eluted with ether–methanol (4:1) and was then sublimed at 110° (0.5 mm.). The sublimate (0.77 g., 64%) was recrystallized from ether–ethyl acetate, m.p. 53.0–54.0°. A mixed melting point with an authentic sample of β-1,3-cycloheptanediol[1] was undepressed, and the infrared spectra of the two samples were identical. A portion of the glycol was converted to the bisphenylurethan, m.p. 134.5–135.0° (from cyclohexane–ethyl acetate), undepressed on admixture with an authentic sample of the bisphenylurethan of β-1,3-cycloheptanediol. The infrared spectra of the derivatives were identical.

The isopropylidene ketal was treated with 10 ml. of 90% formic acid at 100° for 2 hr. At the end of this time, 25 ml. of water was added followed by sodium hydroxide pellets (with cooling) until the mixture was alkaline. It was extracted with six 10-ml. portions of ether. Removal of the ether under reduced pressure left 0.20 g. (91%) of a viscous yellow oil. This was sublimed at 130° (1.5 mm.), and the sublimate was recrystallized from ether–cyclohexane, m.p. 57.0–58.0°, undepressed on admixture with authentic *trans*-1,2-cycloheptanediol. The infrared spectra of the two were identical. The bisphenylurethan, m.p. 213.0–214.0° (from methanol–ethyl acetate), did not depress the melting point of an authentic sample of the bisphenylurethan of *trans*-1,2-cycloheptanediol. The infrared spectra of the two were identical.

Proximity Effects. XXXI. Ring Contraction of *trans*-Cycloöctene Oxide[1]

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Received July 25, 1962

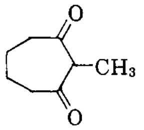
The structures of two glycols formed by ring contraction during the solvolysis of *trans*-cycloöctene oxide in formic acid have been established and confirmed by synthesis. The formation of these compounds contrasts with the absence of ring contraction in the solvolysis of *cis*-cycloöctene oxide. Possible paths leading to these glycols are considered.

The isolation of six products from the solvolysis *trans*-cycloöctene oxide in formic acid has been reported.[3] Four of these compounds were identified as *trans*-1,4-cycloöctanediol, *trans*-1,3-cycloöctanediol, 4-cycloöcten-1-ol, and hexahydro-*o*-tolualdehyde. The two remaining products, isomeric glycols A and B ($C_8H_{16}O_2$), each had one C-methyl group and each gave a negative periodate test. This paper reports the structures of glycols A and B.

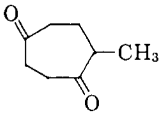
Repetition of the formolysis of *trans*-cycloöctene oxide[3] gave glycols A and B in yields of 4 and 7%, respectively. The glycols were only partially separated by chromatography on alumina, and, therefore, were converted to diacetates which were separated by gas chromatography. The infrared spectra of the glycols obtained by treating the corresponding diacetates with lithium aluminum hydride were identical to those of glycols A and B obtained previously.[3]

The carbon skeleton of the glycols was established by lithium aluminum hydride reduction of the ditosylates. A mixture of the ditosylates of A and B gave in over 90% yield only one hydrocarbon, methylcycloheptane. Thus methylcycloheptanediol structures were established for A and B.

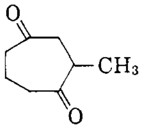
Oxidation of A and B produced the corresponding diketones, A′ and B′. Excluding the 1,2-diketones on the basis of the negative periodate test, there are six possible methylcycloheptanedione structures to be considered (I–IV). To distinguish between these possibilities, the nuclear magnetic resonance spectra of diketones A′ and B′ were obtained. The spectrum of A′ was compatible only with I. The tertiary hydrogen atom resonance appeared as a well resolved quartet centered at $\tau = 6.33$. A doublet at $\tau = 8.95$ was attributed to the methyl protons split by the single tertiary proton. Two multiplets of equal intensity corresponding to the α-methylene protons ($\tau = 7.57$) and the β-methylene protons ($\tau = 8.05$) comprised the remainder of the spectrum.



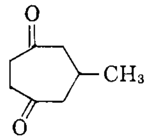
I. A′



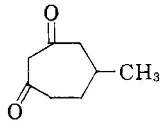
II. B′



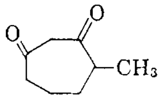
III



IV



V



VI

The n.m.r. spectrum of diketone B′ was less conclusive. However, lack of resonance below $\tau = 7.5$ excluded the 1,3-diketone structures V and VI. Structure IV also was eliminated because the intensity of the β proton signal indicated the presence of more than one β proton. The remaining possible structures, II and III, could not be differentiated on the basis of the spectrum.

Chemical evidence for the structure of glycol B was obtained by pyrolysis of the diacetate. The resulting mixture of dienes exhibited ultraviolet absorption at 248 mμ, indicating the presence of a 1,3-cycloheptadiene unsubstituted on the chromophore.[4] This suggested structure II for the diketone (B′) derived from glycol B, since the conjugated diene derived from structure III would have a methyl substituent on the chromophore.

Structures I and II for the diketones were confirmed by synthesis. The mixture of glycols obtained by the reaction of 3-hydroxycycloheptene oxide[5] (a mixture of *cis* and *trans* isomers) with methyllithium was treated with acetone and copper sulfate and the resulting mixture of isopropylidene ketal and 1,3-glycol was

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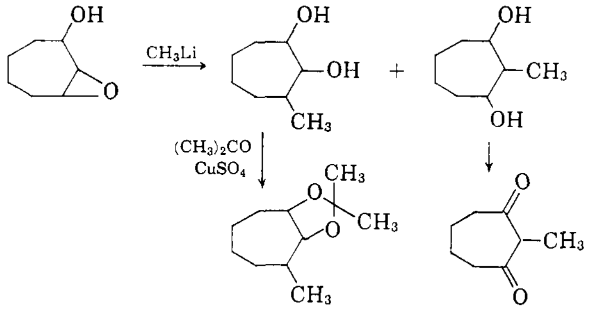
[1] Supported in part by a research grant (NSF-G5055) of the National Science Foundation. Paper XXX, A. C. Cope, S. Moon, C. H. Park, and C. L. Woo, *J. Am. Chem. Soc.*, **84**, 4865 (1962).

[2] (a) National Institutes of Health Postdoctoral Fellow, 1961–1962; (b) National Institutes of Health Predoctoral Fellow, 1960–1961.

[3] A. C. Cope, A. Fournier, Jr., and H. E. Simmons, Jr., *J. Am. Chem. Soc.*, **79**, 3905 (1957).

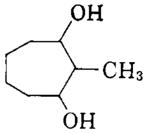
[4] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London, 1958, p. 96.

[5] A. C. Cope, T. A. Liss, and G. W. Wood, *J. Am. Chem. Soc.*, **79**, 6287 (1957).

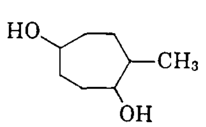


I≡A′

separated by alumina chromatography. (Both *cis*- and *trans*-1,2-cycloheptanediol are known to form isopropylidene ketals by the procedure employed.[5]) Since the 1,3-glycol was a mixture of stereoisomers (and it is probable that the glycols A and B isolated from the solvolysis of *trans*-cycloöctene oxide also were) it was oxidized to a diketone identical with that obtained by oxidation of glycol A. Therefore glycol A was established as 2-methyl-1,3-cycloheptanediol.



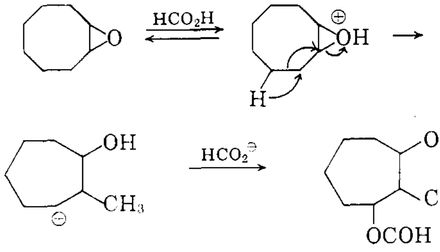
A

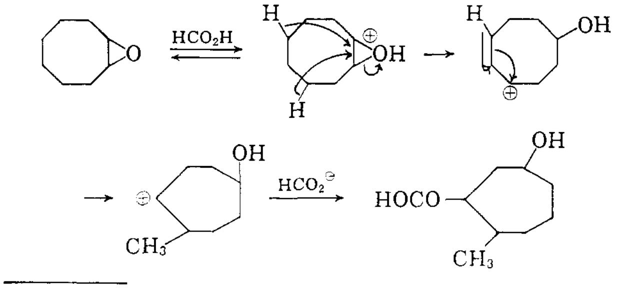


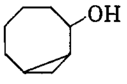
B

Diketone II, synthesized unambiguously by the aluminum chloride-catalyzed reaction of diazoethane[6] and 1,4-cyclohexanedione, proved to be identical to diketone B′. Therefore glycol B is 5-methyl-1,4-cycloheptanediol.

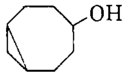
The process of formation of A during the solvolysis of *trans*-cycloöctene oxide may be viewed as a carbon migration to the initially formed electron deficient site, followed by or concerted with a 1,2-hydride shift and attack by solvent. The formation of B probably involves a 1,3- or 1,5-hydride shift[7] with subsequent or simultaneous carbon migration, 1,2-hydride shift and attack by solvent. Whether such processes are stepwise (as illustrated for simplicity) or concerted cannot be ascertained from the information at hand. The stereospecific formation of *trans*-1,4-cycloöctanediol,[3] presumably formed *via* the same hydride migration as glycol B, indicates that the opening of the epoxide ring is concerted with this transannular hydride shift. As no information is presently available regarding the stereochemistry of A and B, the nature of the ring contracting rearrangements remains equivocal. An alternative path to A and B, involving the intermediacy of bicyclo[5.1.0]octanols (VII, VIII) arising from proton elimination, is considered unlikely in view of the isolation of only two methylcycloheptanediols.







VII



VIII

In contrast to the solvolysis of *trans*-cycloöctene oxide, ring contracted products are not formed from the solvolysis of *cis*-cycloöctene oxide.[8] Explanation of the difference must await more detailed conformational information in the *cis* and *trans*-cycloöctene oxide systems, but the higher energy of the ion formed from the (strained) *trans* oxide undoubtedly is a factor.

Experimental[9]

Solvolysis of *trans*-Cycloöctene Oxide with Formic Acid.—*trans*-Cycloöctene oxide (15.1 g.) was solvolyzed with formic acid using the procedure reported previously.[3] Glycols A and B were obtained in 4 and 7% yields respectively, calculated from gas chromatograms of the diacetates.

Diacetates of Glycols A and B.—The glycols were not completely separated by chromatography on alumina and therefore were converted to a mixture of diacetates (93% yield) by treatment with acetic anhydride and pyridine at room temperature overnight. The diacetates were separated and isolated by gas chromatography using columns of silicone grease (200–220°), 1,2,3-tris-(β-cyanoethoxy)-propane (140–160°), and Viton A-HV (210–240°). Glycol A gave a liquid diacetate, $n^{25}\text{D}$ 1.4552, and glycol B gave a solid diacetate, m.p. 45–50°.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found (diacetate A): C, 63.31; H, 8.66. Found (diacetate B): C, 63.21; H, 8.64.

Treatment of each of the pure diacetates with lithium aluminum hydride gave the glycols in yields of *ca.* 90%. Infrared spectra of these glycols were identical to those obtained previously.[3]

Reduction of the Ditosylates of Glycols A and B.—A mixture of the glycols (150 mg.) was treated with 570 mg. of *p*-toluenesulfonyl chloride in 5 ml. of pyridine and gave 444 mg. (99%) of a mixture of ditosylates. This material in ether solution was treated with lithium aluminum hydride. An ether solution of the product, analyzed by gas chromatography (silicone oil, 110°) showed only one hydrocarbon peak. From 25% of the ether solution of the product, 27 mg. of hydrocarbon was collected, indicating a yield of over 90%. The infrared spectrum of the hydrocarbon was identical to that of authentic methylcycloheptane.

Pyrolysis of Diacetate B.—Diacetate B (290 mg.) in 4 ml. of pentane was pyrolyzed at 540–555° by passage in a nitrogen steam (*ca.* 6 ml. per min.) through a 50 × 12-cm. Pyrex tube packed with glass helices. The pentane solution was added dropwise during 5 min. The pyrolysate was washed with water, dried over magnesium sulfate, and analyzed by gas chromatography on a silver nitrate–tetraethylene glycol column at 75°. It contained at least 13 components. An ultraviolet absorption spectrum of the mixture in isooctane solution showed λ_{max} 248 mμ, $\epsilon = 1{,}610$.

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[6] E. Müller, M. Bauer, and W. Rundel, *Tetrahedron Letters*, **4**, 136 (1961).

[7] A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *J. Am. Chem. Soc.*, **82**, 6366 (1960).

[8] A. C. Cope, J. M. Grisar, and P. E. Peterson, *ibid.*, **81**, 1640 (1959).

[9] Melting points are corrected. Methods used for gas chromatography are those described by A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1647 (1959), footnote 24, with stationary phases as specified. Microanalyses were by Dr. S. M. Nagy and his associates.

Oxidation of Glycols A and B.—Glycol A (43 mg.) was oxidized with excess chromic acid–sulfuric acid in acetone.[10] After the dilution of the reaction mixture with water, the product was extracted with ether. Evaporation of the dried (magnesium sulfate) solution gave 26 mg. of crude diketone A′. An analytical sample was collected from a Viton A-HV column at 220°, $n^{25}\text{D}$ 1.4743. A similar oxidation of glycol B (81 mg.) afforded 28 mg. of crude diketone B′. An analytical sample, $n^{25}\text{D}$ 1.4775, was collected on the same chromatographic column.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found, A′: C, 68.45; H, 8.71. Found, B′: C, 68.72; H, 8.41.

N.m.r. Spectra of Diketones A′ and B′.[11]—Diketone A′: $\tau = 8.95$ (doublet, $J = 11$ c.p.s.), $\tau = 8.05$ (multiplet), $\tau = 7.57$ (multiplet), $\tau = 6.33$ (quartet, $J = 11$ c.p.s.). Diketone B′: $\tau = 9.00$ (doublet, $J = 3$ c.p.s.), $\tau = 8.21$ (multiplet), $\tau = 7.51$ (multiplet).

2-Methyl-1,3-cyclohexanedione (A′).—A solution of 1.97 g. of 3-hydroxycycloheptene oxide[5] in 10 ml. of ether was added dropwise with stirring in a nitrogen atmosphere to a filtered solution of methyllithium, prepared from 1.4 g. of lithium wire and 5 ml. of methyl iodide in *ca.* 100 ml. of ether. The solution was stirred at room temperature for 24 hr., then poured onto ice and extracted with four 20-ml. portions of ether. The combined extracts were washed with water until neutral and then dried (magnesium sulfate). Removal of the solvent under reduced pressure left 1.12 g. (50%) of an oil. It was dissolved in 50 ml. of acetone, 4 g. of anhydrous copper sulfate was added, and the suspension was stirred for 42 hr. at room temperature in a stoppered flask. The solids were removed by filtration and the filter cake was washed several times with acetone. Evaporation of the combined filtrates left 1.16 g. of an oil which was chromatographed on 50 g. of Woelm alumina (activity I). The isopropylidene ketal (0.87 g.) was eluted with 1:1 pentane–ether and a glycol fraction (0.21 g.) was eluted with 1:4 methanol–ether. The glycol fraction (98 mg.) was oxidized with chromic acid–sulfuric acid in acetone[10] and gave 41 mg. (43%) of a diketone mixture. Gas chromatography (Viton A-HV, 245°) showed a peak with the same retention time as diketone A′. Another peak was found to be the 1,2-diketone resulting from 1,2-glycol that had failed to form an isopropylidene ketal. Oxidation of the glycol mixture before treatment with acetone and copper sulfate gave the same compound (1,2-diketone) in a larger proportion to the 1,3-diketone. The compound with the same retention time as diketone A′ was isolated by gas chromatography; its infrared spectrum was identical to that of diketone A′.

5-Methyl-1,4-cycloheptanedione (B′).—1,4-Cyclohexanedione[12] (1.80 g.), dissolved in 160 ml. of ether to which *ca.* 20 mg. of aluminum chloride had been added, was treated at room temperature with an ethereal solution of diazoethane, generated from 5.7 g. of nitrosoethylurea and aqueous potassium hydroxide solution.[7] The solution was stirred for 4.5 hr., then washed with 30-ml. portions of 5% sodium carbonate, dilute hydrochloric acid, and 5% sodium carbonate. After drying over magnesium sulfate, the ether was evaporated, giving 0.34 g. of an oil which was shown by gas chromatography (silicone grease, 159°) to contain at least six materials. The major peak (34% of the product mixture) had a retention time identical to that of the diketone B′. Starting material (11%) also was detected. The infrared spectra of the diketone B′ derived from the *trans*-cyclooctene oxide solvolysis product and the major product, isolated by gas chromatography, were identical.

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[10] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[11] The spectra were obtained for 20% solutions in carbon tetrachloride using a Varian 4300B spectrophotometer with a 60-Mc. oscillator frequency. Tetramethylsilane was the internal standard.

[12] J. R. Vincent, A. F. Thompson, and L. I. Smith, *J. Org. Chem.*, **3**, 603 (1939).

Polynuclear Heterocycles. III. The Chlorination and Nitration of Benzo[*b*]phenazine[1]

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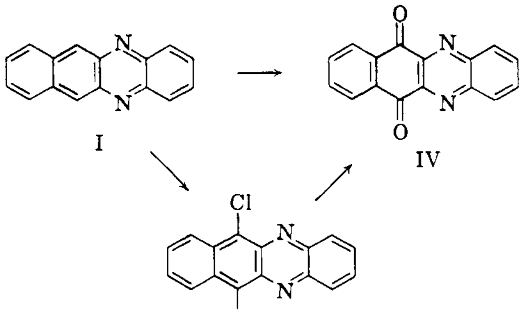
Research Laboratories, Eastman Kodak Company, Rochester, New York

Received July 26, 1962

The structures of several chlorinated and nitrated benzo[*b*]phenazines have been determined. It is shown that substitution occurs exclusively in the 6,11-positions. Benzo[*b*]phenazine-6,11-quinone, a key intermediate in the above structural determinations, has been prepared by the thermal decomposition of 2-azido-3-anilino-1,4-naphthoquinone. Under similar conditions of chlorination and nitration, dibenzo[*a,i*]phenazine gives products with substituents in the 8,13-positions.

In a previous communication,[2] it was shown that the *meso* positions of benzo[*b*]phenazine (I) are reactive toward electrophilic reagents. As an extension of this investigation, I was chlorinated[3] with sulfuryl chloride to give 6,11-dichlorobenzo[*b*]phenazine (II), m.p. 263°. Zincke and Fries[4] have described a substance (m.p. 265°) which they obtained by the condensation of 1,4-dihydro-1,1,4,4-tetrachloro-2,3-naphthoquinone with *o*-phenylenediamine and to which they assign the structure II. To elucidate the structure of our product, we made numerous attempts to repeat their work, but obtained a mixture of chlorophenazine derivatives of which the main component was a trichlorobenzo[*b*]phenazine (III) (m.p. 239°). Since this method of determining the structure failed, II was oxidized with chromic acid in acetic acid to give 6,11-benzo[*b*]phenazinequinone (IV) which was identical with the oxidation product of I. The structure of IV is proved later by an unambiguous synthesis.



Leicester[5] claimed to have obtained 6,11-benzo[*b*]phenazinequinone (IV) by heating 2-(2′-nitroanilino)-1,4-naphthoquinone (V) in a sealed tube with ammonium sulfide. However, Badger and Pettit[6] have dis-

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[1] Contribution no. 2306 from the Kodak Research Laboratories.

[2] J. A. VanAllan, R. E. Adel, and G. A. Reynolds, *J. Org. Chem.*, **27**, 2873 (1962).

[3] In place of I, the corresponding 5,12-dihydrobenzo[*b*]phenazine may be used. Oxidation of the dihydro compound gives I.

[4] T. Zincke and K. Fries, *Ann.*, **334**, 360 (1904).

[5] J. Leicester, *Ber.*, **23**, 2793 (1890).

[6] G. M. Badger and R. Pettit, *J. Chem. Soc.*, 3211 (1951).