Structures of the "Isomers" of 2,3,6,7-Dibenzo-1-thia-4,5-diaza-cyclohepta-2,4,6-triene-1,1-dioxide[1]

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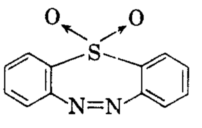
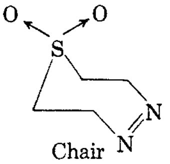
Received July 16, 1959

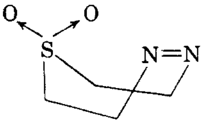
Szmant and Chow[3] originally reported the isolation of three isomers of 2,3,6,7-dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene-1,1-dioxide (I). Shortly thereafter one of the compounds was actually found to be the corresponding hydrazo compound.[4] The two remaining isomers (IA and IB) were assigned structures which differed in the conformation of the center ring, one being a chair and the other a boat form. The more stable isomer was assigned the chair structure.



I



Chair



Boat

It can be argued *a priori* that the chair structure represents an exceedingly improbable situation. There is no authentic case known in which both of a pair of conformers such as these can be isolated as separate stable individual substances. The energy barrier for the interconversion of boat and chair forms is estimated to be only about 10 kcal. for cyclohexane,[5] and since the angular deformation necessary to attain planarity appears to be less with a seven-membered ring, the corresponding barrier should be even smaller here. There is still, however, a more serious objection to the chair structure. In the regular chair form illustrated the dihedral angles between either nitrogen and the sulfur are 93°. Since there are benzene rings fused onto positions 2 and 3, and also 6 and 7, these benzene rings would have to be twisted from planarity to an improbable degree. While such a structure might conceivably exist it would certainly not be expected to be more stable than the boat form and yet the isomerization of IB to IA was reported.[3]

An examination of the experimental data reported by Szmant and Chow showed a surprising similarity between the substances IA and IB. The two compounds did not give a mixture melting point depression. The azo compounds IA and IB were reported to oxidize to the corresponding azoxy compounds IIA and IIB, respectively, and the latter pair likewise showed no mixture melting point depression. The isomerization of IB to IA and the various reactions in which IB was converted to derivatives of IA appeared to suggest that IA and IB were actually the same compound and merely samples of different purity.

The chair structure postulated for IA was sufficiently unusual, and the data upon which the structure was based were sufficiently indecisive that the work of Szmant and Chow was repeated. The materials designated by them as IA and IB were isolated without undue difficulty following a modification of their procedure. Compound IA, m.p. 173°, appeared to be a pure substance. Their compound IB, m.p. 126–130°, which did not appear upon close examination of the crystals to be a single substance, was separated by chromatography on alumina into two compounds, IA and the diamine (III) from which I had been prepared, m.p. 148.5°. Szmant and Chow reported[3] that it gave only one band when chromatographed on alumina. This observation was repeated and confirmed. The amine, being colorless, was not visible on the column, and only the azo compound was seen. The other extensive observations of Szmant and Chow on "isomerizations" can be better interpreted as purification. The rapid oxidation of IB relative to IA is not surprising, since the amine would oxidize very easily. Since IB contains about 50% amine, a large amount of oxidant would be consumed, and the rate was apparently not followed far enough to observe a break in the curve. It is clear therefore that only one isomer of I has in fact been previously isolated, that which corresponds in physical properties to the compound labeled IA by the earlier workers. Only the boat form is regarded by the present authors as a reasonable structure for this compound. It follows that the corresponding azoxy compounds IIA and IIB must also be regarded as identical, and possessing the boat structure.

EXPERIMENTAL

2,3,6,7-Dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene-1,1-dioxide (I). The preparation was similar to that reported by Szmant and Chow.[3] 2,2′-Diaminodiphenyl disulfide was prepared[6] from benzothiazole, and converted to 2-nitro-2′-aminodiphenyl sulfide,[7] which was acetylated[8] and oxidized[8] to the sulfone. This compound was in turn reduced and hydrolyzed to the diamino sulfone III.[9] 2,2′-Diaminodiphenyl sulfone (III), 4.0 g., phenyliodoso acetate,[10] 4.65 g., and 400 ml. of dry toluene were mixed and allowed to stand at room temperature for 5 days with occasional shaking. The mixture was filtered and the brown precipitate

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[1] Supported in part by a research grant from the National Science Foundation.

[2] National Science Foundation Predoctoral Fellow 1956–59.

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was washed with benzene. The filtrate and washings were combined and the solvent was removed under diminished pressure to yield a dark red oil. Crystallization of the oil from methanol as described was attempted, but was unsuccessful. The solution was therefore diluted with water and extracted with ether. The ether layer was washed and dried, and the solvent was evaporated. The residue was a red oil which partially solidified. This material was triturated with 20 ml. of benzene. The insoluble solid (IB) was removed by filtration.

The benzene filtrate was poured onto a column of 200 g. of activated alumina. The column was eluted with 2:8 hexane:ether, and then with ether. The early fractions yielded orange crystals which were combined and recrystallized from methylene chloride–hexane, m.p. 148–149°, wt. 0.27 g. (7%). The mixture melting point with authentic III was undepressed.

A small portion of the benzene-insoluble solid (IB) was recrystallized from methanol, m.p. 127–131° (lit.[3] m.p. 131.5°). The remainder of the crude IB was chromatographed on alumina with gradually increasing concentrations of methylene chloride in hexane, followed by pure ether. From the 4:6 hexane:methylene chloride fractions there was obtained a solid which was crystallized to yield IA as orange needles, m.p. 172.5–173.5°, wt. 0.20 g. From the ether fractions there was obtained material which after recrystallization gave III as colorless plates, m.p. 147–148.5°. The mixed melting point with authentic III was undepressed.

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Synthesis of the *gem*-Dimethylcyclopentenes

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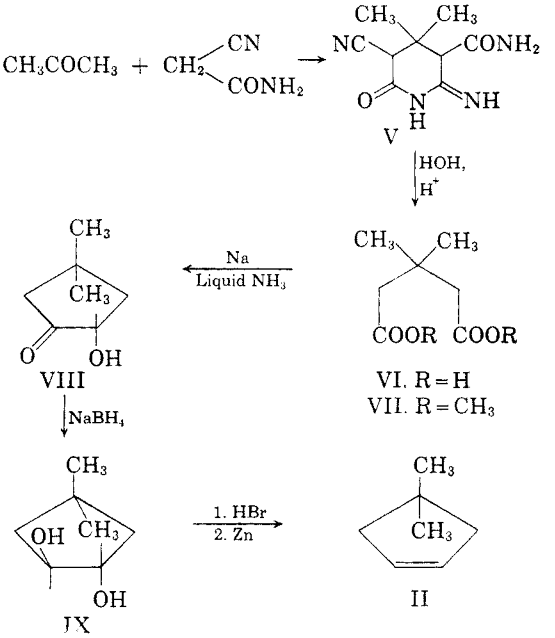
Received July 17, 1959

The two isomeric *gem*-dimethylcyclopentenes were required for an investigation in progress in these laboratories. A method of preparation of 2,2-dimethylcyclopentane (1) has been reported,[2] but apparently the conditions employed for obtaining a significant yield were very exacting. Kizhner[2] has described the formation of (I) by dehydrobromination of 1-bromo-2,2-dimethylcyclopentane, (III), which, as he indicated, resulted from a Demjanov type of rearrangement[3] of cyclobutyldimethyl carbinol (IV) on boiling with fuming hydrobromic acid. When we used 48% aqueous hydrobromic acid instead in the procedure of the Russian author, we obtained chiefly 1,2 dimethylcyclopentene and none of the desired bromo compound (III). Subsequently we found, however, that stirring (IV) with 48% hydrobromic acid at 20–30° (without heating) produced a good yield of (III). Furthermore, upon increasing the reaction time given by Kizhner[2] for the dehydrobromination of (III) we were able to raise the yield of (I) from 42 to 74%



Flow Diagram for Synthesis 3,3-Dimethylcyclopentene

The synthesis of the other isomer, 3,3-dimethylcyclopentene (II), has not been reported. This has now been achieved according to the reactions illustrated in the flow diagram.

The starting material, 5-carbamyl-3-cyano-4,4-dimethyl-6-imino-2-piperidone, (V), was made by condensation of acetone and cyanoacetamide.[4] (V) was hydrolyzed to 3,3-dimethylglutaric acid (VI) by a procedure analogous to that given by Thole and Thorpe.[5] Cyclization of the methyl ester[6] (VII) to 3,3 dimethylglutaroin (VIII) was effected by means of sodium in liquid ammonia. The structure of (VIII) was confirmed by the identity of its osazone with that from 1,1-dimethyl-3,4-cyclopentanedione.[7]

Reduction of (VIII) with sodium borohydride gave 1,1-dimethyl-*trans*-3,4-cyclopentanediol (IX). The trans structure was confirmed by the failure of (IX) to form a cyclic ketal with *p*-nitrobenzaldehyde[8] and the absence of any infrared evidence[9] for intramolecular hydrogen bonding.

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[1] (1) Abstracted from the doctorate thesis of John A. Ford, Jr., submitted to the University of Delaware in partial fulfillment of the requirements of the Ph.D. degree, June, 1958; present address, Eastman Kodak Co., Rochester 4, N. Y.

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[4] (4) F. B. Thole and J. F. Thorpe, *J. Chem. Soc.*, **99**, 430 (1911).

[5] (5) F. B. Thole and J. F. Thorpe, *J. Chem. Soc.*, **99**, 434 (1911).

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[9] (9) See for examples, L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); **76**, 4323 (1954) and H. Kwart and G. C. Gatos, *J. Am. Chem. Soc.*, **80**, 881 (1958).