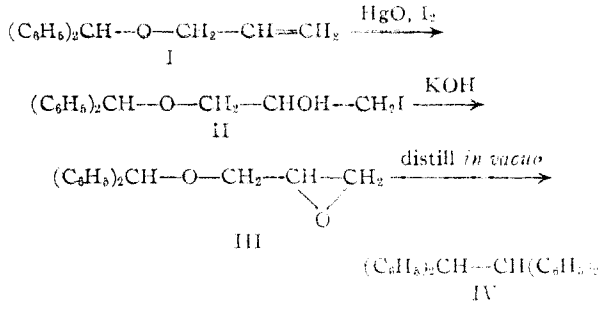
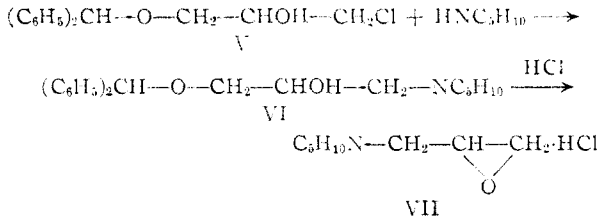


The decomposition was apparently catalyzed by iodine as in the case of isopropyl ether.[5]

The dissociation of benzohydryl ether was again observed in the second case in which the 1-benzohydryl ether of 3-chloro-1,2-propanediol (V) was allowed to react with piperidine.



Most unexpectedly, β-piperidopropylene oxide (VII) instead of the amine-ether (VI) was isolated. The fate of the rest of the molecule was not defined.

Experimental[6]

Benzohydryl Allyl Ether (I).—Diphenylchloromethane (16 g.) was carefully added to allyl alcohol (14 g.) in potassium hydroxide solution (5 g. dissolved in 15 ml. of water). When the reaction had subsided, the mixture was then refluxed on the steam-bath for five hours, cooled, diluted with water (100 ml.) and extracted three times with 50 ml. of ether. The ethereal extract was dried over calcium chloride and distilled under reduced pressure. The fraction distilling between 172–176° (18 mm.), weighed 16.5 g. (30.5% based on allyl alcohol).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.7; H, 7.2. Found: C, 85.0; H, 7.1.

Attempted Preparation of the Benzohydryl Ether of 1,2-Epoxypropanol (III).—To a solution of benzohydryl allyl ether (11.2 g.) in ether (110 ml.) was added yellow mercuric oxide (6 g.) and a little water (10 ml.). While the mixture was vigorously stirred, iodine (14 g.) was added in small portions. The stirring was continued for half an hour after the addition of all the iodine. The mixture was filtered and washed first with potassium iodide solution and then with a solution of sodium hyposulfite to remove the unreacted iodine. The clear ethereal solution was next shaken vigorously with 50 ml. of a 20% aqueous potassium hydroxide solution. The ethereal layer was dried over magnesium sulfate, then distilled *in vacuo*. It became dark red upon heating, with the visible liberation of iodine. The distillation was subsequently discontinued, and the solution again subjected to the treatment with sodium hyposulfite, extracted with ether, and the ethereal extract again shaken with concentrated potassium hydroxide. Upon redistilling the dried ethereal extract under reduced pressure, iodine was liberated as described before. When all volatile fractions, b.p. below 180° (18 mm.) (unidentified) were distilled off, an almost colorless crystalline residue remained, m.p. 211°, after recrystallizing from acetone. It was shown to be *s*-tetraphenylethane by elementary analyses and also by comparison with an authentic sample.

(5) J. V. S. Glass and C. N. Hinshelwood, *J. Chem. Soc.*, 1815 (1929).

(6) All boiling points and melting points are not corrected. Microanalyses done by Dr. G. Weiler of Oxford, England.

1-Benzohydryl Ether of 3-Chloro-1,2-propanediol (V).[7]—Concentrated sulfuric acid (2 ml.) was very carefully dropped into an equimolecular mixture of benzohydrol (18.4 g.) and epichlorohydrin (9.3 g.). The mixture reacted very vigorously and soon turned dark. After six hours heating on the steam-bath, the solution was cooled, diluted with benzene (50 ml.), and carefully neutralized with barium carbonate (6 g.). It was filtered, dried over magnesium sulfate and fractionated *in vacuo*. The fraction boiling between 150–160° (20 mm.) was collected; it weighed 8 g. (27%).

Anal. Calcd. for $C_{16}H_{17}ClO_2$: Cl, 12.8. Found: Cl, 12.8.

The reaction of epichlorohydrin with the sodio-derivative of benzohydrol failed to give the expected ether.

Condensation of 1-Benzohydryl Ether of 3-Chloro-1,2-propanediol with Piperidine.—The 1-benzohydryl ether of 3-chloro-1,2-propanediol (8 g.) was mixed with piperidine (11.6 g.); evolution of heat was noted. The solution was warmed on the steam-bath for three hours, cooled, poured on ice, and carefully acidified with hydrochloric acid (6 *N*) until blue to congo red. It was extracted with about an equal volume of ether and the ethereal extract discarded. The acid solution was made strongly alkaline with potassium hydroxide solution, whereupon a light reddish, amine-smelling oil separated. This was extracted with benzene, and dried over anhydrous potassium carbonate. The benzene was distilled off leaving the free base as a residue. A colorless hydrochloride prepared from this base had an m.p. 245–247° (darkening at 238°), and weighed 4 g. Upon mixing the piperidine hydrochloride, a depression of 45° in m.p. was observed. The product analyzed correctly for the hydrochloride of β-piperidopropylene oxide (VII).

Anal. Calcd. for $C_8H_{15}NO\cdot HCl$: C, 54.1; H, 9.0; N, 7.9. Found: C, 53.5; H, 9.0; N, 8.1.

Acknowledgment.—This work was done in 1947 during the tenure of a research assistantship at the Department of Pharmacology, University of Oxford, England.

(7) E. Fourneau and I. Ribas, *Bull. soc. chim.*, **39**, 1584 (1926); **41**, 1046 (1927).

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The Separation of Catechol from Steam Distillates and Reaction Mixtures

BY W. WERNER ZORBACH AND J. ELLIOTT WEBER

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During experiments designed to determine yields in the conversion of *o*-aminophenol to catechol,[1] it was found that the product could easily be removed from the bulky steam distillate by precipitating as the barium salt,[2] thus rendering unnecessary tedious extraction procedures. Some difficulty, however, was encountered in attempts to regenerate the catechol in organic solvents by means of hydrogen chloride, but this was overcome by substituting lead for barium. In contradistinction, the lead salt[3] was readily decomposed in benzene with hydrogen chloride to yield catechol and lead chloride. Although this procedure proved quite satisfactory, the over-all yields from the reaction were found to be of a low order.

Applying further this property of catechol to form insoluble salts with heavy metals, a convenient and rapid method was found for the separation of this substance formed in the hydrogen peroxide

(1) Société Chimique des Usines du Rhone, D.R.P. 167,211 (1906).

(2) B. Elsner, *Monatsh.*, **40**, 361 (1919).

(3) C. Zwenger, *Ann.*, **37**, 332 (1841).

oxidation of salicylaldehyde,[4] particularly when small scale syntheses were undertaken. Due to interfering ions, lead acetate could not be used in the recovery. Instead, the catechol thus formed was precipitated directly from the reaction mixture with barium hydroxide and regenerated from the resulting salt with a small quantity of dilute, aqueous hydrochloric acid. Ether extraction gave yields comparable to those noted in the described synthesis. For excellent purity the crude product was vapor distilled with bromobenzene.[5]

Experimental

Catechol from *o*-Aminophenol.—To a solution of 35.6 g. (0.363 mole) of sulfuric acid in 50 ml. of water cooled to −10° was added with constant stirring 15.8 g. (0.145 mole) of *o*-aminophenol. The final solution was brought to about 10% by dilution with ice and then added at a moderate rate to a boiling solution of 50 g. (0.2 mole) of cupric sulfate pentahydrate in 50 ml. of water contained in a flask equipped for distillation. The catechol formed was steam distilled until the distillate gave only a faint test with alcoholic ferric chloride. To this distillate was added a 10% aqueous solution of normal lead acetate until precipitation was complete. The lead catecholate was then collected on a buchner funnel, washed thrice with cold water, then twice with small portions of acetone and finally sucked dry. The dry material was transferred to a 300-ml. round bottom flask, covered with 200 ml. of benzene and then treated with a rapid stream of dry hydrogen chloride. In 15 to 20 minutes the decomposition was complete, leaving a residue of lead chloride which was filtered off. The filtrate was then placed on a steam-bath and distilled at atmospheric pressure until the distillate appeared clear. The remainder of the benzene was evaporated *in vacuo*, leaving a brownish, crystalline residue of catechol which was transferred to a 50-ml. distilling flask, covered with 25 ml. of bromobenzene and vigorously distilled through an air condenser into a flask cooled to 0°. The separating product was filtered by suction and the filtrate returned to the distilling flask which contained undistilled catechol. This was likewise distilled, giving an additional amount of pure material in the distillate, and the process repeated until all the catechol was carried over. In this manner, 2.32 g. (9.7%) of colorless plates, m.p. 104°, was obtained.

Catechol from Salicylaldehyde.—Directions for this preparation, scaled down to 0.05 mole, were employed as noted above.[4] To the final reaction mixture, adjusted to a *p*H of approximately seven with acetic acid and warmed to 40°, was added a solution of 9.45 g. (0.03 mole) of barium hydroxide octahydrate in 30 ml. of water at 80°. Greenish-gold leaflets of barium catecholate separated and were immediately filtered by suction. The funnel and contents were transferred to a clean filter flask, washed with cold water until the washings appeared clear, then twice with acetone and allowed to dry by suction. To the first filtrate was added a solution of 6.30 g. (0.02 mole) of barium hydroxide octahydrate in 20 ml. of water, whereupon more material separated out. This was filtered and washed in a similar manner. The combined quantities of dry salt were crushed, placed in a 100-ml. round bottom flask and covered with 25 ml. of a hydrochloric acid solution containing 2.74 g. (0.075 mole) of hydrogen chloride. The mixture was then warmed on the steam-bath until complete solution was effected and the contents transferred quantitatively to a separatory funnel and extracted with two 100-ml. portions of ether. The ether extract in turn was washed with two 25-ml. portions of 5% potassium bicarbonate, dried for one-half hour over anhydrous magnesium sulfate, filtered and evaporated *in vacuo*, leaving 3.91 g. (71%) of impure, crystalline catechol. Repeated distillation with bromobenzene, as described in the above experiment, gave 3.72 g. (68%) of colorless plates, m.p. 104°.

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(4) H. D. Dakin, "Organic Syntheses," Coll. Vol. I, 2d Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 149.

(5) N. Elliott, U. S. Patent 1,912,626 (1933).

Conductance of Aluminum Chloride in Sulfuryl Chloride on Adding Benzophenone or Sulfur Monochloride[1]

BY A. R. PRAY AND C. R. MCCROSKY

RECEIVED APRIL 28, 1952

Kraus, Van Dyke and their collaborators have recently reported studies on the complexes formed by some aluminum (or gallium) halides with other molecules in several non-aqueous solutions.[2] These solutes are of especial interest as their solutions are electrically conducting, the conductance changing in a marked way as the complexing agent is added.

We here report a somewhat similar study on aluminum chloride dissolved in sulfuryl chloride, using benzophenone and sulfur monochloride as complexing agents.

Experimental

Materials.—Sulfuryl chloride[3] was distilled immediately before use. The distilling apparatus, of ordinary kind with ground glass joints, was flushed out with a portion of the fraction boiling at 69° before collection of the portion to be used. The solvent so obtained had a specific conductance of 4×10^{-8} mho.

Aluminum chloride, anhydrous, of reagent grade, was purified by sublimation, the method resembling that given by Archibald[4] but simplified in detail.

Benzophenone was recrystallized three times from alcohol, dried in a current of warm air, and stored over barium oxide.

Sulfur monochloride was twice distilled from excess sulfur. The middle portion of the fraction boiling at 138° was used.

Apparatus and Procedure.—Conductance measurements were made on an assembled apparatus following the circuit of Jones and Josephs.[5] The conductance cell was immersed in an oil thermostat of 20-l. capacity maintained at 25 ± 0.05°. The conductance cell was a test-tube, 15 by 2.5 cm., fitted with a hard rubber cover. Through this cover two parallel glass tubes holding the electrodes passed. The electrodes were shiny platinum plates, about 1 cm. square and separated by about 1 mm. The glass tubes were separated by a glass spacer at the electrode end. The hard rubber cover was drilled to provide entry for a buret tip, by means of which the complexing agent was added. The buret was of 10-ml. volume, graduated in 0.05 ml. It was calibrated at each ml. It was found convenient to fit the top with a microcapillary to restrict air entry.

The addition of complexing agent to the aluminum chloride was carried out as follows. Twenty ml. of sulfuryl chloride was distilled into the conductance cell. From 0.3 to 1 g. of aluminum chloride was weighed out into the cell. The liquid was warmed slightly to hasten solution. The cell was closed with the cap holding the electrodes and immersed in the thermostat. About 10 g. of the complexing agent was weighed into a small (10–25 ml.) calibrated volumetric flask. The flask was made up nearly to the mark with sulfuryl chloride, allowed to stand in the thermostat, and finally adjusted to volume. The contents were then transferred to the buret. The initial conductance of the solution was then measured and discrete amounts of com-

(1) Presented at the 118th National Meeting of the American Chemical Society in Chicago, September 3–8, 1950.

(2) (a) Aluminum bromide with methyl ether in methyl bromide solution, W. J. Jacobs and C. A. Kraus, THIS JOURNAL, **71**, 2409 (1949); (b) Aluminum bromide with other molecules in nitrobenzene solution, R. E. Van Dyke and C. A. Kraus, *ibid.*, **71**, 2694 (1949), and R. E. Van Dyke, *ibid.*, **73**, 398 (1951); (c) gallium chloride with other molecules in nitrobenzene solutions, R. E. Van Dyke, *ibid.*, **72**, 2823 (1950); (d) aluminum bromide with other molecules in benzonitrile solution, R. E. Van Dyke and T. S. Harrison, *ibid.*, **73**, 402, 571 (1951); (e) aluminum chloride with other molecules in nitrobenzene solution, R. E. Van Dyke and H. E. Crawford, *ibid.*, **73**, 2018, 2022 (1951).

(3) Kindly furnished by the Hooker Electrochemical Co., Niagara Falls, New York.

(4) E. H. Archibald, "Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, N. Y., 1932.

(5) G. Jones and R. J. Josephs, THIS JOURNAL, **50**, 1049 (1928).