6·7%), which after recrystallisation from dilute acetone had m. p. 143° and was therefore probably 1-carboxy-*trans-cyclo*hexane-2-propionic acid (cf. Hückel, *Annalen*, 1925, **444**, 1, m. p. 143°); after standing for a further week, a third crop, m. p. 118—122° (6·5 g.), was obtained, probably 1-carboxy-*trans-cyclo*hexane-2-acetic acid (cf. Kandiah, J., 1931, 922).

Another procedure was to keep the crude oxidation product over-night, and wash the separated solid with dilute alcohol (3 vols. of rectified spirit and 8 vols. of water); 30·5 g. (47%) of acid, m. p. 161—162°, were obtained. The mother-liquor, containing the washings, deposited a large crop, m. p. 120—135°, from which no 1 : 2-diacetic acid could be isolated. The pure acid, m. p. 167°, was obtained by recrystallisation from rectified spirit or from acetone-light petroleum (b. p. 60—80°) (1 : 2 by vol.).

Thermal Decomposition of trans-cyclo*Hexane*-1 : 2-*diacetic Acid*.—The apparatus used was that described by Vogel (J., 1929, 726; 1933, 1029), except that the copper turnings were omitted. In order to obtain reproducible results, it is essential in this and the following decompositions to adhere closely to the experimental conditions. 40 G. of the acid were slowly distilled during 6 hours. After the first 2 hours, distillation commenced at 308—317°, the temperature rose gradually during the following 3 hours to 350°—most of the distillate passed over at 315—328°—and during the last hour, the thermometer was raised to the neck of the distilling flask and the bath heated very strongly, only a small quantity of liquid passing over. A tarry residue (2·0 g.) remained in the flask. The aqueous layer was separated, the ketonic layer washed with dilute ammonia and water (the washings being added to the aqueous layer), dried with calcium chloride and distilled; 22·9 g. (83%) of *trans*-hexahydro-β-hydrindone, b. p. 91—92°/13 mm., were obtained. A middle fraction had $d_{4^\circ}^{20^\circ}$ 0·9819, $n_D^{20^\circ}$ 1·4762. The aqueous distillate and washings were heated on the steam-bath until neutral to litmus, and silver nitrate then precipitated 0·43 g. of *silver* trans-1-*methyl*-cyclo*hexane*-2-*acetate* (Found: Ag, 41·1; C, 40·7; H, 5·7. $C_9H_{15}O_2Ag$ requires Ag, 41·1; C, 41·1; H, 5·75%).

Catalytic Decomposition of trans-cyclo*Hexane*-1 : 2-*diacetic Acid*.—*Expt.* 1. 60·0 G. of acid were mixed with 3 g. of finely powdered crystallised baryta and distilled during 3 hours. The temperature rose to 260° after ½ hour, and the distillation was practically completed during the following 1½ hours at 260—290°; the bath was strongly heated during the last hour. The distillate was worked up as above; yield, 36·4 g. (88%) of ketone, b. p. 97·5°/15 mm.

Expt. 2. 80·0 G. of acid and 2·0 g. of baryta were slowly distilled during 10 hours. Most of the ketone passed over at 275—290°, and the total weight of the distillate was 61·6 g. (99%), which yielded 52·2 g. (94·5%) of ketone, b. p. 95—95·5°/13 mm.

Thermal Decomposition of trans-*Decahydronaphthalene*-2 : 2-*diacetic Acid*.—40·0 G. of acid, m. p. 175° (cf. Rao, J., 1929, 1954), were slowly distilled during 12 hours from a 500 c.c. Pyrex distilling flask (Vogel, Part V, J., 1929, 726; Part X, J., 1933, 1029). The acid was completely melted after 1 hour, distillation just commenced at 260° after 2 hours, and after 4½ hours decomposition was appreciable and was largely completed during the following 5½ hours at 400—460°, the rate of distillation being 1—2 drops per minute. The bath was heated as strongly as possible during the last 2 hours, during which a further small quantity passed over. The experiment was repeated with a further 55 g. of acid, the distillates combined, the aqueous layer separated, the " organic " layer washed with dilute ammonia until alkaline, and then with water (the washings being added to the aqueous layer), dried with calcium chloride, and distilled. The following fractions were collected:

(1) B. p. 55—81·5°/13·5 mm.. chiefly 76—81°/13·5 mm., 3·87 g., $d_{4^\circ}^{20^\circ}$ 0·8650, $n_D^{20^\circ}$ 1·4749.

(2) B. p. 86—89°/14 mm., chiefly 87—88°/14 mm., 23·3 g. A middle fraction, b. p. 86—88°/14 mm., had $d_{4^\circ}^{20^\circ}$ 0·8892, $n_D^{20^\circ}$ 1·4855 (Thakur, J., 1932, 2134, gives for 2-methylene-*trans*-decalin b. p. 81—83°/9 mm., $d_{4^\circ}^{16^\circ}$ 0·8928, $n_D^{16^\circ}$ 1·4870).

(3) B. p. 100—142°/10·5 mm., 5·6 g., $d_{4^\circ}^{20^\circ}$ 0·9487, $n_D^{20^\circ}$ 1·5279.

(4) B. p. 142—152°/10·5 mm., 1·3 g., $d_{4^\circ}^{20^\circ}$ 0·9650, $n_D^{20^\circ}$ 1·5225 (Thakur, J., 1932, 2134, gives for *trans*-decahydronaphthylideneacetone, b. p. 149—150°/15 mm., $d_{4^\circ}^{20·3^\circ}$ 0·9734, $n_D^{20^\circ}$ 1·5068) (Found: C, 81·8; H, 10·6. Calc. for $C_{13}H_{20}O$: C, 81·2; H, 10·5%).

(5) B. p. 152—185°/9 mm., a pale yellow viscous liquid, 2·0 g., $d_{4^\circ}^{20^\circ}$ 1·0068, $n_D^{20^\circ}$ 1·5362 (Found: C, 83·2; H, 9·8. Calc. for $2C_{13}H_{20}O–H_2O$: C, 85·2; H, 10·5%).

It is clear that fractions (1) and (2) consisted of almost pure methylene-*trans*-decalin, the yield of which was therefore 27·17 g. (48·4%). The pure compound was prepared by distillation over sodium and had b. p. 82—82·5°/10 mm., $d_{4^\circ}^{20^\circ}$ 0·8897, $n_{D}^{20^\circ}$ 1·4870. No semicarbazone could be prepared from fraction (1), thus proving the absence of acetone.

Thermal Decomposition of trans-*Hexahydrohydrindene*-2 : 2-*diacetic Acid.*—40·0 G. of acid, m. p. 224° (cf. Kandiah, J., 1931, 922), were slowly distilled as described above during 11 hours. The compound was maintained just above the m. p. during the first 2—3 hours, and the temperature gradually raised. The thermometer was raised to the level of the side arm of the flask, and the distillate passed over at 290—350°. The distillate was worked up as for the decalin acid. The following fractions were collected :

(1) B. p. 35—55°/11 mm., chiefly 50—54°/11 mm., 1·16 g., $d_{4^\circ}^{20^\circ}$ 0·8593, $n_{D}^{20^\circ}$ 1·4690.

(2) B. p. 55—67°/11 mm., chiefly 61—63°/11 mm., 6·91 g., $d_{4^\circ}^{20^\circ}$ 0·8683, $n_{D}^{20^\circ}$ 1·4728. A middle fraction, b. p. 59—60°/9·5 mm., had $d_{4^\circ}^{20^\circ}$ 0·8667, $n_{D}^{20^\circ}$ 1·4726.

(3) B. p. 70—118°/11 mm., chiefly 90—112°/11 mm., 2·42 g., $d_{4^\circ}^{20^\circ}$ 0·9106, $n_{D}^{20^\circ}$ 1·4954.

(4) B. p. 115—168°/11 mm., chiefly 128—148°/11 mm., 1·55 g., $d_{4^\circ}^{20^\circ}$ 0·9728, $n_{D}^{20^\circ}$ 1·5306 (Thakur, J., 1932, 2156, gives for *trans*-hexahydrohydrindylideneacetone, b. p. 134°/10 mm., $d_{4^\circ}^{20^\circ}$ 0·9738, $n_{D}^{20^\circ}$ 1·5047) (Found : C, 85·9; H, 9·9. Calc. for $2C_{12}H_{18}O-H_2O$: C, 85·1; H, 10·1%).

Fractions (1) and (2) were clearly 2-*methylene*-trans-*hexahydrohydrindene*, the yield of which was therefore 8·07 g. (35·6%). The pure compound obtained after distillation over sodium had b. p. 59—60°/9·5 mm., $d_{4^\circ}^{20^\circ}$ 0·8663, $n_{D}^{20^\circ}$ 1·4720 (Found : C, 87·8; H, 12·1. $C_{10}H_{16}$ requires C, 88·1 ; H, 11·9%). Oxidation with 3% potassium permanganate in alkaline solution yielded *trans*-hexahydro-β-hydrindone, identified as the semicarbazone. No semicarbazone could be prepared from fraction (1).

The authors' thanks are due to the Chemical Society and Imperial Chemical Industries for grants.

WOOLWICH POLYTECHNIC, LONDON, S.E. 18.

[*Received, May 2nd*, 1934.]