ACKNOWLEDGMENT

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Synthesis of 1-Amino-2-alkanols

3-(2-Propeneoxy)-1-amino-2-propanols and 4,4,4-Trichloro-1-amino-2-butanol Hydrochlorides

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New 3-(2-propeneoxy)-1-amino-2-propanols and 4,4,4-trichloro-1-amino-2-butanol hydrochlorides have been synthesized by the reactions of allyl glycidyl ether and 4,4,4-trichloro-1,2-epoxybutane with primary and secondary amines.

THE REACTIONS of allyl glycidyl ether with a variety of primary and secondary amines in the absence of a solvent yielded the corresponding 3-(2-propeneoxy)-1-amino-2-propanols (I) in good to excellent yields. These compounds (Table I), which were colorless to pale yellow oils, were obtained by reduced pressure distillation of the reaction mixtures. Several compounds of this type have been described (*1*).

The reactions of 4,4,4-trichloro-1,2-epoxybutane with primary and secondary amines (*2*) proceeded smoothly in either boiling toluene or ethanol solutions to yield the corresponding 4,4,4-trichloro-1-amino-2-butanols (II). These compounds were isolated as their hydrochlorides, since the free bases apparently decomposed on attempted reduced pressure distillation. The physical properties of these nicely crystalline colorless salts are listed in Table II.

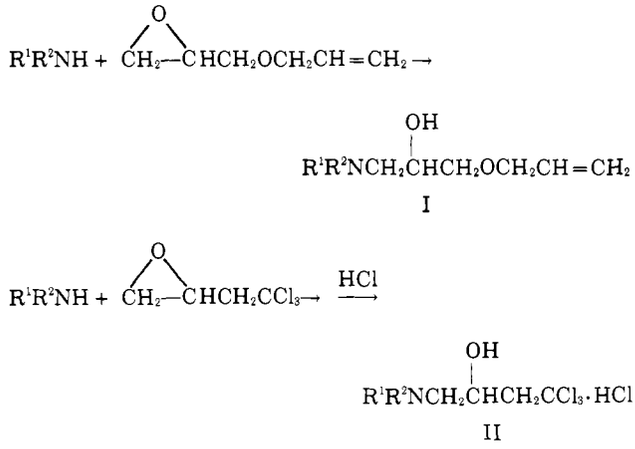

Table I. 3-(2-Propeneoxy)-1-amino-2-propanols[a]

$R^1R^2NCH_2CH(OH)CH_2OCH_2CH=CH_2$

Compd. No.	R^1	R^2	Yield,[b] %	B.P., °C./Mm.	n_D^{25}	Molecular Formula
1	$CH_3O(CH_2)_3$—	H	64	121–3/0.7	1.4587	$C_{10}H_{21}NO_3$
2	Allyl	Allyl	83	112–4/2.6	...	$C_{12}H_{21}NO_2$
3	*n*-C_3H_7	*n*-C_3H_7	90	99–100/1.1	1.4451	$C_{12}H_{25}NO_2$
4	Iso-C_3H_7	Iso-C_3H_7	77	103–4/2.4	1.4482	$C_{12}H_{25}NO_2$
5	*n*-C_4H_9	CH_3	89	94–6/1.5	1.4469	$C_{11}H_{23}NO_2$
6	*n*-C_4H_9	*n*-C_4H_9	92	105–7/0.4	1.4461	$C_{14}H_{29}NO_2$
7	Iso-C_4H_9	Iso-C_4H_9	88	106–9/1.3	1.4445	$C_{14}H_{29}NO_2$
8	Iso-C_5H_{11}	Iso-C_5H_{11}	90	116–20/0.9	1.4475	$C_{16}H_{33}NO_2$
9	$CH_2(CH_2)_2OCHCH_2$—	CH_3	90	120–1/0.5	1.4674	$C_{12}H_{23}NO_3$
10	Cyclohexyl	CH_3	90	126–7/1.0	1.4740	$C_{13}H_{25}NO_2$
11		—$(CH_2)_2$—CH—(CH_3)—$(CH_2)_2$—	85	112–5/1.5	1.4677	$C_{12}H_{23}NO_2$
12		—CH_2—$(CH_2)_4$—CH_2—	84	101–4/0.5	1.4767	$C_{12}H_{23}NO_2$
13	2-ClC_6H_4	H	70	142–4/0.1	1.5513	$C_{12}H_{16}ClNO_2$
14	3-$CF_3C_6H_4$	H	12	...	[c]	$C_{13}H_{16}F_3NO_2$
15	C_6H_5	C_2H_5	89	138–41/0.6	1.5373	$C_{14}H_{21}NO_2$
16	C_6H_5	Iso-C_3H_7	83	119–21/0.07	1.5264	$C_{15}H_{23}NO_2$
17	$C_6H_5CH_2$—	H	64	132–5/0.2	1.5240	$C_{13}H_{19}NO_2$
18	C_6H_5—CH_2—	CH_3	83	116–9/0.15	1.5120	$C_{14}H_{21}NO_2$

[a] Confirming elemental analyses have been obtained for all compounds and deposited with the American Documentation Institute. [b] Yields for once distilled products. [c] M.p. 39–41°.

Table II. 4,4,4-Trichloro-1-amino-2-butanol Hydrochlorides

$Cl_3CCH_2CH(OH)CH_2NR^1R^2 \cdot HCl$

Compd. No.	R^1	R^2	M.P.[a], °C.	Yield,[b] %	Molecular Formula
19	Iso-C_3H_7	H	203	73	$C_7H_{15}Cl_4NO$
20	*n*-C_4H_9	H	230	51	$C_8H_{17}Cl_4NO$
21	*sec*-C_4H_9	H	190	68	$C_8H_{17}Cl_4NO$
22	Iso-C_4H_9	H	224	62	$C_8H_{17}Cl_4NO$
23	*tert*-C_4H_9	H	212	58	$C_8H_{17}Cl_4NO$
24	$CH_2(CH_2)_4CH$—	H	225	71	$C_{10}H_{19}Cl_4NO$
25	Iso-C_3H_7	Iso-C_3H_7	177	39	$C_{10}H_{21}Cl_4NO$
26	$—CH_2CH_2—O—CH_2CH_2—$		182	50	$C_8H_{15}Cl_4NO_2$
27	$—CH_2CH_2CH_2CH_2CH_2—$		191	52	$C_9H_{17}Cl_4NO$

[a] All m.p. for analytical samples; all products melted with decomposition. [b] Yields for recrystallized products.

EXPERIMENTAL

Allyl glycidyl ether was obtained from Matheson, Coleman and Bell and used as received. 4,4,4-Trichloro-1,2-epoxybutane (b.p. 80–81°/25 mm.) was obtained from the Chemicals Division, Olin Mathieson Chemical Corp., and used as received.

3-(2-Propeneoxy)-1-amino-2-propanols. A mixture of 0.40 mole of the amine and 0.30 mole of allyl glycidyl ether was heated at 85° to 125° C. for 4 to 8 hours. A moderately exothermic reaction was usually observed. The reaction mixture was then cooled to room temperature and distilled under reduced pressure. The excess amine was recovered as the first fraction. The amino alcohols were obtained as the second fraction.

4,4,4-Trichloro-1-amino-2-butanol Hydrochlorides. To a well-stirred boiling solution of amine (0.22 mole) in 150 ml. of solvent (ethanol or toluene), 4,4,4-trichloro-1,2-epoxybutane (0.20 mole) was added dropwise over 1 to 2.5 hours. The reaction mixture was boiled under reflux for 2 to 7 hours. The solvent was removed in vacuo, and the residual oil was dissolved in 300 ml. of anhydrous ether. Ethereal hydrogen chloride was then added dropwise (ice bath) until precipitation was complete. The solid product was collected, washed with ether, and recrystallized from ethanol plus ethyl acetate.

ACKNOWLEDGMENT

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Esters of 2,5-Bis(trichloromethyl)-*N*-(1-hydroxy-2,2,2-trichloroethyl)-4-imino-1,3-dioxolane

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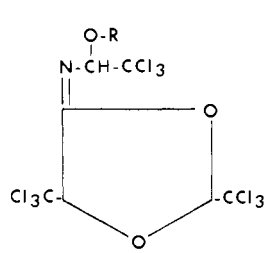
Esters of 2,5-bis(trichloromethyl)-*N*-(1-hydroxy-2,2,2-trichloroethyl)-4-imino-1,3-dioxolane, Wallach's compound, were synthesized.

THE SYNTHESIS of Wallach's compound from chloral or chloral hydrate and potassium cyanide (*2, 3, 6*) and the preparation of its acetate, benzoate, and ethylcarbonate ester derivatives have been described (*1, 3, 4*).

Recently, Franck and Hennessy (*4*) reported the structure of Wallach's compound to be 2,5-bis(trichloromethyl)-*N*-(1-hydroxy-2,2,2-trichloroethyl)-4-imino-1,3-dioxolane (I, R = H). Their conclusion was based on the chemical behavior and infrared and NMR spectra of Wallach's compound and its benzoate ester (I, R = C_6H_5CO).



I

We have synthesized nine new esters of 2,5-bis(trichloromethyl)-*N*-(1-hydroxy-2,2,2-trichloroethyl)-4-imino-1,3-dioxolane. The physical properties of these compounds are summarized in Table I.

The infrared spectra of these esters had two strong absorption bands in the 5.5- to 6-micron region. The first band at 5.60 to 5.70 microns was assigned to the carbonyl group of the ester. This band position is similar to that observed for the carbonyl group in esters of chloral hemimercaptals, R—S—$CH(O_2CR)CCl_3$ (*5*). The second strong absorption band appeared at 5.75 to 5.80 microns and was assigned to the iminocarbonyl group. Franck and Hennessy (*4*) have reported that Wallach's compound had an infrared absorption band at 1745 $cm.^{-1}$ due to the iminocarbonyl group, and that its benzoate ester had a broad infrared absorption at 1750 to 1730 $cm.^{-1}$

EXPERIMENTAL

The infrared spectra were recorded on Perkin-Elmer Model 137 infrared spectrophotometer in KBr disks. The