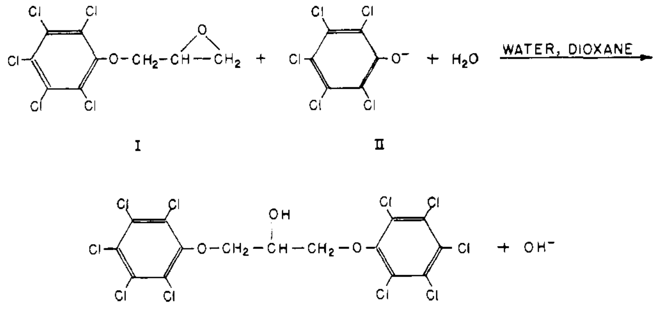
1,3-Bis(Pentachlorophenoxy)-2-Propanol

A. BLAGA and M. J. SKRYPA
Solvay Process Division, Allied Chemical Corp., Syracuse, N. Y.

THE SYNTHESIS of 1,3-bis(pentachlorophenoxy)-2-propanol (III) was accomplished by treating 3-(pentachlorophenoxy)-1,2-epoxypropane (I) (pentachlorophenyl glycidyl ether) with sodium pentachlorophenoxide (II) in accordance with the following reaction:



The N.M.R. spectrum showed two bands: a doublet at 2.6δ and a complex multiplet centered about 4.2δ. The doublet (area ratio 1:1, J = 5 c.p.s.) is assignable to a hydroxylic proton (X) of a secondary alcohol (*2*) split twice by spin-spin coupling with the proton (A) attached to carbon atom 2. This band is part of the spectrum of an AX system which should give rise to a pair of doublets (*3*). The other doublet overlaps with the multiplet. The complex multiplet arises from an AB_4X system made up by the proton (A) attached to carbon 2, the four magnetically equivalent methylenic protons (B), and the hydroxylic proton (X). The proton coupling constants in the complex multiplet could not be determined. The total areas of the multiplet and the doublet are in the ratio of 5:1. This type of spectrum is compatible with structure III. It rules out the structure corresponding to the other possible isomeric product, 2,3-bis(pentachlorophenoxy)-1-propanol (IV); its hydroxylic proton would be split as a triplet by spin-spin coupling with the two protons attached to carbon 1. The triplet would be part of an absorption band of an A_2X system. Furthermore, the spectrum would give rise to bands characteristic of an A_2BC_2 system. The Compound I was prepared by the procedure of Alquist and Slagh (*1*).

EXPERIMENTAL

The N.M.R. spectrum of the product was measured (in *o*-dichlorobenzene at 100° C.) by means of a Varian Associates nuclear magnetic resonance spectrometer at a fixed frequency of 60 mc., using tetramethylsilane as an external standard ($\delta = 0$).

3-(Pentachlorophenoxy)-1,2-epoxypropane (190.0 grams; 0.59 mole) dissolved in 1000 ml. of dioxane was added with stirring over a ½-hour period to 750 ml. of an aqueous solution of sodium pentachlorophenoxide (170.0 grams; 0.59 mole) maintained at 90°–100° C. The reaction mixture was heated with stirring at 95° C. for 4 hours. The white precipitate which formed was filtered and washed with three portions of 300 ml. of methanol. The dried product weighed 158.0 grams (45.6% yield), m.p. 167°–169° C. After recrystallization from 1-butanol, the product melted at 169°–170° C. Anal. Calcd. for $C_{15}H_6Cl_{10}O_3$: C, 30.59; H, 1.03; Cl, 60.22. Found: C, 30.68; H, 1.16; Cl, 60.00. The infrared spectrum (Perkin Elmer 221, KBr technique) showed maxima at 3580 cm.$^{-1}$(w), 3430 cm.$^{-1}$(w), 1353 cm.$^{-1}$(m), 1318 cm.$^{-1}$(m), 1020 cm.$^{-1}$(ms), 785 cm.$^{-1}$(s), 762 cm.$^{-1}$(s), and 712 cm.$^{-1}$(vs).

LITERATURE CITED

(1) Alquist, F.N., Slagh, H.R. (to Dow Chemical Co.), U. S. Patent **2,221,771** (November 19, 1940).
(2) Bhacca, N.S., Williams, D.H., "Applications of N.M.R. Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, 1964.
(3) Jackman, L.M., "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1959.

RECEIVED for review June 17, 1965. Accepted December 22, 1965.

Complex Bromo Lead(II) Salts

R. D. WHEALY and A. Z. HARRIS
Department of Chemistry, Texas A&M University, College Station, Tex.

Sixteen compounds were prepared by the reaction of amine hydrobromide salts with lead(II) bromide. The complex compounds were recrystallized and analyzed for lead and bromide content, their melting points and densities were determined, and qualitative solubilities were observed. Absorption spectra of the complex compounds and of lead perchlorate solutions with varying amounts of sodium bromide were studied.

AMMONIUM pentabromodiplumbate(II) was prepared by Fonzes-Diacon (*3*) and its structure was determined by Powell and Tasker (*8*), using x-ray diffraction methods. Hydrated ammonium tetrabromoplumbate(II) was prepared by Wells and Johnston (*10*). Datta and Sen (*2*) reported the preparation of pyridinium tribromoplumbate(II) and quinolinium tribromoplumbate(II). Bis-brucinium tetrabromoplumbate(II) was prepared by White (*11*).

The reaction of lead ions with bromide ions has been studied by Biggs, Parton, and Robinson (*1*), Fromherz and Lih (*4*), Kivalo (*5*), Nancollas (*6*), Panckhurst and Parton (*7*), Vasilev and Proukhina (*9*), and Yatsimirskiĭ (*12*). The reported values for pK₁ (−log K_1) vary from 1.15 to 1.85 for the reaction at 25° C., with the ionic strength corrected to zero. Kivalo (*5*) was the only investigator who reported values for K_2 and K_3. He found $pK_1 = 1.11$, $pK_2 =$