

potassium hydroxide, cooled to 7° in an ice-bath, was stirred vigorously while a rapid stream of air was introduced. After 2 hours the ice-bath was removed. The stirring accompanied by the introduction of air was continued for an additional 10 hours. The mixture was diluted with 1 l. of hot water and filtered with suction. The residue, while still on the filter, was washed first with boiling water and then with ethanol. The product crystallized from acetic acid as yellow needles, m.p. 225–227.5°, yield 85.1 g. (71.5%). Recrystallization of the dinitro compound from acetic acid raised the melting point to 227–228.5°.

4,4'-Diamino-2,2'-dimethylbibenzyl.—A mixture of 87.9 g. of 4,4'-dinitro-2,2'-dimethylbibenzyl, 200 g. of powdered iron, 500 ml. of ethanol and 500 ml. of water was heated to boiling. To this boiling mixture was added dropwise, with stirring, a solution of 12.1 ml. of concentrated hydrochloric acid in 100 ml. of 50% aqueous ethanol. The resulting mixture, after having been boiled under reflux, with stirring, for 16 hours, was made alkaline by the addition of 30 ml. of 6 *N* aqueous sodium hydroxide in 500 ml. of ethanol. The mixture was filtered while hot. The cold filtrate deposited 36.5 g. of tan needles, m.p. 164–167°. Concentration of the mother liquor afforded an additional crop of the diamine; total yield 43.5 g. (62%). A boiling ethanolic solution of the product, after decolorization with Norit, was chilled to give the pure diamine as white needles melting at 169–170.5°.

Anal. Calcd. for $C_{16}H_{20}N_2$: C, 79.98; H, 8.39; N, 11.66. Found: C, 79.90; H, 8.12; N, 11.82.

4,4'-Diphenylsulfonamido-2,2'-dimethylbibenzyl.—A solution of 23.3 g. of 4,4'-diamino-2,2'-dimethylbibenzyl and 45 ml. of benzenesulfonyl chloride in 200 ml. of pyridine was heated to boiling. The solution, after having been allowed to cool, was poured, with stirring, into 1.5 l. of cold water. The crude sulfonamide was dissolved in warm, dilute, aqueous sodium hydroxide, the alkaline solution decolorized with Norit and the product reprecipitated with hydrochloric acid. The disulfonamide crystallized from ethanol as tan prisms; m.p. 172–174°, yield 42.3 g. (82.1%). It was obtained as colorless prisms, m.p. 173–174°, by slowly cooling a decolorized solution of the crude product in boiling ethanol.

Anal. Calcd. for $C_{26}H_{28}N_2O_4S_2$: C, 64.60; H, 5.42; N, 5.38; S, 12.32. Found: C, 64.65; H, 5.37; N, 5.33; S, 12.17.

Most attempts to recrystallize the material from ethanol resulted in the deposition of an alternative crystalline form, large rectangular prisms melting at 159–160° with a simultaneous transition to the higher melting form. The substance would melt completely only if it were plunged into a bath heated to a temperature of 161° or more. When the recrystallizing solvent was benzene or acetic acid, the lower-melting crystalline form resulted. The infrared spectra of the two forms are identical and the composition of the lower-melting form corresponds to that of the desired product.

Anal. Calcd. for $C_{26}H_{28}N_2O_4S_2$: C, 64.60; H, 5.42; N, 5.38; S, 12.32. Found: C, 64.74; H, 5.59; N, 5.31; S, 12.26.

2,2'-Dimethyl-4,4'-(hexamethylenediimino)-bibenzyl (Ib).—A solution of 30.9 g. (0.0593 mole) of 4,4'-diphenylsulfonamido-2,2'-dimethylbibenzyl and 15.0 g. (0.0614 mole) of hexamethylene bromide in 200 ml. of dimethylformamide was added in high dilution and with stirring, over a 13-hour period, to a suspension of 150 g. (1.08 moles) of anhydrous potassium carbonate in 500 ml. of refluxing dimethylformamide. After the addition was complete, the mixture was boiled under reflux, with stirring, for an additional 8 hours, cooled, diluted with 1 l. of water and poured into 3 l. of cold water. The crude product was taken up in boiling chloroform, the solution decolorized with Norit and the solvent removed on a steam-bath. A mixture of the residue, a viscous yellow oil, with 20 g. of phenol and 150 ml. of 48% hydrobromic acid was boiled under reflux, with stirring, for 1 hour. The cyclic diamine, isolated in the usual fashion,² crystallized from ethanol as white needles, m.p. 185.5–187.5°, yield 5.05 g. (26.4%). An additional recrystallization of the compound from ethanol sharpened the melting point to 186.5–187.5°.

Anal. Calcd. for $C_{22}H_{30}N_2$: C, 81.92; H, 9.38; N, 8.70; mol. wt., 323. Found: C, 81.66; H, 9.23; N, 8.72; mol. wt. (Rast), 352.

Concentration of the mother liquor yielded no additional material having the composition of the cyclic diamine.

The diacetate of the heterocyclic compound was prepared by boiling, under reflux for 4 hours, a mixture of 0.50 g. of the diamine, 1.0 g. of anhydrous sodium acetate and 20 ml. of acetic anhydride. After the excess acetic anhydride had been hydrolyzed the mixture was poured into 300 ml. of dilute, aqueous sodium hydroxide. The product separated as an oil which solidified when chilled. A solution of the compound in boiling ethanol was decolorized with Norit, the solvent removed and the residue taken up in boiling petroleum ether (b.p. 30–60°). The diamide crystallized from the cold solution as white cubes, m.p. 126–127°, yield 0.48 g. (74%).

Anal. Calcd. for $C_{26}H_{34}N_2O_2$: C, 76.83; H, 8.43; N, 6.89. Found: C, 76.93; H, 8.51; N, 6.79.

The infrared spectrum of the product closely resembles the spectrum of *N*,3,4-trimethylacetanilide.

2,2'-Dimethyl-4,4'-(tetramethylenediimino)-bibenzyl (Ia).—A solution of 6.10 g. (0.0117 mole) of 4,4'-diphenylsulfonamido-2,2'-dimethylbibenzyl and 3.24 g. (0.0150 mole) of tetramethylene bromide in 100 ml. of dimethylformamide was added in high dilution and with stirring, over a period of 7.5 hours, to a suspension of 55.2 g. (0.40 mole) of anhydrous potassium carbonate in 500 ml. of refluxing dimethylformamide. After the addition was complete, the mixture was boiled under reflux, with stirring, for an additional 7 hours and then worked up as in the previous case. A mixture of the crude cyclic disulfonamide, a viscous, yellow oil obtained from the chloroform extract, with 5.0 g. of phenol and 75 ml. of 48% hydrobromic acid was boiled under reflux, with stirring, for 1 hour. The cyclic diamine crystallized from a methanol-water mixture as white needles, m.p. 174–176°, yield 0.19 g. (5.5%). Recrystallization of the heterocyclic compound from aqueous methanol raised the melting point to 175.5–176.5°.

Anal. Calcd. for $C_{20}H_{26}N_2$: C, 81.59; H, 8.90; N, 9.52; mol. wt., 294. Found: C, 81.70; H, 8.94; N, 9.68; mol. wt. (Rast), 318.

No other product could be isolated from the mother liquor.

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The Conformation of 2-(2,3-Dimethoxyphenyl)-cyclohexane-1,2-diol, a *cis*-Glycol

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It has been shown that hydroxylation of the double bond of 1-(2,3-dimethoxyphenyl)-cyclohexene by performic acid and by osmium tetroxide leads to the same glycol, 2-(2,3-dimethoxyphenyl)-cyclohexane-1,2-diol, presumed to be a *cis*-glycol.² It is generally believed that the performic acid and osmium tetroxide hydroxylation methods lead to *trans*- and to *cis*-glycols, respectively. Clearly, in the case under discussion one conformation is considerably more stable than the other and therefore only one glycol is isolated.

It seems reasonable to assume that in the present case, the bulkier dimethoxyphenyl group at C₂ of the cyclohexane ring and the hydroxyl group at C₁ will both assume the equatorial conformation and will thus be *trans* with respect to each other. The hydroxyl group at C₂ must necessarily adopt the polar conformation and constitute with the adjacent hydroxyl group, a *cis*-glycol system. Although both *cis*- and *trans*-2-phenylcyclohexane-1,2-diol are known, it has been shown that the

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(2) E. D. Bergmann, R. Pappo and D. Ginsburg, *J. Chem. Soc.*, 1369 (1950).

latter may be readily converted to the former. Conformational analysis of the *trans*-glycol requires the arrangement: 2-phenyl (e), 2-hydroxyl (p), 1-hydroxyl (p) while in the *cis*-glycol the following arrangement obtains: 2-phenyl (e), 2-hydroxyl (p), 1-hydroxyl (e). It is implied in the work of Beckett, Pitzer and Spitzer³ that the energy difference in similar systems between 2(p), (e) and (p), 2(e) is of the order of 1 kcal./mole. It has, indeed, been shown that the molar heat of combustion in the case of the *cis*-glycol is 1563.1 kcal. and that of the *trans*-glycol, 1564 kcal.⁴

A novel method has recently been employed by Woodward for the synthesis of *cis*-glycols⁵ based upon Winstein's work on neighboring group effects.⁶ The method involves the *trans* addition of iodine to a double bond followed by attack by silver acetate to give the *trans*-iodoacetoxy compound. The presence of water in the acetic acid used as solvent leads to the formation of the *cis*-glycol monoacetate. Finally, saponification leads to the *cis*-glycol.

When applied to 1-(2,3-dimethoxyphenyl)-cyclohexene, this method led to the same glycol obtained by the standard hydroxylation procedures. That the stable conformation in this case is, indeed, the *cis*-glycol was shown by the preparation of an acetonide using anhydrous copper sulfate as catalyst. Acetonide formation proceeds at a slow rate because one of the hydroxyl groups is tertiary, but is practically complete within 96 hours. Although cases of *trans*-glycols forming acetonides are known when mineral acid is used as catalyst⁷ due to prior rearrangement to the *cis*-glycol, no such cases have been reported when copper sulfate is used as catalyst.

Experimental

cis-2-(2,3-Dimethoxyphenyl)-cyclohexane-1,2-diol.—1-(2,3-Dimethoxyphenyl)-cyclohexene (4.77 g.) was dissolved in analytical glacial acetic acid (100 ml.) in a three-necked flask equipped with stirrer, reflux condenser and thermometer. Silver acetate (8.22 g.) was added followed by finely powdered iodine (5.85 g.) in small portions to the vigorously stirred reaction mixture over a period of 30 minutes at room temperature. During this time the temperature rose from 26 to 33°. When all the iodine had been absorbed, as indicated by the color of the mixture, aqueous acetic acid (9.85 ml. prepared by dilution of 2.0 ml. of water up to 50 ml. with glacial acetic acid) was added and the reaction mixture was heated in a boiling water-bath with vigorous stirring for 3 hours. After cooling, sodium chloride (20 g.) was added, the mixture was stirred for 30 minutes more and the insoluble precipitate was removed by filtration. The precipitate was washed with hot benzene and the combined filtrate was evaporated under reduced pressure. The residue was treated with methanol, filtered to remove a small amount of insoluble material, and to the filtrate was added a solution of potassium hydroxide (2 g.) in methanol (10 ml.). After hydrolysis had proceeded overnight, the methanol was removed under reduced pressure, water was added and the mixture was extracted with ether. Removal of the solvent and trituration of the residue with methylcyclohexane yielded 3.2 g. (56%) of *cis*-2-(2,3-dimethoxy-

phenyl)-cyclohexane-1,2-diol, m.p. 104–105°, identical with the product described by Bergmann, *et al.*²

2-(2,3-Dimethoxyphenyl)-cyclohexane-1,2-diol Acetonide.—The glycol (2 g.) was dissolved in acetone (200 ml., distilled from anhydrous potassium carbonate) and was shaken mechanically with anhydrous copper sulfate (10 g.) for 96 hours. After filtration and evaporation of the solvent under reduced pressure, the residue was dissolved in chloroform and chromatographed over alumina. The acetonide (2.1 g.) passed through the column readily and any glycol still present remained in the column. The analytical sample of the oily acetonide was prepared by heating the material in a high vacuum at 70° for 24 hours.

Anal. Calcd. for C₁₇H₂₄O₄: C, 69.83; H, 8.27. Found: C, 70.10; H, 8.16.

In the infrared spectrum, the hydroxyl band present in the glycol at 2.86 μ , was completely absent. A strong band at 9.68 μ and a band of medium intensity at 11.35 μ were present.⁸

(8) For the position of the ether bands in the infrared spectra of acetonides, see R. B. Woodward, *et al.*, THIS JOURNAL, **74**, 4241 (1952).

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Reaction of Some Metallic Oxides with Liquid Dinitrogen Tetroxide. Oxides of the First and Second Periodic Groups and Lead¹

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This is the first of a planned series of studies being undertaken at this Laboratory on the reaction of liquid dinitrogen tetroxide with various oxides. Other workers have studied reactions of the oxides CaO,² CuO and Cu₂O,^{3,4} PbO,⁴ HgO⁴ and ZnO,⁵ with gaseous or liquid N₂O₃ or N₂O₄. The oxides studied in this series are listed in Table I.

Experimental

Materials.—Pb₃O₄, PbO₂, BaO₂, BaO (71% Ba(OH)₂), Cu₂O, HgO, Hg₂O and Hg(NO₃)₂ were reagent grade chemicals. PbO, ZnO, PbO and MgO were prepared by the thermal decomposition of the respective carbonates and CaO and SrO from their oxalates. Ag₂O and CuO were prepared by precipitation from solution with NaOH, followed by drying to the oxide. N₂O₄ (cylinder) was dried before use by passing through a P₂O₅ drying tower.

Analyses.—Dinitrogen tetroxide content (as NO₂) in the reaction products was determined by cerate oxidation, as previously described.⁶ Copper and mercury determinations were done by standard electrolytic procedures. Calcium, cadmium, lead, zinc and magnesium were determined gravimetrically by ignition of the reaction product to the oxide. Water analyses were done by the standard Karl Fischer procedure.

Apparatus and Procedure.—The apparatus and experimental procedure have been described elsewhere.⁶ The reactants were heated to 87° at 14.5 atm. NO₂ pressure except for Ca(OH)₂, HgO, Hg₂O and Hg(NO₃)₂ which reacted completely at 25° and 1.1 atm. NO₂ pressure. All transfers or operations on the products were carried out in a dry-box.

(1) Presented in part at the 122nd Meeting of the American Chemical Society, September, 1952.

(2) M. Ostwald, *Ann. chim.*, (IX) **1**, 32 (1914); J. R. Partington and F. A. Williams, *J. Chem. Soc.*, **125**, 947 (1924); E. Briner, J. P. Lugin and R. Monnier, *Helv. Chim. Acta*, **13**, 64 (1930).

(3) E. Divers and T. Shimidzu, *J. Chem. Soc., Trans.*, **47**, 630 (1885); J. R. Park and J. R. Partington, *J. Chem. Soc.*, **125**, 72 (1924); J. R. Partington, *ibid.*, **125**, 663 (1924).

(4) G. Boh, *Ann. chim.*, **20**, 421 (1945).

(5) C. C. Addison, J. Lewis and R. Thompson, *J. Chem. Soc.*, 2829, 2838 (1951); C. C. Addison and J. Lewis, *ibid.*, 2833 (1951).

(6) G. Gibson and J. J. Katz, THIS JOURNAL, **73**, 5436 (1951).

(3) C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

(4) P. E. Verkade, *et al.*, *Ann.*, **467**, 217 (1928).

(5) We are indebted to Dr. R. B. Woodward for making this information available to us and for kindly assenting to its disclosure prior to his own publication of the details of the method.

(6) Cf. S. Winstein and R. E. Buckles, THIS JOURNAL, **64**, 2787 (1942).

(7) Cf. A. A. Petrov, *J. Gen. Chem. (U.S.S.R.)*, **10**, 981 (1940); C. A., **35**, 3603 (1941).