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

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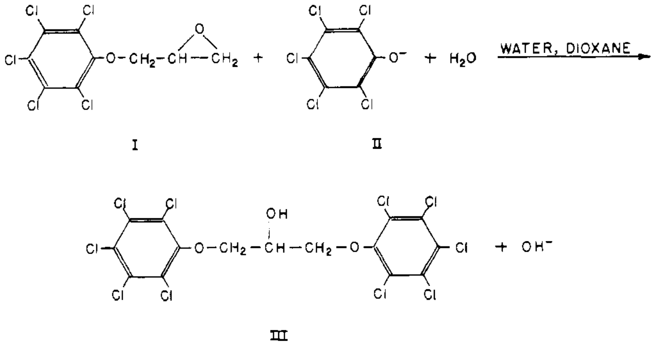
THE SYNTHESIS of 1,3-bis(pentachlorophenoxy)-2-propanol (III) was accomplished by treating 3-(pentachlorophenoxy)-1,2-epoxypropane (I) (pentachlorophenyl glycidyl ether) with sodium pentachlorophenoxide (II) in accordance with the following reaction:



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.

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Complex Bromo Lead(II) Salts

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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 $pK_1 = 1.11$, $pK_2 =$

0.32, and $pK_3 = 0.75$ by polarographic studies in a $NaClO_4$-NaBr system with constant ionic strength of 1. He found no evidence of the formation of $PbBr_4^{-2}$ ions in 1.0*M* NaBr solutions.

EXPERIMENTAL PROCEDURES

The lead(II) bromide solutions, 0.025*M* with respect to lead and 0.18*M* with respect to hydrobromic acid, were prepared by dissolving reagent grade lead carbonate in 48% hydrobromic acid. The amine hydrobromide salts were prepared by adding an excess of hydrobromic acid to the respective amines. The amine hydrobromide salt was 0.25*M* in all preparations. An aliquot of the lead(II) bromide solutions of 50 ml. was added slowly with vigorous stirring to approximately the same volume of the amine hydrobromide solutions. This procedure ensured a very large excess of the bromide ion and amine ion, compared with the concentration of the lead ion. The resulting solutions were diluted to a total volume of 200 ml. by the addition of methanol. This procedure was adopted after repeated failure to prepare relatively pure compounds from aqueous solutions. The precipitates were separated by filtration through sintered glass crucibles and rinsed with ethanol. The product was dried in a vacuum desiccator with sodium hydroxide as the desiccant. These original products were analyzed for lead and bromide content. If the results did not indicate a rather pure compound, the precipitates were redissolved in a small volume of concentrated hydrobromic acid and sufficient methanol was added to give a total volume of 200 ml. The recrystallized product was allowed to remain in contact with the solution for several days with frequent vigorous stirring. It was then filtered, washed with ethanol, and dried in a vacuum desiccator over sodium hydroxide.

Analytical Procedures. The lead content was determined by direct titration with the disodium salt of (ethylenedinitrilo)tetraacetic acid (EDTA) using xylenol orange as an indicator. The samples were dissolved in 5 ml. of concentrated nitric acid and digested on a low temperature hot plate to oxidize and remove the organic material. The dissolved product was diluted to 100 ml. with ion-exchange water and the pH adjusted to 5.5. The results of these analyses are given in Table I.

The bromide content was determined by titration with silver nitrate. A Beckman Zeromatic pH meter equipped with a silver-indicating electrode and a mercury-mercurous sulfate reference electrode was used to follow the course of the titration (Table I).

PHYSICAL PROPERTIES OF COMPOUNDS

The compounds are all white, finely divided solids, soluble in water and methanol, slightly soluble in 2-propanol, and insoluble in low dieletric solvents such as benzene, carbon tetrachloride, and chloroform. The compounds all decompose in any solvent in which they will dissolve, unless an appreciable excess of bromide ion is present.

The melting points or decomposition temperatures were determined using a modified Thiele-Dennis melting point tube containing Dow Corning 550 silicone oil. A set of total immersion thermometers with appropriate corrections was used for the temperature measurement. The melting points or decomposition temperatures ranged from 177° to over 350° C. (upper limit of apparatus was 350° C.) and are recorded in Table I.

The densities of the compounds were determined with calibrated pycnometers by a displacement technique using carbon tetrachloride as the displaced liquid. Duplicate accurately weighed samples of approximately 3.0 grams were used for each compound (Table I).

The absorption spectra of the compounds all have a maximum at 300 *M* in solutions which have a bromide concentration 4*M* or greater. The wavelength of maximum absorption decreases as the bromide concentration is decreased. Dilute lead perchlorate with varying concentrations of bromide was studied to relate the different absorption maxima with particular ionic species. $Pb(ClO_4)_2$ in 1.0*M* $HClO_4$ has a sharp absorption maximum at 207 ± 2 mμ with a molar absorptivity of 8.5 (±0.1) × 10^3 liters/mole cm. As the bromide concentration is increased, a second maximum is observed at 245 mμ, which has been identified as the result of absorption by $PbBr^+$ by Biggs, Parton, and Robinson (*1*). As the bromide concentration is increased, the absorption maximum is continuously shifted to longer wavelengths until in 4.0*M* bromide the peak is at 300 mμ. No measurable change in the wavelength of the absorption maximum was found on further increasing the bromide concentration.

DISCUSSION

Attempts to make the complex salts in relatively concentrated aqueous solutions always gave impure products which were mixtures of tribromo and tetrabromo complex salts. A number of different hydrobromic acid concentrations were tried without success. The dilution with methanol decreased the concentration and lowered the dielectric constant of the solution. Both of these factors would favor the

Table I. Results of Analyses

	Density, G./Cc.	% Lead		% Bromine		M. P. Range, ° C.
		Theor.	Exptl.	Theor.	Exptl.	
$C_2H_5NH_3PbBr_3$	2.69	42.02	42.07 ± 0.07	48.63	48.63 ± 0.02	317-318[a]
$(CH_3)_2NH_2PbBr_3$	3.49	42.02	41.97 ± 0.02	48.62	48.41 ± 0.06	348-349[a]
$(C_2H_5)_2NH_2PbBr_3$	3.05	39.76	39.79 ± 0.06	46.00	45.88 ± 0.10	177-178
$(CH_3)_3NHPbBr_3$	2.81	40.86	41.18 ± 0.24	47.28	47.02 ± 0.02	>355[a]
$(C_2H_5)_3NHPbBr_3$	2.71	37.73	37.77 ± 0.01	43.65	43.34 ± 0.08	268-269
2-$CH_3 \cdot C_5H_4NHPbBr_3$	3.06	38.29	38.14 ± 0.01	44.33	44.32 ± 0.06	231-232
4-$CH_3 \cdot C_5H_4NHPbBr_3$	2.44	38.29	38.30 ± 0.02	44.33	44.48 ± 0.28	252-253
$O(CH_2CH_2)_2NH_2PbBr_3$	3.27	38.73	38.45 ± 0.03	44.80	44.47 ± 0.03	254-255[a]
$(CH_2)_5NH_2PbBr_3$	3.01	38.87	38.88 ± 0.02	44.97	44.87 ± 0.07	>347
$(C_4H_9)_2NH_2PbBr_3$	2.35	35.90	36.48 ± 0.10	41.54	41.37 ± 0.07	194-195
$HOCH_2CH_2(C_2H_5)_2NHPbBr_3$	2.30	36.59	36.14 ± 0.06	42.33	42.29 ± 0.06	212-213
$HOCH_2CH_2(CH_3)_2NHPbBr_3$	2.74	38.57	39.09 ± 0.25	44.65	44.57 ± 0.07	243[a]
$[(CH_3)_2CHCH_2]_2NH_2PbBr_3$	3.84	35.90	35.60 ± 0.16	41.52	41.17 ± 0.13	213-214
$(CH_3)_2NHCH_2CH_2CH_2NH_3PbBr_4$	2.69	32.83	32.69 ± 0.05	50.65	50.91 ± 0.05	282-283
$[CH_3(CH_2)_2NH_3]_2PbBr_4$	2.46	32.02	31.83 ± 0.04	49.42	49.36 ± 0.01	309-311[a]
$(C_6H_5CH_2NH_3)_2PbBr_4$	2.40	27.88	27.94 ± 0.10	43.01	43.32 ± 0.04	270-271

[a] Melted with decomposition.