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PERHYDROTRIPHENYLENE

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From a configurational point of view, cyclic compounds can be considered as useful models of linear stereoregular polymers. This topic is being discussed elsewhere; in this paper we wish to report research done on a low-molecular-weight°) polycyclic system, with particular reference to some of its stereochemical properties. We have approached this field of investigation starting from a discussion recently published in this journal (1) concerning the type of asymmetric carbon atom present in certain optically active cyclic polymers, such as polybenzofuran. A careful examination of the stereochemical properties made us realize that the same type of asymmetric carbon atom is present also in low-molecular-weight polycyclic compounds such as perhydrotriphenylene.

Both the synthesis and the stereochemistry of perhydrotriphenylene $C_{18}H_{30}$ have so far claimed little attention. This hydrocarbon was synthesized by Schrauth and Görig (2) and recognized to be equal to one of the degradation products of lignin. It is described as a liquid compound boiling at 175°C at 7 mmHg. Mannich (3) had previously tried, without success, to obtain perhydrotriphenylene by reduction of dodecahydrotriphenylene $C_{18}H_{24}$. The same negative result was also obtained by the Authors quoted (2).

We have found that hydrogenation of dodecahydrotriphenylene is possible under drastic conditions (150-250 atm., 300°C), using Palladium-Carbon as catalyst. After 4 days, the reaction was practically complete: the reaction product consisted of a crystalline substance (A)(30%), which

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°) This term is used in contrast to "macromolecular".

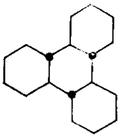
after repeated crystallization from benzene and acetone melted at 124°C (uncorrected), and of a liquid (B) (about 70%) boiling at 148–150°C at 0.2 mmHg, which became solid below room temperature after a long period (m.p. ≃ 20°C). Both products were completely saturated as revealed by IR and UV examinations.

The hydrogenations accomplished under less drastic conditions (200–240°C) gave only a liquid product in far lower yields.

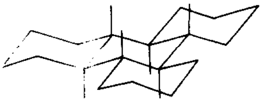
The elementary analyses of products A and B and also molecular weight determinations confirm the formulae $C_{18}H_{30}$ (calculated C 87.73%, H 12.27 %, MW 246; found for A: C 87.66%, H 12.22 %, MW (cryoscopic) 243; for B: C 87.76 %, H.12.14 %, MW 236)

The low-melting compound B can be transformed into A in high yields by heating to 300°C, in the presence of palladium-carbon and under hydrogen pressure. Compound A can, in its turn, be catalytically dehydrogenated (palladium-carbon) at high temperature with production of triphenylene $C_{18}H_{12}$ (m.p. 196° after purification via the picrate, IR spectrum identical with that reported in literature (4)).

Therefore, it can be concluded that both compounds A and B correspond to the skeleton of perhydrotriphenylene of which they constitute stereoisomers. Considering the physical and chemical properties mentioned, compound A appears to be the most stable isomer and should show a high symmetry. Therefore it can be considered that this compound is the trans-anti-trans-anti-trans-perhydrotriphenylene (I).



Ia



Ib

In fact, isomer (I) possesses one ternary symmetry axis and three binary axes; it can exist in a completely equatorial chair conformation without strain or steric hindrances (Ib). This structure of compound A is confirmed by a preliminary X-ray examination of the crystals and by the NMR spectrum. In the latter, it is possible to observe three bands at 229.4, 192.0 and 180.6 ± 1 cps (external reference benzene; Varian 4310 C 40 MC) whereas only one band at 207 ± 1 is observed in the spectrum of B .

In spite of the high symmetry, (I) does not possess alternating axes of any order, and therefore can exist in optically active enantiomers.

The examination of the symmetry properties of the tertiary carbon atoms of (I) permits the conclusion that these atoms are asymmetric in the full sense of the word and belong to the type of asymmetric atoms recently discussed (1) and already observed in the optically active polymers of benzofuran (5). Their asymmetry is caused by the different relationship existing between the atom considered and the two adjacent tertiary atoms (which are identical if considered by themselves): one of these belongs to the same ring as the atom under examination (endo) and the other does not (exo). The existence of the cyclic substituents makes this system essentially different from the hexa-substituted monocyclic cyclohexanes of analogous configuration (e.g. hexamethylcyclohexanes). The compound with trans configuration in this last series has in fact centre and planes of symmetry and therefore cannot exist in optically active forms.

Following the proposal put forward in the previous communication (1) (endo precedes exo) it is possible to define the absolute configurations in the compound corresponding to Ia and Ib: all the tertiary atoms have (R) configuration.

From a conformational point of view, it is possible to consider compound (I) as constituted by three ortho-bisubstituted cyclohexanic rings in rigid chair conformation and having both substituents in equatorial positions. Such a structure is intrinsecally asymmetric and is repeated with the same "chirality" in the three rings.

An examination of the compound according to the Brewster scheme (6) allows prediction of an optical activity of positive sign for the (R) isomer: the separation into antipodes of (I) and of its derivatives is now in progress in our laboratory.

Some interesting crystallographic properties of perhydrotriphenylene are referred to in another paper.

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