[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Proximity Effects. IV. Reaction of Cycloöctene Dibromide with Silver Acetate[1]

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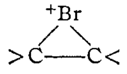
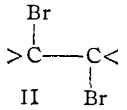
The reaction of cycloöctene dibromide with silver acetate in dry acetic acid has been shown to yield 3-cycloöcten-1-yl acetate, 4-cycloöcten-1-yl acetate, *cis*-1,4-cycloöctanediol diacetate, *trans*-1,4-cycloöctanediol diacetate and only a small amount of the expected *trans*-1,2-cycloöctanediol diacetate. The structures of the cycloöctenyl acetates have been elucidated by ozonolysis of the corresponding phenylurethans and reduction of the ozonides with sodium borohydride, followed by treatment with phenyl isocyanate to form the corresponding octanetriol tris-phenylurethans. Authentic specimens of 1,3,8- and 1,4,8-octanetriol tris-phenylurethans have been prepared for comparison. The course of the reactions leading to the abnormal products listed above is interpreted as resulting from the spatial proximity of opposite sides of the eight-membered ring.

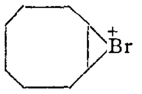
The existence of a "transannular effect" (which we also term a "proximity effect") that influences the course of the reaction between cyclic olefins with medium-sized rings and performic acid has been reported recently.[2-4] In the case of *cis*-cycloöctene this influence results in the formation of a 1,4-cycloöctanediol as well as the expected *trans*-1,2-cycloöctanediol,[2] whereas with both *cis*- and *trans*-cyclononenes and cyclodecenes only the formation of abnormal products has been reported.[3,4] This paper describes the reaction between cycloöctene dibromide and silver acetate in dry acetic acid, which also has been found to be influenced by a "proximity effect."

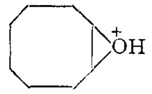
Addition of bromine to *cis*-cycloöctene has been reported to give *trans*-1,2-dibromocycloöctane (V).[5-7] The addition of bromine to simple olefins is known to proceed *via* an intermediate bromonium ion (I), which then reacts with bromide ion to yield a *trans*-1,2-dibromide (II) (or the *threo* isomer from acyclic olefins).

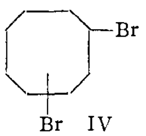

I

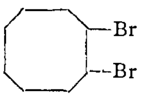

II

In the addition of bromine to *cis*-cycloöctene the similarity between the structure of the intermediate bromonium ion Ia and that of protonated *cis*-cycloöctene oxide (III) suggested that the reaction of Ia with bromide ion might give a 1,x-dibromocycloöctane (IV) as well as *trans*-1,2-dibromocyclooctane (V). Evidence concerning the structure of the dibromide was obtained by considering the products formed by treating the dibromide with dimethylamine. This reaction has been found[5,8] to yield 1-bromocycloöctene in 70–77% yield. These observations indicate that the crude dibromide obtained by the addition of bromine to *cis*-cycloöctene probably contains at least 77% of V, although the possibility exists that other dibromides (IV) could be dehydrobrominated abnormally forming 1-bromocycloöctene.


Ia


III


IV


V

The cycloöctene dibromide described above was treated with silver acetate in dry acetic acid[9] to yield a mixture of acetates, which could be separated by distillation into two fractions. The lower boiling fraction (56–58%) on redistillation afforded material which proved to be a mixture of isomers with the molecular formula $C_{10}H_{16}O_2$. The infrared absorption spectrum of this material contained bands indicative of an isolated ethylenic linkage (3000 and 1620 cm.$^{-1}$) and of an acetoxyl group (1725 and 1200 cm.$^{-1}$) and showed that it was different from the isomeric 2-cycloöcten-1-yl acetate[10] and 1-cycloöcten-1-yl acetate. A specimen of the latter compound was prepared from cycloöctanone and isopropenyl acetate.[11] Saponification of the mixture of acetates gave the corresponding unsaturated alcohols ($C_8H_{14}O$), which on hydrogenation over a platinum catalyst absorbed one mole of hydrogen and formed cycloöctanol, characterized as the phenylurethan. These results established the fact that the unsaturated alcohol fraction was 3-cycloöcten-1-ol (VI) or 4-cycloöcten-1-ol (VII) or a mixture of VI and VII.

The unsaturated alcohol fraction gave a mixture of phenylurethans, which was partially separated by chromatography over alumina into 3-cycloöcten-1-yl phenylurethan (IX), m.p. 101.5–102.5°, and a phenylurethan with m.p. 73–74° that is shown in the following paper to be a mixture of the isomers IX and X. The structures of the phenylurethans IX and XI and the presence of X in the mixture with m.p. 73–74° were proved by ozonolysis, followed by reduction of the ozonides to give (after treatment with phenyl isocyanate) the corresponding *n*-octanetriol tris-phenylurethans XII, XIII and XIV. Some trial ozonizations with XI

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[1] Supported by a research grant (NSF-G990) of the National Science Foundation. Presented at the Fourteenth National Organic Chemistry Symposium, Lafayette, Ind., June 14, 1955.

[2] A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952).

[3] V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952).

[4] V. Prelog, K. Schenker and W. Kung, *ibid.*, **36**, 471 (1953).

[5] E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, THIS JOURNAL, **61**, 1057 (1939).

[6] M. W. Lister, *ibid.*, **63**, 143 (1941).

[7] R. Willstätter and E. Waser, *Ber.*, **43**, 1176 (1910).

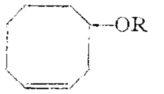
[8] A. C. Cope and M. Brown, unpublished observation.

[9] Conditions employed in a similar case by S. Winstein and R. E. Buckles, THIS JOURNAL, **64**, 2780 (1942).

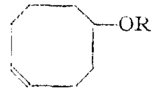
[10] A. C. Cope, M. R. Kinter and R. T. Keller, *ibid.*, **76**, 2757 (1954).

[11] Conditions employed in a similar case by H. J. Hagemeyer and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

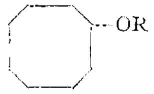
indicated that the ozonide was very unstable, decomposing before it could be reduced to the corresponding triol monophenylurethan by a catalytic hydrogenation procedure. It was found that when a solution of ozone in ethyl acetate at −70°[12]



VI, R = H
IX, R = $\mathrm{OCNHC_6H_5}$



VII, R = H
X, R = $\mathrm{OCNHC_6H_5}$



VIII, R = H
XI, R = $\mathrm{OCNHC_6H_5}$

$\mathrm{RO(CH_2)_5CH(OR)(CH_2)_2OR}$
XII, R = $\mathrm{OCNHC_6H_5}$

$\mathrm{RO(CH_2)_4CH(OR)(CH_2)_3OR}$
XIII, R = $\mathrm{OCNHC_6H_5}$

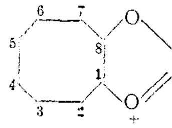
$\mathrm{RO(CH_2)_5CH(OR)CH_2OR}$
XIV, R = $\mathrm{OCNHC_6H_5}$

was added to a solution of XI in ethyl acetate at −70° until a faint blue color persisted, followed by the immediate addition of an excess of sodium borohydride dissolved in methanol, that XIV could be isolated after treatment with phenyl isocyanate in 90% yield.

In a similar manner IX and the mixture melting at 73–74° that contained X were ozonized, reduced and treated with phenyl isocyanate to give XII and XIII, respectively. It was found that the higher melting phenylurethan corresponded to IX and that it was identical with the phenylurethan prepared from the mixture of cyclooctenols formed in the solvolysis of *cis*-cyclooctene oxide.[13] The identities of XII and XIII were established by a comparison of their melting points and infrared absorption spectra with those of authentic specimens described below.

The physical properties and infrared absorption spectrum of the high boiling fraction (23%) from the reaction of cyclooctene dibromide with silver acetate indicated that it was a mixture of cyclooctanediol diacetates. Hydrolysis of this fraction gave a mixture of the corresponding diols. It was possible to separate all of the 1,2-cyclooctanediol from the diol mixture as the isopropylidene ketal, formed by treating the mixture with acetone and anhydrous cupric sulfate.[14] Chromatography of the resultant mixture separated the less polar isopropylidene ketal from the more polar, and hence more strongly absorbed, cyclooctanediols. This chromatographic procedure for the separation of isopropylidene ketals from glycols has been found to be more convenient than the previous method which involved distillation[2] and has been used throughout this work. The isopropylidene ketal obtained in this way was shown to be derived from *trans*-1,2-cyclooctanediol by comparison of boiling point, index of refraction and infrared absorption spectrum with data for an authentic specimen. Solvolysis of the isopropylidene ketal with formic acid, followed by hydrolysis of the monoformate which was formed, gave *trans*-1,2-cyclooctanediol in 10% yield from the crude diol mixture (2.3% from cyclooctene dibromide). This compound was further characterized by conversion to the bis-*p*-nitrobenzoate. After removal of all of the *trans*-1,2-cyclooctanediol from the crude diol mixture, the residue was chromatographed over alumina and thereby separated into four main fractions. The first fraction (36%, or 8.3% from cyclooctene dibromide) on crystallization from ethyl acetate yielded a material with m.p. 90–91°, which depressed the melting point of the known *cis*-1,4-cyclooctanediol. Elemental analysis and conversion to a bis-phenylurethan indicated that this material was a cyclooctanediol. The diol was identified as *trans*-1,4-cyclooctanediol by preparation of the bis-*p*-nitrobenzoate.[15] Continued development of the chromatogram yielded an intermediate fraction (20%, 4.6% based on cyclooctene dibromide) followed by pure *cis*-1,4-cyclooctanediol (10%, 2.3% based on cyclooctene dibromide), which was further characterized as the bis-*p*-nitrobenzoate. Further development of the chromatogram gave a more polar fraction (17%, 3.9% based on cyclooctene dibromide), which could not be induced to crystallize and has not been identified.

It is of interest that only a 2.3% yield of the "normal" product of reaction of cyclooctene dibromide and silver acetate (*trans*-1,2-cyclooctanediol diacetate) could be isolated while larger amounts of the "abnormal" products, acetates of VI and VII and diacetates of *cis*- and *trans*-1,4-cyclooctanediols, were isolated. Since as previously noted the cyclooctene dibromide employed probably contained at least 77% of *trans*-1,2-dibromocyclooctane (V), most or all of these abnormal products are believed to be formed in the reaction of V with silver acetate. Winstein and Buckles[9] have shown that *trans*- or *threo*-1,2-dibromo compounds react with silver acetate *via* a cyclic acetoxonium ion. In this case the intermediate may be represented by XVII. This intermediate has a structure somewhat similar to the protonated epoxide III, which is an intermediate in the "abnormal" hydroxylation of *cis*-cyclooctene. XVII would be expected to



XVII

undergo a normal displacement reaction with acetate ion forming a *trans*-1,2-diacetate. It is suggested, however, that because of the steric hindrance at C_1, which retards the approach of acetate ion, a transannular hydride shift from C_3 or C_5 to C_1 occurs with concomitant attack by an acetate ion at the relatively unhindered C_3- or C_5-position, forming both stereoisomeric 1,4-cyclooctanediol diacetates. As in the case of *cis*-cyclooctene oxide,[2] it is thought that a 1,3(or 1,5)-hydride shift will be particularly facile because of the close spatial

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(12) P. Bladon, H. B. Henbest, E. R. H. Jones, G. W. Wood and G. F. Woods, *J. Chem. Soc.*, 4890 (1952).

(13) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, THIS JOURNAL, **79**, 3900 (1957).

(14) C. Niemann and C. D. Wagner, *J. Org. Chem.*, **7**, 230 (1942).

(15) A. C. Cope, A. Fournier, Jr., and H. E. Simmons, Jr., THIS JOURNAL, **79**, 3905 (1957).

proximity of the transannular hydrogen atoms. The loss of a proton from C_2, C_4 or C_6 instead of attack by acetate ion at C_3 or C_5 would give rise to the 3- and 4-cycloöcten-1-yl acetates.

Authentic specimens of the *n*-octanetriol *tris*-phenylurethans obtained from the ozonolysis of IX and X were prepared by the following methods.

Lithium aluminum hydride reduction of dimethyl 4-ketosuberate[16] gave 1,4,8-octanetriol, which on treatment with phenyl isocyanate gave XIII identical with the product obtained from X.

Condensation of the magnesium derivative of diethyl malonate with δ-carbethoxyvaleryl chloride gave after hydrolysis the substituted malonic ester XV. This compound when heated with a catalytic amount of 2-naphthalenesulfonic acid[17] at 200–220° for 7 hr. decomposed to give diethyl 3-ketosuberate (XVI).

$EtOOC(CH_2)_4COCH(COOEt)_2$ XV

$EtOOC(CH_2)_4COCH_2COOEt$ XVI

Since the reduction of β-ketoesters with lithium aluminum hydride sometimes gives anomalous results,[18] the carbonyl group in XVI was first reduced with sodium borohydride. The resulting hydroxyester on reduction with lithium aluminum hydride gave 1,3,8-octanetriol, which on treatment with phenyl isocyanate gave XII identical with the product obtained from IX.

Experimental[19,20]

Cycloöctene Dibromide.—A solution of bromine (32 g., 10.9 ml.) in carbon tetrachloride (100 ml.) was added dropwise, with stirring. to a solution of *cis*-cycloöctene (22 g.) in carbon tetrachloride (50 ml.). The internal temperature was maintained between 0–5° during the course of the addition with an external ice–salt cooling bath. The reaction mixture was kept at room temperature for either 1 hr. or overnight, after which the solvent was removed under reduced pressure below 30°. The residue on distillation afforded cycloöctene dibromide (43.5 g., 80%), b.p. 70° (0.15 mm.), $n^{25}D$ 1.5526.

Reaction of Cycloöctene Dibromide with Silver Acetate.—A suspension of silver acetate (44 g.) in glacial acetic acid (100 ml.) and acetic anhydride (5 ml.) was heated at 110° in an oil-bath, with stirring and exclusion of atmospheric moisture for 90 minutes. Cycloöctene dibromide (27 g.) was added dropwise to the foregoing suspension, and the stirring and heating were continued for 14 hr. The reaction mixture was then cooled, diluted with ether and filtered. The organic extract was washed with seven 150-ml. portions of water, with sodium bicarbonate solution until acid free and finally with water. After drying over anhydrous magnesium sulfate, the ether was removed on a steam-bath. The residue on distillation afforded a low boiling fraction (A) (9.8 g., 58%), b.p. 62–65° (0.1 mm.), $n^{25}D$ 1.4694–1.4720, and a high boiling residue (B) (5.2 g., 23%). In three similar experiments the yields of A were 56, 56 and 58%, while the yields of B were 24, 23 and 24%.

Fraction A.—Fractional distillation of A through a semimicro column[21] yielded a mixture of isomeric cycloöctenyl acetates, b.p. 50° (0.14 mm.), $n^{25}D$ 1.4691.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.20; H, 9.71.

Hydrolysis of Fraction A.—Fraction A (15.8 g.) in methanol (220 ml.) was heated under gentle reflux for 1 hour with a solution of sodium hydroxide (20 g.) in water (25 ml.). After removal of the bulk of the methanol under reduced pressure, the residue was diluted with water (150 ml.) and extracted with six 75-ml. portions of ether. After drying the extract with magnesium sulfate, the ether was removed on a steam-bath. The residue (10.96 g., 87%) was distilled through a column with a spinning band (30 × 0.8-cm.) to give five fractions, b.p. 69–69.2° (3.00 mm.), $n^{27.5}D$ 1.4958–1.4965. Fraction 3 ($n^{25}D$ 1.4960) was submitted for analysis.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.36; H, 11.26.

Hydrogenation of a sample of the unsaturated alcohol (252 mg.) in acetic acid (17 ml.) in the presence of 200 mg. of prereduced platinum oxide was complete after the absorption of 102% of one molar equivalent of hydrogen in 1 hr. The reduction product was identified as cycloöctanol by conversion to the phenylurethan, m.p. 56–58°, which was undepressed on admixture with an authentic specimen.

Phenylurethans of the Alcohols Obtained from Fraction A.—The mixture of alcohols (500 mg.) was warmed on a steam-bath with phenyl isocyanate (650 mg.) in a sealed flask for 5–10 minutes. After keeping at room temperature overnight the excess phenyl isocyanate was removed under reduced pressure (50° at 0.01 mm.) to give the phenylurethans as a white solid (1.0 g.). The foregoing solid was dissolved in benzene and passed onto a column of alumina (120 g. of Grade "H"). Elution with benzene:ether (9:1) and benzene:ether (3:1) mixtures afforded a series of crystalline fractions. The early fractions were combined and crystallized from aqueous methanol to give 140 mg. of a mixture (see following paper), m.p. 73–74°, containing the phenylurethans IX and X.

Anal. Calcd. for $C_{15}H_{19}O_2N$: C, 73.43; H, 7.81. Found: C, 73.21; H, 7.76.

The last fractions from the chromatograms were combined and recrystallized from aqueous methanol to give 3-cycloocten-1-yl phenylurethan (IX) (140 mg.), m.p. 101.5–102.5°.

Anal. Calcd. for $C_{15}H_{19}O_2N$: C, 73.43; H, 7.81. Found: C, 73.17; H, 7.68.

Ozonolysis of 2-Cycloöcten-1-yl Phenylurethan.—A saturated solution of ozone in ethyl acetate at −70° was added dropwise with swirling to a solution of the phenylurethan (200 mg.) in ethyl acetate (15 ml.) at −70° until a faint blue color persisted. A solution of sodium borohydride (0.5 g.) in methanol (15 ml.) was then added in one portion and the solution was allowed to warm to room temperature. After 2 hr. it was poured into dilute hydrochloric acid and extracted with ether. Removal of the ether gave a gum (220 mg.), which on treatment with phenyl isocyanate gave 1,2,8-octanetriol tris-phenylurethan (390 mg., 92%), m.p. 122–124°. An analytical sample that was crystallized from aqueous methanol had m.p. 134.5–135.5°.

Anal. Calcd. for $C_{29}H_{33}O_6N_3$: C, 67.02; H, 6.40. Found: C, 67.10; H, 6.14.

Treatment of 3-cycloöcten-1-yl phenylurethan in a similar manner gave 1,3,8-octanetriol tris-phenylurethan, m.p. 143.5–145° (from aqueous methanol).

Anal. Calcd. for $C_{29}H_{33}O_6N_3$: C, 67.02; H, 6.40. Found: C, 67.06; H, 6.55.

Treatment of the mixture of phenylurethans, m.p. 73–74° (see the following paper), in a similar manner gave 1,4,8-octanetriol tris-phenylurethan, m.p. 127–128° (from aqueous methanol), proving that it contained X. Neither of the above tris-phenylurethans depressed the melting points of the corresponding authentic specimens (see below). The mixed melting points of mixtures of *n*-octanetriol tris-phenylurethans are: 1,2,8 and 1,3,8, mixed m.p. 118–122°; 1,2,8 and 1,4,8, mixed m.p. 115–118°; 1,3,8 and 1,4,8, mixed m.p. 113–117°.

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[16] A. C. Cope and W. R. Schmitz, This Journal, **72**, 3059 (1950).

[17] B. Riegel and W. M. Lilienfeld, *ibid.*, **67**, 1273 (1945).

[18] A. S. Dreiding and J. A. Hartman, *ibid.*, **75**, 939 (1953).

[19] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

[20] Unless stated otherwise, the alumina used for chromatography was supplied by Merck and Co., Inc. It was first neutralized and deactivated by treating with ethyl acetate and methanol and then reactivated by heating under reduced pressure before use. The "Grades" used in defining the activity of the alumina are those given by H. Brockmann and H. Schodder, *Ber.*, **74**, 73 (1941). Grade "H" alumina was supplied by Peter Spence and Sons (Widnes, England) and was used directly. It had activity Grade I–II on the above scale.

[21] C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

1,4,8-Octanetriol Tris-phenylurethan.—An excess of diazomethane in ether was added with gentle swirling to a suspension of 4-ketosuberic acid[16] (850 mg.) in ether. After the vigorous reaction had subsided, the solvent was removed under reduced pressure to give the corresponding dimethyl ester as an oil (980 mg.). The foregoing ester was dissolved in anhydrous ether (50 ml.) and added to a solution of lithium aluminum hydride (600 mg.) in dry ether (100 ml.). The solution was heated under gentle reflux for 2 hr., after which the excess lithium aluminum hydride was decomposed with ethyl acetate. Dilute sulfuric acid was added to dissolve the inorganic salts, and the reaction mixture was then extracted continuously with chloroform for 5 days to give 1,4,8-octanetriol as a viscous gum. The foregoing triol (330 mg.) was treated with phenyl isocyanate as described before to give a gum (950 mg.), which crystallized with difficulty from aqueous methanol to give 1,4,8-octanetriol tris-phenylurethan, m.p. 127.5–128.5°.

Anal. Calcd. for $C_{29}H_{33}O_6N_3$: C, 67.02; H, 6.40. Found: C, 66.71; H, 6.44.

Diethyl 3-Ketosuberate.—Diethyl malonate (16.2 g.), absolute ethanol (10.5 ml.), dry ether (30 ml.), carbon tetrachloride (0.1 ml.) and clean magnesium turnings (2.5 g.) were heated under gentle reflux with stirring for 3 hr. The reaction mixture was protected from atmospheric moisture with calcium chloride tubes. To the above mixture was added a solution of δ-carbethoxyvaleryl chloride (21 g.) in dry ether (50 ml.) at such a rate that the ether boiled gently. The mixture was then stirred and heated under gentle reflux for 1 hr. Sulfuric acid (40 ml. of 10% by volume) was added slowly with stirring after which the mixture was extracted with ether. Removal of the ether, after drying over magnesium sulfate, gave a residue (34 g.), which was heated with 2-naphthalenesulfonic acid (1.5 g.) in an oil-bath at 190–200° for 4 hr. and at 220° for 3.5 hr., by which time the evolution of carbon dioxide had ceased. The reaction mixture was cooled, diluted with ether and washed with saturated sodium bicarbonate solution. Removal of the ether gave a dark residue, which was flash distilled to give 20.2 g. of a colorless distillate, b.p. 45–140° (0.5 mm.). Fractionation gave substantially pure diethyl 3-ketosuberate (11.1 g., 45%). A sample redistilled for analysis had b.p. 118° (0.55 mm.), n^{25}D 1.4480.

Anal. Calcd. for $C_{12}H_{20}O_5$: C, 58.99; H, 8.25. Found: C, 59.31; H, 8.26.

1,3,8-Octanetriol Tris-phenylurethan.—Diethyl 3-ketosuberate (1.25 g.) was dissolved in methanol (10 ml.) and added dropwise to a stirred solution of sodium borohydride (0.5 g.) in methanol (35 ml.) containing one drop of 3 *N* sodium hydroxide solution. The mixture was stirred at room temperature for 45 minutes and then acidified with dilute hydrochloric acid and extracted with ether. The dried ether extract was concentrated under reduced pressure at room temperature and then dissolved in anhydrous ether and added to a solution of lithium aluminum hydride (1.0 g.) in dry ether (50 ml.). The mixture was stirred and heated under gentle reflux for 1 hr. After the excess reagent had been decomposed with ethyl acetate, the reaction mixture was acidified with hydrochloric acid, the ether removed under reduced pressure and the residue extracted continuously with chloroform for 36 hr. to give 1,3,8-octanetriol as a viscous gum (1.1 g.). Treatment of the foregoing triol (300 mg.) with phenyl isocyanate afforded (after crystallizing from aqueous methanol) 1,3,8-octanetriol tris-phenylurethan, m.p. 142.5–144.5°.

Hydrolysis of Fraction B.—Fraction B (7.75 g.) in methanol (200 ml.) was heated under gentle reflux for 1 hr. with a solution of sodium hydroxide (20 g.) in water (25 ml.). After removal of the bulk of the methanol under reduced pressure, the residue was diluted with water (75 ml.) and then extracted continuously with chloroform overnight to give a mixture of diols (4.8 g.). The foregoing diols were dissolved in acetone (150 ml.) and stirred overnight in a stoppered flask with anhydrous cupric sulfate (12 g.). After removal of the cupric sulfate and the acetone the residue was dissolved in benzene and passed onto a column of alumina (100 g., Grade III). Elution with benzene afforded *trans*-1,2-cycloöctanediol isopropylidene ketal (700 mg.), b.p. 109° (22 mm.), n^{25}D 1.4585. Elution with ether: methanol (3:1) afforded a mixture of cycloöctanediols (4.12 g.). The foregoing *trans*-1,2-cycloöctanediol isopropylidene ketal (700 mg.) was dissolved in 88% formic acid (20 ml.) and heated on a steam-bath for 2 hr. After removal of the bulk of the formic acid under reduced pressure, the residue was dissolved in methanol (50 ml.) and heated under gentle reflux with a solution of sodium hydroxide (8 g.) in water (15 ml.) for 30 minutes. After removal of the methanol under reduced pressure, the residue was diluted with water (30 ml.) and then extracted continuously with chloroform for 18 hr. Removal of the chloroform gave *trans*-1,2-cycloöctanediol (480 mg.) as a sirup. The bis-*p*-nitrobenzoate formed short needles from ethyl acetate:methanol with m.p. 105–106°, which was undepressed on admixture with an authentic specimen.

The mixture of cycloöctanediols (4.14 g.) after removal of all of the *trans*-1,2-cycloöctanediol as the isopropylidene ketal was dissolved in the minimum amount of chloroform and passed onto a column of alumina (350 g., Grade III). Elution with ether:methanol (1600 ml., 99:1) gave *trans*-1,4-cycloöctanediol (1.6 g.), which after crystallizing from ethyl acetate had m.p. 90–91°.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.18. Found: C, 66.45; H, 10.94.

The foregoing diol gave a bis-*p*-nitrobenzoate, which after crystallizing from ethyl acetate:methanol formed needles, m.p. 156–156.6°, undepressed on admixture with an authentic specimen.[15] Treatment of the diol with phenyl isocyanate in the manner described for the alcohols obtained from fraction A afforded (after crystallizing from ethyl acetate) *trans*-1,4-cycloöctanediol bis-phenylurethan, m.p. 180.2–181.7°.

Anal. Calcd. for $C_{22}H_{26}O_4N_2$: C, 69.09; H, 6.85. Found: C, 69.16; H, 6.95.

Continued elution with the same solvent mixture gave an intermediate fraction (960 mg.), m.p. 70–78°. Elution with ether:methanol (98:2) gave *cis*-1,4-cycloöctanediol (450 mg.), m.p. 82–83°, which was undepressed on admixture with an authentic specimen. Elution with ether:methanol (3:1) afforded a more polar material (820 mg.) which has not been identified.

1-Cycloöcten-1-yl Acetate.—Cycloöctanone (2.52 g.), isopropenyl acetate (4.0 g.) and *p*-toluenesulfonic acid (50 mg.) were heated together at a bath temperature of 95° for 3 hr. Acetone (0.7 ml.) was removed through a semimicro column. The reaction mixture was poured into water and extracted with ether. After removal of the ether, the residue was fractionated under reduced pressure to yield the enol acetate, b.p. 50° (0.15 mm.), n^{25}D 1.4697.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.52; H, 9.60.

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