acetophenone and carbinol (approx. 0.02 mole), 30%; and α-cumyl benzoate (0.07 mole), 40%.

Reaction of valeraldehyde, benzoyl peroxide, and carbon tetrachloride in the presence and absence of cuprous salts. (a) A mixture of valeraldehyde (0.0475), benzoyl peroxide (0.0246 mole) and carbon tetrachloride (0.25 mole) was heated at 76° for 6 hr. At the end of that time, all gas evolution (0.02 mole) had ceased. The benzoic acid (0.003 mole) formed in the reaction was separated by the usual procedure. The chloroform formed in the reaction was separated by distillation and identified. The formation of hydrogen chloride during the course of the reaction was also demonstrated.

The major reaction product was a mixture (0.29 mole) of the unsymmetrical benzoyl valeroyl anhydride and the two symmetrical anhydrides.

(b) A mixture of valeraldehyde (0.1 mole), benzoyl peroxide (0.05 mole), carbon tetrachloride (0.3 mole) and cuprous chloride (0.2 gram) was heated to 76° for less than 1 hr. The gas evolution (carbon dioxide 0.017 mole) ceased at the end of 30 min. The benzoic acid (0.032 mole) formed during the reaction was separated by the usual procedure. Under the conditions described in (a), no chloroform and hydrogen chloride (volatile acid) were formed in the reaction. The reaction product (0.05 mole) appeared to be valeroyl benzoyl anhydride (b.p. 100°/15 mm., n_D^{20} 1.4835) and a mixture of the two symmetrical anhydrides.

Reaction of tert-butyl peroxide in benzaldehyde in the presence and the absence of cuprous salts. (a) A mixture of benzaldehyde (0.47 mole) and *tert*-butyl peroxide (0.068 mole) was heated at 140° for 24 hr. The evolved methane gas (0.0043) was collected. The low boiling materials (benzaldehyde and unreacted peroxide) were removed by distillation at reduced pressure. The residue (0.054 mole, calculated on the basis that it was a mixture of the *meso* and racemic forms of benzopinacol dibenzoate) was crystallized from methanol. The *meso* form of benzopinacol dibenzoate (0.015 mole) obtained melted at 244°. The methanol filtrate was evaporated, leaving an oily residue. Repeated crystallization of this residue material from a mixture of ether and petroleum ether gave a solid material (0.018 mole), which melted quite sharply in an evacuated melting point tube at 115°. This solid was presumed to be the racemic form of benzopinacol dibenzoate.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.6; H, 5.3; mol. wt. 422. Found: C, 79.8; H, 5.5; mol. wt. 440 (camphor).

(b) A mixture of benzaldehyde (0.45 mole), *tert*-butyl peroxide (0.072 mole) and cuprous chloride (0.7 g.; 0.001 mole) was heated at 140° for 6 hr. The reaction mixture was worked up in the usual way. The major reaction product (83%) was *tert*-butyl benzoate (b.p. 92°/10 mm.; n_D^{20} 1.4915). *Tert*-butyl benzoate is known to boil at 94°/10 mm.[24]

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.9. Found: C, 74.3; H, 7.9.

The minor reaction products were the *meso* and racemic forms of benzopinacol dibenzoate (5%).

The infrared spectrum of the *tert*-butyl benzoate obtained with peaks at 1710 cm.$^{-1}$ (benzoate), and 1375 cm.$^{-1}$ and 1395 cm.$^{-1}$ (*tert*-butyl group) was in agreement with the structure assigned to this compound. *Tert*-butyl benzoate was stable when warmed in an alcoholic solution of potassium hydroxide. However, an acetic acid solution of the ester was rapidly hydrolyzed by strong acids.

Acknowledgment. The authors are indebted to Otto B. May, Inc. for the financial support which made this work possible.

CHICAGO, ILL.

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[24] V. R. Stimson, *J. Chem. Soc.*, 2673 (1955) states that *tert*-butyl benzoate boils at 50°/0.5 mm. (n_D^{20} 1.4900).

[CONTRIBUTION FROM SOUTHERN REGIONAL RESEARCH LABORATORY[1] UNITED STATES DEPARTMENT OF AGRICULTURE]

Reaction of Epichlorohydrin with Cyclohexylamine

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The addition of epichlorohydrin to cyclohexylamine through the epoxide group has been reinvestigated. Two chlorohydrins, *N*-(3-chloro-2-hydroxypropyl)cyclohexylamine and *N,N*-bis(3-chloro-2-hydroxypropyl)cyclohexylamine, have been isolated. These compounds have been converted to their respective epoxides and hydrochlorides.

Modern research[3,4,5] has shown various amines react with epichlorohydrin to form *N*-(3-chloro-2 hydroxypropyl)amines. In view of these findings it seemed advisable to reconsider the earlier investigation of Wedekind and Bruch.[6] These latter investigations showed that when cyclohexylamine was treated with epichlorohydrin (3.5 to 1 mole ratio of amine to epoxide) on a water bath, small yields of 1,3-bis(cyclohexylamino)-2-propanol were obtained, in addition to considerable quantities of cyclohexylamine hydrochloride and unidentified tars. We have confirmed this observation, since the reaction easily gets out of hand even when the correct ratio of amine to epoxide is used. However, this investigation has demonstrated that a slow, smooth reaction, which gave the desired products, occurred when mutual solvents were used at room temperature.

In order to prepare the mono- and diepichlorohydrin derivatives of cyclohexylamine, increasing mole ratios of epichlorohydrin to amine were in-

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[3] N. S. Drozdov and O. M. Cherntzov, *J. Gen. Chem.* (*U.S.S.R.*), **4**, 969 (1934); through *Chem. Abstr.*, **29**, 2148 (1935).

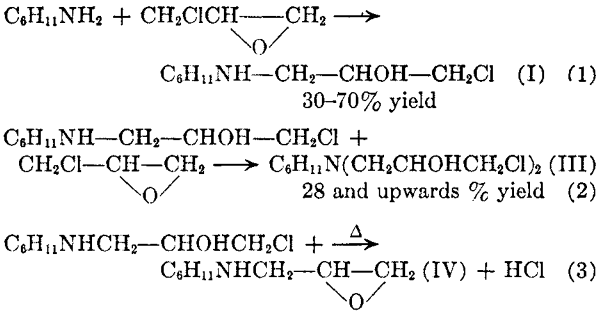
[4] R. Rothstein and K. Binovic, *Compt. rend.*, **236**, 1050 (1953).

[5] G. Chanpetier, G. Montegudet, and J. Petit, *Compt. rend.*, **240**, 1896 (1955).

[6] E. Wedekind and E. Bruch, *Ann.*, **471**, 95 (1929).

vestigated. At a 1:1 (epichlorohydrin to amine) molar ratio a 60–63% yield of *N*-(3-chloro-2-hydroxypropyl)cyclohexylamine (I) was obtained; but the investigation was laregly made at a 2:1 (epichlorohydrin to amine) molar ratio. When the latter molar ratio was used with petroleum ether as a solvent, and the reaction mixture kept at 25° or below, a large quantity of crystalline precipitate formed after 4–5 hours. If the reaction was allowed to continue for 16–20 hours, or if the temperature was lowered to 8–10°, a highly viscous liquid was also precipitated. The isolated crystals were largely I. In addition to this compound, there were small quantities of crystals (II) insoluble in hot petroleum ether, which were identified as the hydrochloride of I. The viscous liquid formed was composed mainly of *N*,*N*-bis(3-chloro-2-hydroxypropyl)cyclohexylamine (III). When the reaction was carried out in petroleum ether, there was no evidence to show the formation of cyclohexylamine hydrochloride[7] (V) (lit. m.p. 204°). In experiments conducted in dioxane, however, trace quantities of V were isolated. Whether it forms as in reaction 5 or by amine attack on carbon with the displacement of the chloride group is not known. No 1,3-dicyclohexylamino-2-propanol, the only compound identified by Wedekind and Bruch,[6] was observed under the mild conditions of this investigation.

In view of the products obtained, the following reaction scheme appears probable at temperatures less than 25°:



$$C_6H_{11}NH_2 + CH_2ClCH\underset{\diagdown O \diagup}{——}CH_2 \longrightarrow C_6H_{11}NH—CH_2—CHOH—CH_2Cl \text{ (I)} \quad (1)$$

30–70% yield

$$C_6H_{11}NH—CH_2—CHOH—CH_2Cl + CH_2Cl—CH\underset{\diagdown O \diagup}{—}CH_2 \longrightarrow C_6H_{11}N(CH_2CHOHCH_2Cl)_2 \text{ (III)}$$

28 and upwards % yield (2)

$$C_6H_{11}NHCH_2—CHOHCH_2Cl + \xrightarrow{\Delta} C_6H_{11}NHCH_2—CH\underset{\diagdown O \diagup}{—}CH_2 \text{ (IV)} + HCl \quad (3)$$

$$C_6H_{11}NHCH_2CHOHCH_2Cl + HCl \longrightarrow C_6H_{11}NHCH_2CHOHCH_2Cl{\cdot}HCl \text{ (II)} \quad (4)$$

less than 1%

$$C_6H_{11}NH_2 + HCl \xrightarrow{\text{dioxane}} C_6H_{11}NH_2{\cdot}HCl \text{ (V)} \quad (5)$$

The relative yields of I, II, and III were apparently dependent on speed and temperature of the reaction; a high yield of the monosubstituted product I occurring when the reaction was run at 20–25°, and the lower yield when the reaction mixture was maintained at 8–10°. At the higher temperature, the insoluble monochlorohydrin formed faster but precipitated quickly from the reaction medium. When the medium was initially colder, the monochlorohydrin formed slowly enough that it was converted to the dichlorohydrin before its solubility was exceeded. Compound III formed in either case. If the reaction temperature was increased, and this was especially true when no solvent was used, polymer formation with further evolution of heat occurred from the epoxide formed (reaction 3).

Compounds I and II were dehydrochlorinated with commercial sodium orthosilicate (a thick gummy paste) in dioxane solution.[8] With this method, 80% conversion to epoxide based on oxirane oxygen analyses was obtained. On distillation of the epoxides, however, these yields were greatly reduced owing to polymerization of the monomeric epoxide probably due to traces of dissolved alkali. A second distillation showed that the epoxides are thermally stable.

EXPERIMENTAL

When cyclohexylamine (0.2 mole) and epichlorohydrin (0.4 mole) were dissolved in 100 ml. of dioxane and kept at 8° overnight, a small amount (1.4 g.) of cyclohexylamine hydrochloride (m.p. 203°) precipitated and was filtered off. The dioxane solution was treated with sodium orthosilicate paste for 1 hr. at 45–50°. After the solution was filtered and stripped of dioxane, only 26.1 g. of product remained. The product was a pitch-like, reddish polymer. Therefore, the use of dioxane as a reaction medium was abandoned in favor of petroleum ether.

Preparation of N-(3-chloro-2-hydroxypropyl)cyclohexylamine I and its hydrochloride II. To 99 g. (1.0 mole) of distilled (b.p. 133°) Eastman[9] White Label cyclohexylamine in 500 ml. of petroleum ether (b.p. 62–69°) were added 185 g. (2.0 moles) of reagent grade epichlorohydrin. The agitated two-phase system was kept at 20–25° for 17 hr. and filtered. Approximately 137 g. of washed snow-white crystals was obtained (71.5% yield based on cyclohexylamine). The compound I after crystallization in hot petroleum ether melted at 79–80°.

Anal. Calcd. for $C_9H_{18}ClNO$: Cl, 18.0; N, 7.30. Found: Cl, 18.0; N, 7.25.

Another crystalline solid (1.8 g.) present was insoluble in hot petroleum ether and melted at 155° when purified (II). Compound I was unstable above its melting point, leading first to a clear liquid, and, finally, to a waxy white solid having a wide melting range 80–185°. Pure compound I was only very slightly soluble in water and gave no chloride ion test. After decomposition, the material was partially water-soluble and showed a strong chloride ion test. Note Reactions 3 and 4. With identical amounts of reagents but at 8–10° a much lower yield of monochlorohydrin I was obtained (38%). At the lower temperature, the dichlorohydrin III yield was approximately 40% and 4.5 g. of compound (II) were formed.

Compound II (m.p. 155°) was water-soluble and gave a test for chloride ions.

Anal. Calcd. for $C_9H_{19}Cl_2NO$: total Cl, 31.1; ionic Cl, 15.5; N, 6.2. Found: total Cl, 30.0; ionic Cl, 15.5; N, 6.1.

Compound II was synthesized, also, by passing dry HCl. into an ether solution of I.

Preparation of N,N-bis(3-chloro-2-hydroxypropyl)cyclohexylamine (III) *and its hydrochloride.* When the 2 liquid phases formed in the preparation of I were separated, either

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[7] A. Skita and W. Berendt, *Ber.*, **52**, 1519 (1919).

[8] N. V. de Bataafsche Petroleum Maatschappij, Brit. Patent **779,092** (July 17, 1957).

[9] Trade names have been used to identify materials used in the work, and such use does not imply endorsement or recommendation by the U. S. Department of Agriculture over other products not mentioned.

spontaneously or by the evaporation of some of the petroleum ether, the heavy viscous liquid was mainly compound III. A small quantity of II also was isolated from it by taking up the oil in chloroform and diluting with petroleum ether. Removal of the solvents led to product III.

Anal. Calcd. for $C_{12}H_{17}Cl_2NO_2$: Cl, 25.0; N, 4.93. Found: Cl, 24.85; N, 4.52.

Compound III was also prepared by reacting equimolar quantities of I and epichlorohydrin at room temperature in chloroform solution for 2 days.

Anal. Found: Cl, 26.2; N, 4.72.

Compound III was soluble in alcohol, chloroform, and dioxane, but insoluble in petroleum and ethyl ethers. Attempts to vacuum-distill compound III resulted in decomposition. A micro boiling point determination resulted in no definite b.p. up to 165° at 2.5 mm. pressure; and a solid brown resin resulted.

A *hydrochloride* (m.p. 174–175°) was formed when HCl gas was passed into a chloroform solution of III and allowed to cool. The solid was crystallized from chloroform or dioxane.

Anal. Calcd. for $C_{12}H_{23}Cl_2NO_2 \cdot HCl$: ionic Cl, 11.08. Found: ionic Cl, 11.13.

Dehydrochlorination of I. To 0.1 mole of I in dioxane were added 30 g. of commercial sodium orthosilicate paste. After the suspended silicate was stirred, the temperature rose to 40°, and was maintained for 1 hr. at 55–60°. The silicates and chlorides were removed by filtration and the solvent removed under vacuum. The yield of crude epoxide was 12.3 g. (79%) as determined by titration with hydrobromic acid.[10] Over 50% of the yield was lost during vacuum distillation due to polymer formation. The distilled epoxide, b.p. 90° (3.5 mm) was a clear mobile liquid (d_4^{26} 0.9934). The product was water-soluble (*p*H 8) and polymerized in water on standing to form a soft deformable solid. It self-polymerized on standing at room temperature in a few days to a clear, colorless resin, soluble in acetone.

Anal. Calcd. for *N*-(2,3-epoxypropyl)cyclohexylamine (IV): oxirane oxygen, 10.3; N, 8.92. Found: oxirane oxygen 10.6; N, 8.8.

When HCl was passed into an ether solution of IV, compound II was formed (m.p. 155°). It should be noted that an amine-epoxide such as IV requires two equivalents of HBr in Durbetaki's oxirane method.[10]

Dehydrochlorination of III. When 0.1 mole of III was dehydrochlorinated,[8] an 82% conversion to epoxide based on oxirane oxygen analyses was obtained. Vacuum distillation at 126–128° at 4 mm. resulted in the formation of *N,N*-bis(2,3-epoxypropyl)cyclohexylamine.

Anal. Calcd. for $C_{12}H_{21}NO_2$: oxirane oxygen, 15.1; N, 6.6. Found: oxirane oxygen, 14.9; N, 6.44.

The product was a colorless mobile liquid which yellowed slightly on exposure to air, but did not polymerize on standing. The distilled product (d_4^{24} 1.0403) was largely insoluble in water (*p*H 7). The polymers formed on distillation were acetone- and methanol-soluble.

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NEW ORLEANS, LA.

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[10] A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LOYOLA UNIVERSITY]

Studies on 1-Phenylcycloalkyl Derivatives: A New Aldehyde Synthesis

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The synthesis and properties of some 1-phenylcycloalkyl derivatives in the three-, five- and six-membered ring systems are reported. These materials constitute intermediates in a useful conversion of acids with α-quaternary carbon centers into β-substituted acetaldehyde derivatives.

During our investigation of the synthesis and peroxide-induced, liquid-phase decarbonylation of some 1-phenylcycloalkylacetaldehydes[2] we have had occasion to prepare a number of 1-phenylcycloalkyl derivatives, heretofore unreported, which constitute intermediates in a new interesting aldehyde synthesis.

The sequence is illustrated in formulas I–VII. The transformation of the known 1-phenylcycloalkylcarbonitriles (I) into their corresponding acid chlorides III follows established routes.[3] In an effort to construct the aldehyde side chain *via* the acids II by the Rosenmund method, the attempted homologation of these acids by the Arndt-Eistert sequence[4] failed. The formation of the α-methoxy ketones (IV) by the catalyzed interaction of methanol and the diazo ketones derived from III proceeds quite satisfactorily.[5] In these reactions the customary[6] use of excess diazomethane is advisable. Otherwise, subsequent reaction of the diazo ketone with the methanol is immediate, with little or no boron trifluoride

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[1] An Arthur Schmidt Pre-doctoral Fellow, 1957–58.

[2] Paper presented at the Fall Chemistry Conference of the *American Chemical Society*, Kansas City, Mo., November 14, 1958.

[3] Among many references to these substances are: (a) F. Case, *J. Am. Chem. Soc.*, **56**, 715 (1934); (b) A. W. Weston, *J. Am. Chem. Soc.*, **68**, 2345 (1946); and (c) R. E. Lyle and G. G. Lyle, *J. Am. Chem. Soc.*, **74**, 4061 (1952).

[4] W. E. Bachmann and W. S. Struve, *Org. Reactions*, 1, 38 (1942).

[5] The method of M. S. Newman and P. F. Beal, III, *J. Am. Chem. Soc.*, **72**, 5161 (1950).

[6] W. J. Hickinbottom, *Reactions of Organic Compounds*, Second Edition, Longmans, Green and Co., London, 1948, p. 259.