was analyzed for deuterium by the float method for determining the density of a mixture of the combustion water diluted with 30–250 volumes of purified "standard water." The resistance (R_s) of a platinum thermometer is read at the balancing temperature where the float neither sinks nor rises. Details for the method have been described.[10] Results are summarized in Table II. W_0 is the weight of the combustion water, and W' the weight of the standard water used as diluent. ΔR represents $R_s - R_0$, R_0 being the resistance for the standard water. D is the density difference between the diluted and standard samples in parts per million. $n^{\circ}_{D_2O}$ is the number of moles of D_2O in the undiluted sample, and N'_{D_2O} and $N^{\circ}_{D_2O}$ represent mole fractions, respectively, of D_2O in the diluted and undiluted samples.

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[10] Hurd and Azörlosa, This Journal, **72**, 33 (1950).

Summary

By use in the Elbs reaction of *o*-methylbenzophenones with an ortho deuterium substituent, it has been possible to demonstrate that the hydrogen atom appearing at the 9-position in anthracene comes from the ortho nuclear position, not from the methyl group.

Evanston, Illinois

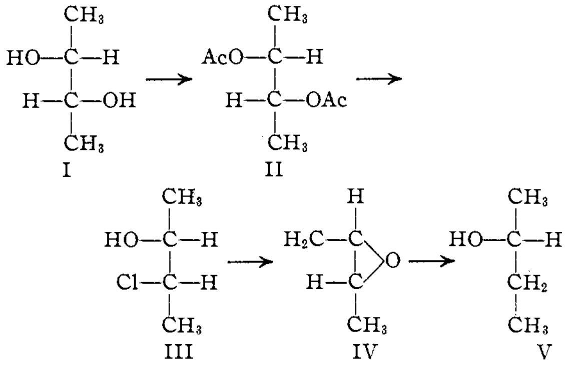
Received May 3, 1950

[Contribution No. 1425 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology]

L(−)-2-Butanol from D(−)-2,3-Butanediol

By P. J. Leroux and H. J. Lucas

The ready availability of D(−)-2,3-butanediol, I, through fermentation methods[1] and the satisfactory yields realized in former work with active and inactive compounds[2,3] have led to the preparation of L(−)-2-butanol, 99% optically pure, from the active glycol in 49% yield through the steps: D-(−)-2,3-butanediol[4] (I), D(+)-2,3-diacetoxybutane[3] (II), L(+)-*erythro*-3-chloro-2-butanol[2,3b] (III), D(+)-2,3-epoxybutane[2] (IV), and L(−)-2-butanol (V). The last step, the reduction of the oxide to the alcohol, has been accomplished with lithium aluminum hydride, following the procedure of W. G. Brown and co-workers.[5] As solvent absolute ethyl ether gave the best results; the yield was 80%. Tetrahydrofuran is less satisfactory, largely because separation by distillation is more difficult. Reduction of L(+)-*erythro*-3-chloro-2-butanol was attempted but the yield was low with either tetrahydrofuran or ethyl ether as solvent.



The conversion of D(+)-2,3-epoxybutane to L-(−)-2-butanol is a confirmation of the configuration of the oxide.[2] The over-all conversion from D(−)-2,3-butanediol requires more steps than were involved in the original determination of the glycol configuration by Morell and Auernheimer,[6] but the high temperature required in the decomposition of the glycol diacetate caused some racemization. Moreover the intermediate methylvinylcarbinol that they reduced to 2-butanol was a by-product, not the main reaction product.

An over-all yield of 45 to 48% would be expected by way of the oxide, in view of the yield at the last step and previous results, some with active compounds,[2] others with inactive compounds.[3] By raising the yield of chlorohydrin from 70 to 77%, an over-all yield of 49% has been obtained. The yield at the last step probably can be increased to 90% to bring the over-all yield to over 50%.

The active alcohol has d^{25}_4 0.8042, n^{20}_D 1.3970, n^{25}_D 1.3949, α^{25}_D −10.67°, $[\alpha]^{25}_D$ −13.51°. This compares with d^{27}_4 0.8025 (d^{25}_4 0.8041, interpolated) n^{20}_D 1.3954, $[\alpha]^{27}_D$ +13.52 ($[\alpha]^{25}_D$ + 13.63, interpolated) for the purest dextro alcohol described.[7] If the active alcohol of Pickard and Kenyon is taken as 100%, the product from 2,3-butanediol has about 1% impurity (including any DL-alcohol), calculated from the specific rotation. The density of our alcohol checks that of theirs, but the refractive index is not in good agreement.[8]

The advantages of the method are convenience, reasonably good yield and high optical purity. The preparations are easy and with the exception of 3-chloro-2-butanol can be carried out with reasonable rapidity. Although the chlorohydrin requires a standing time of two to three weeks, the actual preparation is not laborious. The standard method of resolution of the acid phthalate of 2-butanol with brucine[9] gives about a 40% yield of (+)-alcohol after five to seven crystalliza-

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[1] (a) G. E. Ward, O. G. Pettijohn, L. B. Lockwood and R. D. Coghill, This Journal, **66**, 541 (1944); (b) A. C. Neish, *Can. J. Research*, **23B**, 10 (1945); (c) J. W. Knowlton, N. C. Schieltz and D. Macmillan, This Journal, **68**, 208 (1946).

[2] H. J. Lucas and H. K. Garner, *ibid.*, **70**, 990 (1948).

[3] (a) C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936); (b) H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).

[4] Since the configuration of the higher numbered asymmetric carbon atom determines the family, the glycol is called D, in conformity with the Report of the Committee on Nomenclature, *Chem. Eng. News*, **26**, 1623 (1948). The glycol should be assigned to the family to which the threitol of the same configuration belongs.

[5] R. Nystrom and W. G. Brown, This Journal, **70**, 3738 (1948); L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

[6] S. A. Morell and A. H. Auernheimer, *ibid.*, **66**, 792 (1944).

[7] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911); **103**, 1923 (1913).

[8] We obtain for redistilled DL-2-butanol, also dried with potassium carbonate, n^{20}_D 1.3969, n^{25}_D 1.3949, in good agreement with our values for the active alcohol, and with n^{25}_D 1.39495, obtained with thoroughly dried DL-2-butanol, b. p. (760 mm.) 99.259°; R. Brunel, This Journal, **45**, 1337 (1923).

[9] A. W. Ingersoll, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 376.

tions, $[\alpha]^{27}$D +10.83°. Thus although the percentage yields are comparable, the new method is less laborious and gives a much purer product.

Experimental

D(+)-2,3-Diacetoxybutane (II).—The glycol,[10] I, was distilled at 10 mm., b. p. 77.5–78°, α^{25}D −12.92°, $[\alpha]^{25}$D[11] −13.09°. To 180 g. (2 moles) of I were added 450 g. (4.4 moles) of freshly distilled acetic anhydride and 800 g. freshly distilled pyridine. After the mixture stood overnight, the volatile impurities were removed by distillation at 10 mm., followed by II; b. p. 82°, α^{25}D +13.87°, slightly lower than +14.10° of recrystallized product[2]; yield 319 g., 91.5%.

L(+)-erythro-3-Chloro-2-butanol (III).—Gaseous hydrogen chloride was passed into a solution of 315 g. (1.81 moles) of II in 460 g. concentrated hydrochloric acid at −18 to −20° in two 1-liter ampoules until 162 g. was absorbed by the two. The ampoules were sealed, and the solutions allowed to stand at room temperature for three weeks. The solutions were poured over one kilo of powdered technical sodium bicarbonate, the inorganic solids were removed by suction filtration, the organic liquid was separated, the salt cake was washed with isopropyl ether, and the aqueous phase was extracted with isopropyl ether. After the combined organic phase was washed with aqueous sodium bicarbonate, it was filtered through Dry Ice to remove water. Distillation gave 150 g. of crude III (yield 76.5%, over-all, 70%), b. p. (10 mm.) 56–62°, α^{25}D (obsd.) +9.77°. The boiling range and high rotation[12] can be ascribed to the presence of some chlorohydrin acetate, but this is no particular detriment because it is converted into IV at the next step.

D(+)-2,3-Epoxybutane (IV).—Into a 125-ml. flask containing a solution of 250 g. of potassium hydroxide pellets in 125 ml. of water maintained at 90 to 95° was slowly added 37.6 g. (0.348 mole) of III; IV distilled as formed. Finally the temperature was raised to boiling, to drive over all oxide. After drying the two-phase distillate (without separation) with potassium hydroxide, 22 g. of IV distilled at 53.5° at 746 mm., α^{25}D +46.75°, slightly lower than previous value[2] of +47.23°; yield 88%, over-all, 61.6%.

L(−)-2-Butanol (V).—To a solution of 5 g. (0.132 mole) of lithium aluminum hydride (Metal Hydrides, Inc.)[13] in 150 ml. of absolute ether, 22 g. (0.306 mole) of IV was added slowly with stirring over a period of 1 hour, at a rate to produce gentle boiling of the solvent. Refluxing was continued for another hour. After addition of 20 ml. water during cooling, the mixture was poured into 50 ml. of 10% aqueous potassium hydroxide, and the aqueous phase was extracted four times with ethyl ether. After drying with anhydrous potassium carbonate, fractional distillation gave 18.1 g. of V, b. p. (745 mm.) 97.5–98.0°, α^{25}D −10.67°, $[\alpha]^{25}$D −13.51°; yield 80%, over-all, 49.3%.

Summary

The reduction of D(+)-2,3-epoxybutane to L-(−)-2-butanol with lithium aluminum hydride proceeds smoothly and gives a good yield of active alcohol having an optical purity of 99%. The over-all yield of alcohol from D(−)-2,3-butanediol is about 50%.

PASADENA, CALIFORNIA RECEIVED MAY 22, 1950

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[10] We are indebted to Dr. G. A. Ledingham, Director, and to Drs. A. C. Neish and J. A. Wheat of the Division of Applied Biology, National Research Council of Canada, for a supply of the active glycol, obtained by fermentation of starch with *Aerobacillus polymyxa*. We take this occasion to express our appreciation of this courtesy.

[11] Previous values,[illegible] −13.0°, −13.34° and −13.19°; also −12.85°.

[12] Previous value[2] for L(+)-*erythro*-3-chloro-2-butanol, α^{25}D (obsd.) +9.47°.

[13] An excess was taken to ensure a sufficient amount, because the container had been opened a number of times, with possible deterioration of the reagent.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OKLAHOMA]

Ketimines. III. ω-Cyclohexylalkyl Alkyl Type[1]

BY P. L. PICKARD AND C. W. YOUNG[2]

Previous reports[3,4] from this Laboratory have described a method for synthesis of ketimines under anhydrous conditions. The compounds reported were all prepared from aromatic nitriles and aryl or alkyl Grignard reagents. Since the catalytic methods of ketimine synthesis reported by Mignonac[5,6] had failed for dialkyl compounds, it seemed judicious to test the generality of the method used in this Laboratory by the synthesis of such ketimines.

The series of ω-cyclohexyl aliphatic acids obtained from Dow Chemical Company was selected as a source of nitriles. A study of the literature indicated that data on these acids and the corresponding acid halides, amides and nitriles were far from complete. The intermediate compounds were synthesized by non-ambiguous methods and purified before using them in further work.

The nitriles were treated with a 25% excess of *s*-butylmagnesium bromide and the ketimines isolated

TABLE I

ACID CHLORIDES

Acid chloride R = cyclohexyl	Yield, %	B. p., °C.	Mm.	d^{20}_4	n^{20}D	Chlorine, % Calcd.	Chlorine, % Exptl.
R—CH_2—CO—Cl[a]	87.0	64	4	1.0528	1.4698	22.07	22.16
R—$(CH_2)_2$—CO—Cl[b]	94.5	74	1	1.0345	1.4768	20.30	20.15
R—$(CH_2)_3$—CO—Cl	92.5	83	1	1.0175	1.4710	18.79	18.68
R-$(CH_2)_4$—CO—Cl[c]	93.5	94	1	1.0053	1.4710	17.49	17.31
R—$(CH_2)_5$—CO—Cl	96.0	106	1	0.9987	1.4714	16.35	16.49

[a] Darzens and Rost, *Compt. rend.*, **153**, 774 (1911), gives b. p. (23 mm.) as 98–100°. [b] Mastagli and Metayer, *ibid.*, **224**, 1779 (1948), lists the b. p. (35 mm.) as 124–126° and the b. p. (17 mm.) as 108°. [c] Katsnel'son and Dubinin, *Compt. rend. acad. sci.* (*U. R. S. S.*) (*N. S.*), **4**, 405 (1936), gives the b. p. (15 mm.) as 139°.

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[1] From a thesis presented in partial fulfillment of the requirements for the Master of Science Degree at The University of Oklahoma.

[2] William Earl Schlueter Fellow at The University of Oklahoma, 1949-1950.

[3] P. L. Pickard and D. J. Vaughan, THIS JOURNAL, **72**, 876 (1950).

[4] P. L. Pickard and D. J. Vaughan, *ibid.*, **72**, 5017 (1950).

[5] G. Mignonac, *Compt. rend.*, **169**, 237 (1919).

[6] G. Mignonac, *ibid.*, **170**, 936 (1920).