ml. of absolute ethanol and the insoluble residue (1.9 g.) filtered off. The residue contained 0.57 g. (0.0097 mole) of sodium chloride, as determined by the chloride analysis. The alcoholic extract was taken to dryness and the syrupy residue dissolved in 17 ml. of water. This aqueous solution showed an ultraviolet absorption spectrum different from the starting pyrimidine and different from 2,4-diamino-6-hydroxypyrimidine. This solution was used directly for the next step.

Ultraviolet absorption spectrum of XXIV (at a dilution of 1:1000): At *p*H 1, λ_{max} 276 mμ, O.D. 0.99. At *p*H 11, λ_{max} 275 mμ, O.D. 0.75.

Spectrum of 6-chloro-2,4-diaminopyrimidine: At *p*H 1, λ_{max} 298 mμ. At *p*H 11, λ_{max} 282 mμ.

6-Carbethoxymethoxy-5-*p*-chlorobenzeneazo-2,4-diaminopyrimidine (XXV).—To the above aqueous solution was added a *p*-chlorobenzenediazonium chloride solution (prepared from 220 mg. of *p*-chloroaniline and 125 mg. of sodium nitrite) and 2 g. of sodium bicarbonate. The mixture was kept at 0° overnight and the bright yellow precipitate collected, washed with water and dried in a vacuum desiccator (230 mg.). A portion of this azo compound was purified by solution in 8 ml. of absolute ethanol at room temperature, filtration and dilution with 6 ml. of water.

Anal. Calcd. for $C_{14}H_{15}N_6O_3Cl$: C, 48.2; H, 4.3; N, 24.1. Found: C, 47.8; H, 3.8; N, 24.6.

2,4-Diamino-6-hydroxy-*p*-oxazino(2,3-d)pyrimidine (VII).—A boiling solution of 100 mg. of the crude azo compound (XXV) in 20 ml. of 50% aqueous ethanol was treated with 500 mg. of zinc dust and 2 ml. of 2 *N* hydrochloric acid. After boiling for five minutes, the solution was filtered. A small aliquot of this solution was examined spectrophotometrically. At *p*H 1 the spectrum closely resembled that of XIX[1]; at *p*H 11, that of "β-dihydroxanthopterin." Reacidification of the alkaline solution showed that the spectrum in acid solution now corresponded to that of "β-dihydroxanthopterin," indicating that ring closure had occurred in alkaline solution.

The reaction mixture was made alkaline with 3 ml. of 2 *N* sodium hydroxide, a slight precipitate filtered off and the solution acidified to *p*H 5 with acetic acid. After chilling, the precipitate was centrifuged off, washed with water, alcohol and ether and dried in a vacuum desiccator (23 mg.). After recrystallization from water, from which it crystallized very slowly, the compound was found to be identical in all respects with "β-dihydroxanthopterin."

Anal. Calcd. for $C_6H_7N_5O_2$: C, 39.7; H, 3.9. Found: C, 39.4; H, 4.0.

Ultraviolet absorption spectrum: At *p*H 1, λ_{max} 263, 312 mμ, E_m 13,200, 8800; λ_{min} 290 mμ. At *p*H 11, λ_{max} 275 mμ, E_m 13,700.

Ultraviolet Absorption Spectra.—The spectra were measured with a Beckman spectrophotometer, model DU, using solutions containing 10 mg. per liter. For solutions of *p*H 1, 0.1 *N* hydrochloric acid was used; for *p*H 11, a glycine-sodium hydroxide buffer.

Acknowledgment.—We are indebted to Samuel W. Blackman and Nicholas Martinez, Jr., for the microanalyses reported here.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, BUCKNELL UNIVERSITY]

The Dehydration of Some Glycols Derived from 1-Cyclohexyl-1-phenylethane[1]

BY CHARLES A. RUSSELL,[2] LUTHER T. STROUP AND JAMES ENGLISH, JR.

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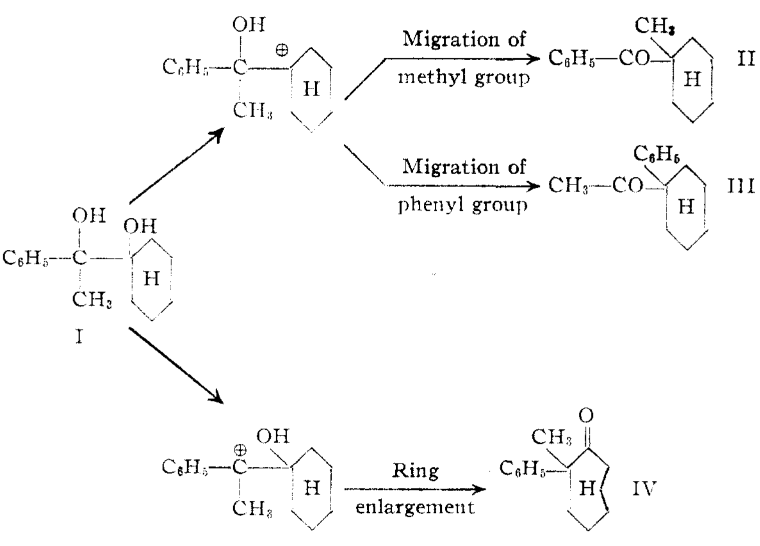
1-(Cyclohexanol-1)-phenylethanol and 1-cyclohexyl-1-phenyl-1,2-ethanediol have been prepared by the performic acid hydroxylation of the corresponding olefins. It was found that the dehydration of cyclohexylphenylmethylcarbinol gave a mixture of α-cyclohexylidene-ethylbenzene and α-cyclohexylstyrene. The dehydration of the glycols showed no abnormalities due to the steric hindrances of the cyclohexyl and phenyl groups.

In connection with earlier studies[3] on glycol rearrangements, it was felt of interest to investigate the rearrangement of 1-(cyclohexanol-1)-1-phenylethanol (I), an open chain analog of the glycols studied in the tetralin and decalin series.[3,4] Depending on which hydroxyl group was removed first, three products were considered possible.

The glycol (I) was prepared by the hydroxylation of α-cyclohexylidene-ethylbenzene (V). Although it has been reported[5] that the dehydration of cyclohexylmethylphenylcarbinol gave (V), we found upon ozonolysis of the resulting hydrocarbon that the product was a mixture of about 10% α-cyclohexylidene-ethylbenzene (V) and 90% α-cyclohexylstyrene (VI). No ozonolysis products were found which would indicate that the double bond had migrated out of conjugation into the cyclohexane ring.



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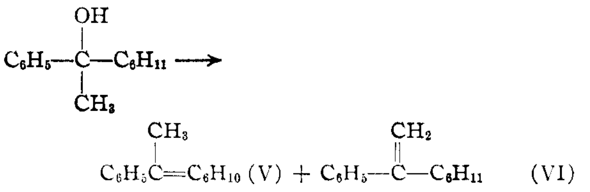
[1] This paper is based in part on the thesis presented by Charles A. Russell to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, and in part on the thesis submitted by Luther T. Stroup to the faculty of Bucknell University in partial fulfillment of the requirements for the degree of Master of Science.

[2] Department of Chemistry, Bucknell University.

[3] J. English and G. Cavaglieri, THIS JOURNAL, **65**, 1085 (1943).

[4] G. Cavaglieri, Ph.D. Thesis, Yale University, 1942.

[5] E. D. Venus-Danilova and I. A. Bol'shukin, *J. Gen. Chem.* (*U.S.S.R.*), **12** 73 (1942).

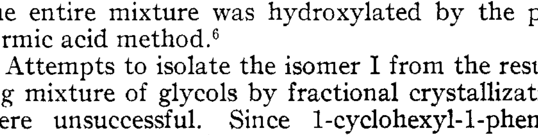


$$C_6H_5\text{—}\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle OH}{|}}{C}}\text{—}C_6H_{11} \longrightarrow C_6H_5\overset{\overset{\textstyle CH_3}{|}}{C}{=}C_6H_{10}\ (V) + C_6H_5\text{—}\overset{\overset{\textstyle CH_2}{\|}}{C}\text{—}C_6H_{11}\quad (VI)$$

Since the two olefins could not be separated readily by fractionation under reduced pressure, the entire mixture was hydroxylated by the performic acid method.[6]

Attempts to isolate the isomer I from the resulting mixture of glycols by fractional crystallization were unsuccessful. Since 1-cyclohexyl-1-phenyl-1,2-ethanediol (VII) contains a primary hydroxyl group while I does not, a separation by means of the selective formation of phthalate half esters[7] was tried. The glycols were readily separated and recovered in about the same ratio as that of the corresponding olefins. The structure of each glycol was confirmed by lead tetraacetate cleavage.

The dehydration of 1-(cyclohexanol-1)-1-phenylethanol (I) gave a ketone which gave no iodoform test, although the melting point of the oxime was that reported by Sackur[8] for the oxime of 1-phenylcyclohexyl methyl ketone (III). It was found that the ketone prepared by Sackur's procedure also gave no iodoform test. Since one of the steps in Sackur's synthesis was the rearrangement of a Grignard complex and undoubtedly involves the same type of reaction intermediate as in the rearrangement of the diol, I, either 1-methylcyclohexyl phenyl ketone (II) or 1-phenylcyclohexyl methyl ketone (III) could have been formed in this case also.



Because of the lack of an iodoform test, it was decided to prepare (II) by a method not involving a rearrangement and see whether this compound was different from, or corresponded to, Sackur's ketone. We first attempted to prepare (II) by the reaction between benzonitrile and 1-methylcyclohexylmagnesium chloride. The only product isolated from the reaction mixture, however, was the cyclic trimer of benzonitrile, cyaphenine.[9] A more successful procedure was the oxidation of 1-methylcyclohexylphenylcarbinol prepared by the action of 1-methylcyclohexylmagnesium chloride of benzaldehyde. A considerable amount of benzyl alcohol was formed by the reduction of the aldehyde in the latter step. Although 1-methylcyclohexyl phenyl ketone (II) would not crystallize, the oxime and 2,4-dinitrophenylhydrazone were prepared and were found different from the corresponding derivatives of Sackur's ketone.

Inasmuch as it is the halogen which is lost from halohydrins in basic media,[10] the possibility of ring enlargement may be eliminated, and the structure given by Sackur for his product appears to be correct. Fuson and Bull[11] report that methyl ketones which have the CH_3–CO– group attached to a group having a large amount of steric hindrance frequently fail to give an iodoform test. This would explain the failure of the iodoform test in this case.

Although the sample of the oxime of the rearrangement product of 1-(cyclohexanol-1)-1-phenylethanol (I) was inadvertently lost before a mixed melting point with the oxime of 1-phenylcyclohexyl methyl ketone (III) could be made the close correspondence of their melting points and the nine-degree higher melting point of the oxime of II indicate that the major product of the rearrangement of I was III. It would seem, therefore, that the phenyl group in I is not as effective as might be expected in facilitating the release of the adjacent hydroxyl group, and that the steric effects in the molecule are not important enough to prevent the phenyl group migrating to the cyclohexyl ring at its point of attachment to the remainder of the molecule.

Dehydration of the primary-tertiary diol, 1-cyclohexyl-1-phenyl-1,2-ethanediol (VII) with 30% sulfuric acid at 100° resulted in the formation of a colorless solid having the empirical formula $C_{14}H_{18}O$. The structure of this compound has not been established, although it appears to contain no carbonyl group. Somewhat more drastic conditions, using 50% sulfuric acid at reflux temperature, gave an aldehyde indicating that, in all probability, the tertiary hydroxyl group was cleaved giving rise to α-cyclohexylphenylacetaldehyde.

Experimental[12]

α-Cyclohexylidene-ethylbenzene (V) and α-Cyclohexylstyrene (VI).—A mixture of 305 g. (1.5 moles) of crude cyclohexylmethylphenylcarbinol, prepared as previously described,[13] and 300 g. of ground, fused potassium bisulfate was heated for eight hours at 130–140°. The product was extracted with ether and washed free of acid with sodium bicarbonate.

After drying the ether solution over calcium chloride the ether was removed and the product fractionated under vacuum. A total of 98.0 g. (35%) of a colorless liquid was obtained; b.p. 92° (2 mm.), n^{20}_D 1.5402, d^{20}_4 0.9561 (reported for V, n^{20}_D 1.5401, d^{20}_4 0.9573). There was a considerable amount of tarry residue remaining in the still-pot which was apparently polymeric material.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.3; H, 9.68. Found: C, 90.2; H, 9.75.

Ozonolysis[14] of the product gave only formaldehyde, acetophenone and cyclohexyl phenyl ketone which were identified by comparison of their 2,4-dinitrophenylhydrazones with authentic samples.

1-(Cyclohexanol-1)-1-phenylethanol (I) and 1-Cyclohexyl-1-phenyl-1,2-ethanediol (VII).—A performic acid solution was prepared by adding 7.5 g. of 30% hydrogen peroxide to 40 ml. of 98% formic acid containing five drops of concd. sulfuric acid. After allowing the solution to stand at room temperature for five minutes, it was slowly added with stir-

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(6) D. Swern, G. N. Billen, T. W. Findley and J. T. Scanlan, This Journal, **67**, 1786 (1945); D. Swern, G. N. Billen and J. T. Scanlan, *ibid.*, **68**, 1504 (1946); J. English and J. D. Gregory, *ibid.*, **69**, 2120 (1947).

(7) A. C. Chibnall, S. N. Piper, A. Pollard, J. A. B. Smith and E. F. Williams, *Biochem. J.*, **25**, 2095 (1931); H. Schinz and H. L. Simon, *Helv. Chim. Acta*, **28**, 744 (1945).

(8) M. O. Sackur, *Compt. rend.*, **208**, 1092 (1932).

(9) A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 278 (1941).

(10) M. Tiffeneau, *Compt. rend.*, **145**, 595 (1907); *ibid.*, **146**, 29 (1908).

(11) R. C. Fuson and B. A. Bull, *Chem. Revs.*, **15**, 279 (1934).

(12) All melting and boiling points are corrected.

(13) J. English, Jr., C. A. Russell and F. V. Brutcher, Jr., This Journal, **72**, 1653 (1950).

(14) F. C. Whitmore and J. M. Church, *ibid.*, **54**, 3710 (1932).

ring to the olefin mixture (V and VI) at such a rate that the temperature was kept between 45 to 50°. The mixture was poured into 400 ml. of cold water and the excess acid neutralized with solid sodium bicarbonate. The organic product was extracted with ether, washed with water, and dried over anhydrous sodium sulfate. After removal of the ether, the formic esters were saponified by refluxing for 30 minutes with 3.2 g. of sodium hydroxide dissolved in 20 ml. of water and enough ethanol to effect solution. After adding another 50 ml. of water the glycols were extracted with ether. The ether solution was dried over sodium sulfate and then the ether removed. Recrystallization from ligroin gave 4.6 g. (42%) of a colorless mixture of I and VII melting at 81–84°.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.1; H, 9.56. Found: C, 76.1; H, 9.42.

One gram of this glycol mixture was cleaved by lead tetraacetate following the procedure of Oesper and Deasy[15] giving formaldehyde, cyclohexyl phenyl ketone, cyclohexanone and acetophenone, all of which were identified by their 2,4-dinitrophenylhydrazones. The ratio of acetophenone to cyclohexyl phenyl ketone was about 1 to 9.

Separation of I and VII.—An attempted fractional crystallization of 13 g. of a mixture of I and VII, prepared by the performic acid oxidation of the olefins gave only 0.9 g. of VII, m.p. 94.7–95.0°, which was identified by lead tetraacetate cleavage. All other fractions were found to be mixtures.

Eight grams (0.054 mole) of phthalic anhydride was added to 9.5 g. (0.043 mole) of the mixture of I and VII dissolved in 30 ml. of dry pyridine. After heating to 100°, the mixture was allowed to stand overnight. The resulting clear solution was placed in a separatory funnel, and an excess of saturated sodium bicarbonate solution was added with stirring. The water-insoluble material was then extracted with two 50-ml. portions of ether. After washing the ether extract with water and drying over anhydrous sodium sulfate, the ether was removed leaving 1.0 g. of I. Recrystallization to a constant melting point gave 0.9 g. of colorless crystals, m.p. 101–101.5°.

A total of 15 g. of sodium hydroxide was added to the aqueous solution containing the sodium salt of VII phthalate half ester. After refluxing for 15 minutes, the organic material was extracted with ether. A total of 7.9 g. of VII melting at 95.5° after recrystallization was obtained.

The glycols were identified by their lead tetraacetate cleavage products.

Rearrangement of I.—Seven-tenths gram of I, m.p. 101.5° was refluxed for two hours with 20 ml. of 50% sulfuric acid. The mixture gradually darkened and became homogeneous. After adding 50 ml. of water, the organic material was extracted with ether, washed free of acid and dried over anhydrous sodium sulfate. The dark solution was partially decolorized by treatment with norite. Removal of ether under reduced pressure left 0.59 g. of a pleasant smelling yellow sirup.

Eleven milligrams of this sirup did not decolorize 0.5 ml. of a 1% solution of bromine in carbon tetrachloride. The sirup gave a positive carbonyl color test.[16] Treatment of 0.02 g. of the sirup with sodium hypoiodite following the procedure by Fuson and Tullock[17] gave no precipitate of iodoform. An oxime was prepared by the pyridine method[18] from 0.540 g. of the sirup and 0.55 g. of hydroxylamine hydrochloride. A total of 0.18 g. of a colorless solid was obtained which, after recrystallization to constant melting point from ethanol, melted at 139.5 to 140° (reported[8] for 1-phenylcyclohexyl methyl ketone oxime 137–138°).

Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.6; H, 8.76. Found: C, 77.9; H, 8.74.

1-Phenylcyclohexyl Methyl Ketone (III).—A total of 6.0 g. of this ketone was prepared by the method of Sackur.[8] The crude, brown solid product melted at 30–42° (reported 35°). Recrystallization from dilute ethanol to constant melting point gave colorless crystals, m.p. 124.5°. No iodoform test could be obtained. The 2,4-dinitrophenylhydrazone melted at 188° and the oxime at 137° (reported[8] for the oxime 137–138°).

1-Methylcyclohexyl Chloride.—1-Methylcyclohexanol was prepared by the usual Grignard procedure from cyclohexanone and methylmagnesium iodide. A total of 228 g. of this alcohol was treated with a slight excess of thionyl chloride (238 g.) added at such a rate as to keep the temperature below 35°. At the end of this time, pyridine was added to destroy the excess thionyl chloride. The product was washed free of acid with a saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. Distillation at reduced pressure gave 180 g. (70%) of 1-methylcyclohexyl chloride; b.p. 51–56° (40 mm.), $n^{17}\mathrm{D}$ 1.4580 (Beilstein, b.p. 54° (40 mm.), $n^{17}\mathrm{D}$ 1.4582).

1-Methylcyclohexyl Phenyl Ketone (II).—A total of 18.5 g. (0.18 mole) of redistilled benzaldehyde (b.p. 179–180°) dissolved in 50 ml. of anhydrous ether was slowly added to an excess of 1-methylcyclohexylmagnesium chloride prepared by adding 47.6 g. (0.35 mole) of 1-methylcyclohexyl chloride to 8.5 g. of magnesium turnings. The mixture was kept gently refluxing throughout the addition by a water-bath. The refluxing was continued for 27 hr. after the addition was complete. After hydrolysis with satururated ammonium chloride solution, the product was extracted with ether, washed free of iodine with thiosulfate, then washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the mixture was distilled at reduced pressure (b.p. 158–160° (7 mm.)). The forefractions consisted of methylcyclohexane (b.p. 99–102° (760 mm.)) and benzyl alcohol (b.p. 200–210° (760 mm.)). A total of 3.5 g. (9.8%) of the 1-methylcyclohexylphenylcarbinol was obtained as a pale yellow sirup which partly solidified on standing. This alcohol was oxidized without further purification by adding a solution of 2.7 g. of sodium dichromate and 4 ml. of sulfuric acid in 3 ml. of water. The temperature was kept at 75° for 15 minutes after the addition was complete. The crude oily product (3.1 g.) was separated. Attempts to crystallize this ketone failed.

A 2,4-dinitrophenylhydrazone was prepared which melted at 169–170° after recrystallization from ethanol. A mixed melting point with 2,4-dinitrophenylhydrazone of Sackur's ketone (III) gave a depression of 20°.

The oxime was also prepared and, after recrystallization to constant melting point from ethanol, melted at 147°. A mixture of this oxime and the oxime of III melted at 115–118°.

Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.6; H, 8.76; N, 6.45. Found: C, 77.3; H, 8.58; N, 6.47.

Rearrangement of VII.—A total of 2.3 g. (0.01 mole) of VII, m.p. 94.5–95.5°, was heated to 100° for four hours with 50 ml. of 30% sulfuric acid. After extracting the product with ether and washing free of acid, it was dried over anhydrous sodium sulfate. Removal of the ether left a yellowish oil which crystallized on shaking with ligroin. Recrystallization from ligroin to constant m.p. gave 1.4 g. (69.5% of theory) of colorless crystals, m.p. 128–128.5°. The crystals gave no positive test with Schiff reagent, carbonyl group color test, 2,4-dinitrophenylhydrazine or a 1% solution of bromine in carbon tetrachloride.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.2; H, 8.91. Found: C, 82.9; H, 8.76.

Refluxing 0.65 g. of VII with 15 ml. of 50% sulfuric acid for 4.5 hours gave, after dilution with water and isolating the product as above, 0.10 g. of a yellow oil which could not be crystallized. The oil gave a positive carbonyl test and a positive Schiff test. There was insufficient material for further tests.

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[15] R. E. Oesper and C. L. Deasy, *ibid.*, **61**, 972 (1939).

[16] F. R. Duke, *Anal. Ed.*, **16**, 110 (1944).

[17] R. C. Fuson and C. W. Tullock, THIS JOURNAL, **56**, 1638 (1934).

[18] R. L. Shriner and R. C. Fuson, "Identification of Pure Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., p. 167.