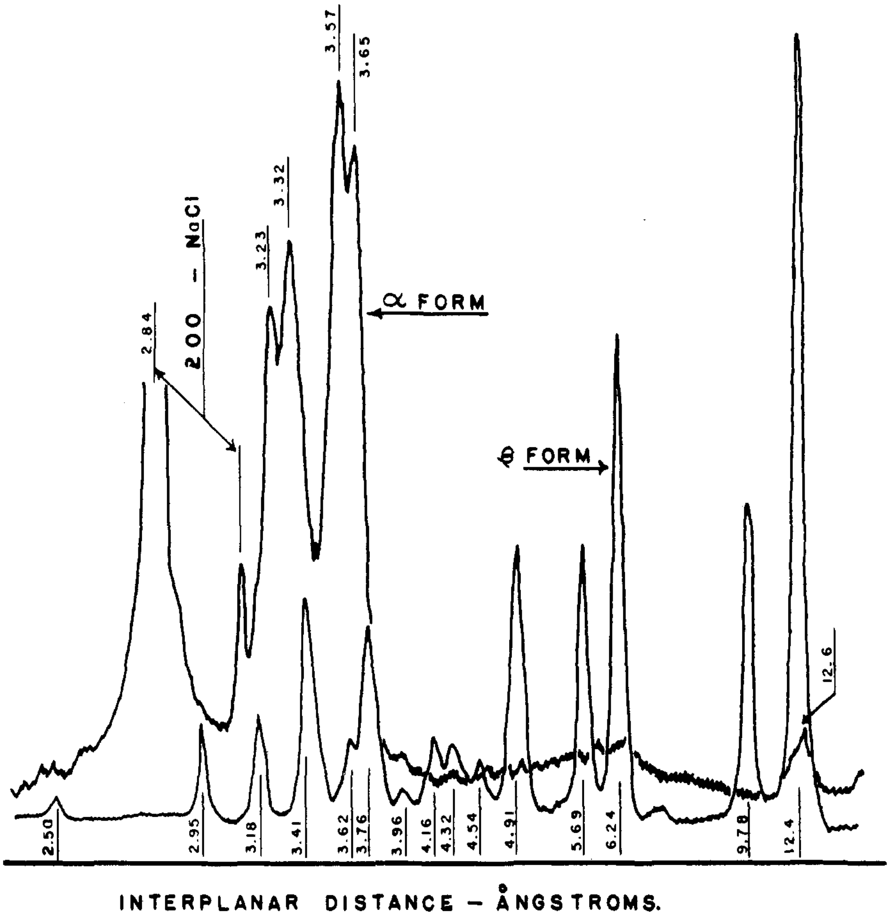

Fig. 1.—X-Ray diffraction patterns of metal-free phthalocyanine.

study of the infrared spectrum[4] and X-ray diffraction pattern of this material revealed that this technique produces the α-form of a phthalocyanine. The average particle size appears to be of the order of a few microns as evidenced by low scattering losses at wave lengths of 3 microns and above. Figure 1 illustrates the X-ray diffraction pattern of the β-form of metal-free phthalocyanine obtained as a powder, and superimposed on the same scale is that of the α-form deposited on a rock salt plate. The decrease in the relative intensity of the diffraction line at 12.6 Å. as compared with the results of Ebert and Gottlieb[5] may be attributed to partial orientation of the crystals produced by sublimation. The β-pattern agrees quite well with that calculated from the data of Robertson.

A preliminary investigation of the pressure dependence of the phase change indicated that the alpha form of metal-free phthalocyanine is produced at sublimation pressures up to 50 mm. The α-form of copper phthalocyanine is produced at pressures up to 0.1 mm.; above this pressure sublimation produces the β-form.

German scientists discovered that an α-β-phase transition occurs for the metal-free and copper phthalocyanine at temperatures above 200°.[6] Barrett's condensation temperature was 400°, which explains why the α-form of metal-free phthalocyanine was never produced by his procedure.

CORVALLIS, OREGON

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[4] D. N. Kendall, 119th A.C.S. Meeting, April, 1951, Abstracts Division of Phys. and Inorg. Chem., 2p.

[5] A. A. Ebert, Jr., and H. B. Gottlieb, THIS JOURNAL, **74**, 2806 (1952).

[6] Fiat, Final Report 1313 Vol. III, U. S. Dept. of Commerce, Washington, D. C., 1948, pp. 345-439.

The Dissociation of Certain Benzohydryl Ethers

BY TI LI LOO

RECEIVED MARCH 20, 1952

The report by Kaye[1] and by Harms and Nauta[2] of the dissociation of certain benzohydryl ethers to afford *s*-tetraphenylethane finds support from work performed by the present author in 1947 in connection with other studies, first during preparation of the oxide of benzohydryl allyl ether, and again during the reaction of 1-benzohydryl ether of 3-chloro-1,2-propanediol with piperidine.

In the first instance, an unsuccessful attempt was made to prepare by the procedures of Brunel[3] and Bougault[4] the oxide (III) from benzohydryl allyl ether (I), through the iodohydrin (II) (not isolated). Upon distilling *in vacuo* an ethereal solution containing the supposed iodohydrin (II), a small amount of *s*-tetraphenylethane (IV) was obtained.

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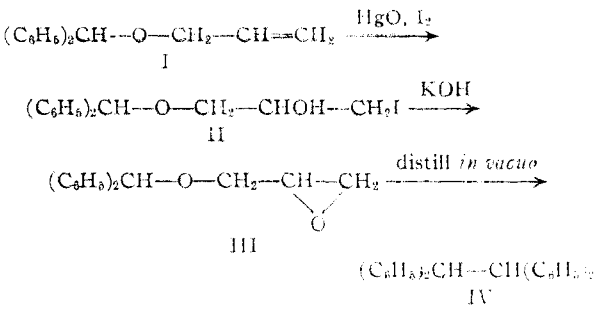
[1] I. A. Kaye, THIS JOURNAL, **73**, 5468 (1951); I. A. Kaye, I. C. Kogon and C. Parris, *ibid.*, **74**, 403 (1952).

[2] A. F. Harms and W. T. Nauta, *Rec. trav. chim.*, **71**, 431 (1952).

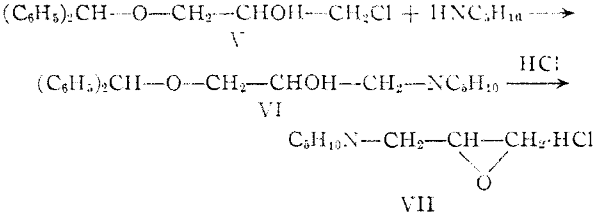
[3] L. Brunel, *Compt. rend.*, **135**, 1055 (1902).

[4] J. Bougault, *Bull. soc. chim.*, **25**, 444 (1901).



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.

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.

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[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.

[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

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[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).