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2,4,4,4-TETRACHLORO-1-BUTANOL AND ITS DERIVATIVES—I

REACTION WITH AMINES

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Abstract—2,4,4,4-Tetrachloro-1-butanol gives with amines substituted 2-amino-3-buten-1-ols and very small amounts of 1-amino-3-buten-2-ols. 4,4,4-Trichloro-1,2-epoxybutane, in contrast to this, gives exclusively the latter. The proof of structure of the products utilized evidence of hydrogenolysis and comparison with the authentic compounds. A unified picture of reactions of 2,4,4,4-tetrachloro-1-butanol is presented and discussed.

The recent availability of 2,4,4,4-tetrachloro-1-butanol[1] (I) in large quantities and in good yield prompted us to examine some of its reactions. In this paper we describe its reactions with amines.

When 2,4,4,4-tetrachloro-1-butanol (I) was heated at 100° with excess of morpholine, dehydrochlorination took place and about 2 equivs of morpholine hydrochloride was isolated. The liquid product was shown to be pure by g l c except for about 5% of an impurity with a shorter retention time. Its IR spectrum showed a strong hydroxyl band and a medium band at 6·22 μ, assignable to a dichloromethylene group.[2] The NMR spectrum of the compound showed an ethylenic proton as a doublet centred at $4{\cdot}23\tau (J \sim 8$ c/s) and two multiplets at $6{\cdot}5\tau$(8 H's) and $3{\cdot}5\tau$(4 H's).[3] The compound reacted exothermically with phenyl isocyanate to give a solid phenylurethane. Crystalline methiodide, hydrochloride and picrate could also be readily obtained.

On the basis of this evidence the structure of 2-morpholino-4,4-dichloro-3-buten-1-ol (II) was assigned to the product resulting from the reaction of 2,4,4,4-tetrachlorobutanol (I) and morpholine.

In accord with the proposed structure, II absorbed 3 equivs of hydrogen[4] in the presence of Raney nickel and potassium hydroxide and gave a halogen-free amino alcohol, 2-morpholino-1-butanol (III). Although its benzoate was liquid, its picrate was crystalline and was different from the isomeric 1-morpholino-2-butanol (VIII) prepared independently (see below).

In order to define the scope and the limitations of the reaction of I with morpholine other amines were studied. As with morpholine, fair to good yields of products

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[1] M. Asscher and D. Vofsi, *J. Chem. Soc.* 1887 (1963). An improved synthesis of I as well as of some of its derivatives is given in the Experimental.

[2] E.g., K. Pilgrim and F. Korte, *Tetrahedron Letters* 883 (1962).

[3] For the NMR spectrum of morpholine itself, see NMR Spectra Catalog, Varian Associates, 1962, Spectrum No. 83.

[4] For hydrogenating dehalogenation of vinylic chlorides, cf. L. Horner, L. Schläfer and H. Kämmerer, *Chem. Ber.* **92**, 1700 (1959).

TABLE 1. REACTION OF 2,4,4,4-TETRACHLORO-1-BUTANOL AND AMINES
$CCl_3CH_2CHClCH_2OH + HNR'R'' \rightarrow CCl_2{=}CHCH\,(NR'R'')CH_2OH$

Amine	B.p., °C (mm)	n_D^t	Yield, %	Empirical formula	Analysis							
					Carbon		Hydrogen		Chlorine		Nitrogen	
					Calc.	Found	Calc.	Found	Calc.	Calc.	Calc.	Found
Morpholine	103 (0·3)	^{28}1·5212	88	$C_8H_{13}Cl_2NO_2$	42·49	42·18	5·79	5·84	31·36	31·12	6·20	6·08
Piperidine	85–87 (0·1)[a]	—	74	$C_9H_{15}Cl_2NO$	48·23	48·22	6·75	6·86	31·63	31·47	6·25	6·32
N-Methylpiperazine	110 (0·2)	—	73	$C_9H_{16}Cl_2N_2O$	45·18	44·99	6·74	6·79	29·64	29·59	11·71	11·57
Hexamethyleneimine	90–94 (0·05)	—	86	$C_{10}H_{17}Cl_2NO$	50·43	50·31	7·20	7·12	29·78	29·70	5·88	5·85
Pyrrolidine	80–83 (0·15)[b]	—	80	$C_8H_{13}Cl_2NO$	45·73	45·97	6·24	6·31	33·75	33·61	6·67	6·51
Diethylamine	69–71 (0·5)	^{27}1·4841	86·5	$C_8H_{15}Cl_2NO$	45·30	45·33	7·13	7·03	33·43	33·34	6·61	6·49
Di-n-butylamine	105–106 (0·5)	^{26}1·4769	44	$C_{12}H_{23}Cl_2NO$	53·73	53·44	8·64	8·53	26·43	25·69	5·22	4·83
2-Methylamino-1-ethanol	111–115 (0·2)	^{25}1·5083	65·5	$C_7H_{13}Cl_2NO_2$	39·27	39·24	6·12	6·16	33·12	33·17	6·54	6·49
2-Amino-1-ethanol	134–135 (0·2)	^{26}1·5185	63	$C_6H_{11}Cl_2NO_2$	36·02	36·15	5·54	5·56	35·44	35·27	7·00	7·17
Ethylenediamine	132–138 (0·2)	—	10	$C_6H_{12}Cl_2N_2O$	36·20	36·98	6·08	6·30	35·62	33·34	14·07	13·42

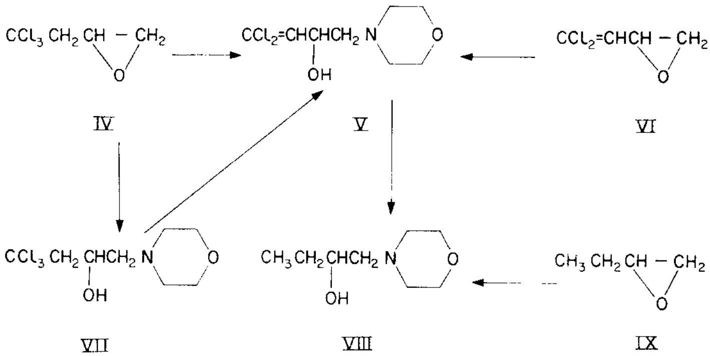
[a] Methiodide, m.p. 126–127° (acetone containing a small amount of MeOH). (Found: C, 32·69; H, 4·99; Cl, 19·29; I, 34·76; N, 3·68. Calc. for $C_{10}H_{18}Cl_2INO$: C, 32·81; H, 4·95; Cl, 19·37; I, 37·67; N, 3·83%).

[b] After recrystallization from petroleum pentane the sample had m.p. 76–77°.

could be obtained (Table 1). The reaction could be carried out with or without solvents or diluents (such as toluene of 1,2-dimethoxyethane), but it was found that the amount of amine should be at least 3 equiv, and generally a slight excess of this amount was used. Secondary amines gave best yields, but the primary diamine ethylenediamine gave a low yield, no doubt reflecting its higher functionality.

When IV and morpholine were subjected to the conditions under which II was obtained from I, the product was isomeric with II and identical with the contaminant present in the reaction product of I and morpholine. It reacted very slowly with phenyl isocyanate and gave no solid phenylurethane. In contrast to II, it reacted more rapidly with methyl iodide to give a methiodide. Its hydrochloride, m.p. 174–175°, showed no $CCl_2=$ in the IR, thereby indicating addition of HCl to the double bond. The final proof of structure of the product of IV and morpholine was obtained as shown in Chart I.

Chart I



An analogous series of reactions was carried out with epoxide IV and piperidine. Thus, IV and piperidine gave 1-piperidino-4,4-dichloro-3-buten-2-ol (X) which was characterized by its crystalline methiodide and hydrochloride. Hydrogenation of X gave 1-piperidino-2-butanol (XI) which was identical with the amino alcohol obtained from the reaction of 1,2-epoxybutane and piperidine. The two samples also led to the same hydrochloride.

The fact that IV gave rise to VII under the milder conditions[5] suggests that the latter is an intermediate in the reaction of IV with morpholine at 100° to give V. An attempt was made to isolate an analogous intermediate from the reaction of I and morpholine at room temperature, but although one equivalent of morpholine hydrochloride could be obtained, the product consisted of a complex mixture of compounds, including unused I. Although the epoxide IV would seem reasonable as an intermediate in the reaction of I and morpholine, it is apparent that it is not formed there, since IV leads to the isomeric alcohol V, and not to II.

Clearly, then, two different paths are involved in the reaction of I and of IV with morpholine. Furthermore, it is very unlikely for a simple displacement to occur in I and to produce a good yield of II. Therefore, the dichotomy in the reactions of I and of IV with morpholine may be rationalized as shown in Chart II.

Alcohol I may react in two distinct ways, *viz.* (1) by formation of the epoxide

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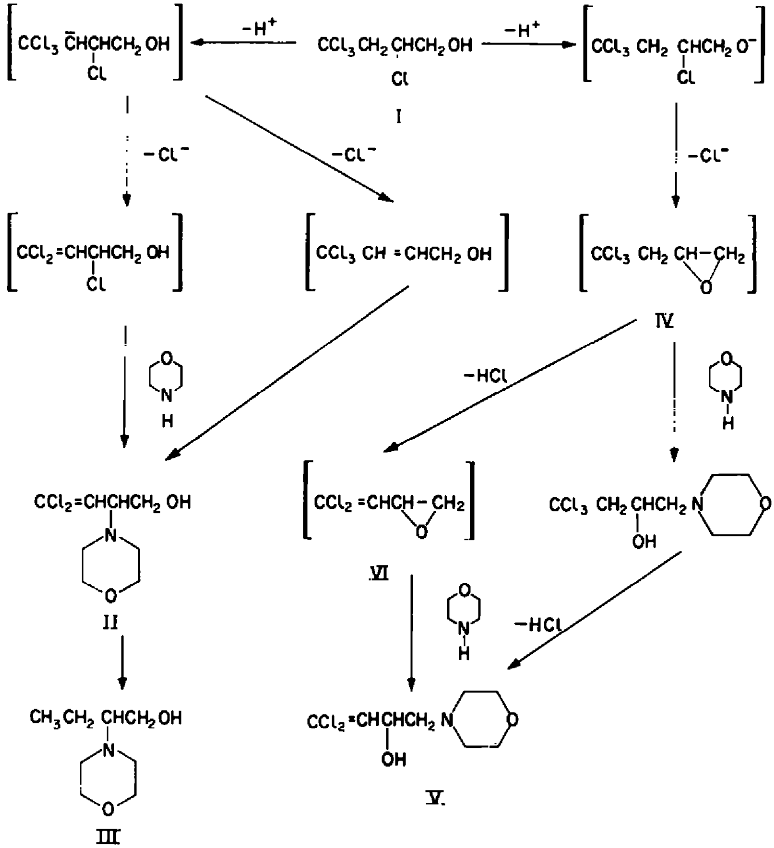
[5] Cf. W. Reeve and L. W. Fine, *J. Amer. Chem. Soc.* **86**, 880 (1964) for a similar reaction of 3,3,3-trichloro-1,2-epoxypropane with amines.

Chart II



IV, and (2) by dehydrochlorination. The former route is not important since it furnishes only about 5% of the product V which is formed predominantly by way of VII. The more important route is dehydrochlorination to form the two intermediates shown of which the chlorohydrin, being an allylic chloride, is probably the one leading to the product II.

EXPERIMENTAL

Reaction of 2,4,4,4-*tetrachloro*-1-*butanol* (I) *and morpholine*

2-*Morpholino*-4,4-*dichloro*-3-*buten*-1-*ol* (II). To 87·1 g (1·00 mole) morpholine there was added with stirring over a period of 30 min 20·2 g (0·095 mole) I, the temp being held below 30°. The mixture was then gradually heated to 100° and stirred at this temp for 3 hr. It was then cooled and the solid was filtered off, washed with a small amount of ether and dried to obtain 25·0 g (0·20 mole) morpholine hydrochloride, m.p. 173–175°. Distillation of the filtrate gave 16·8 g (78%) II, b.p. 110–135° (0·3 mm). Redistillation gave 15·1 g II, b.p. 103–106° (0·2 mm) showing a strong hydroxyl band at 2·94 μ, a medium band at 6·22 μ and weak absorption at 5·6 to 6·1 μ in the IR. The compound, a viscous yellowish oil, was partly soluble in water and showed two peaks in gas chromatography in the ratio of about 95:5. (Found: C, 42·65; H, 5·99; Cl, 31·12; N, 6·38. Calc. for $C_8H_{13}Cl_2NO_2$: C, 42·49; H, 5·79; Cl, 31·36; N, 6·20).

Purification of II through crystallization of the hydrochloride, liberation of the free base by potassium carbonate and distillation gave the product which showed only one band in gas chromatography, b.p. 103° (0·3 mm), n_D^{28} 1·5212. (Found: C, 42·18; H, 5·84; Cl, 31·12; N, 6·08%).

2-*Morpholino*-4,4-*dichloro*-3-*buten*-1-*yl phenylcarbamate* was prepared by the exothermic reaction of II and phenyl isocyanate, a white solid, m.p. 136–137° (from benzene and petroleum hexane), medium band at 3·10 μ, strong band at 5·82 μ and a strong doublet at 6·27 μ in the IR. (Found: C, 52·17; H, 5·19; Cl, 20·54; N, 8·05. Calc. for $C_{15}H_{18}Cl_2N_2O_3$: C, 52·18; H, 5·25; Cl, 20·54; N, 8·12%).

2-*Morpholino*-4,4-*dichloro*-3-*buten*-1-*ol methiodide*, m.p. 170–172° (dec) was crystallized from MeOH and ether, strong bands at 3·04 μ and 6·20 μ in the IR. (Found: C, 29·35; H, 4·34; Cl, 19·21; I, 34·43; N, 3·84. Calc. for $C_9H_{16}Cl_2INO_2$: C, 29·37; H, 4·38; Cl, 19·27; I, 34·48; N, 3·81%).

2-*Morpholino*-4,4-*dichloro*-3-*buten*-1-*ol hydrochloride* was prepared by mixing 20·0 g II and 40 ml conc. HCl, evaporating *in vacuo* and recrystallizing from a mixture of MeOH and acetone, yielding 22·8 g (98%), nearly white solid, m.p. 202–204° (dec), sharp strong band at 3·04 μ, strong complex absorption at 3·4–4·2 μ and a medium sharp band at 6·16 μ. (Found: C, 36·64; H, 5·45; Cl, 40·26; N, 5·30. Calc. for $C_8H_{14}Cl_3NO_2$: C, 36·59; H, 5·37; Cl, 40·51; N, 5·34%).

2-*Morpholino*-4,4-*dichloro*-3-*buten*-1-*ol picrate* was a yellow solid, m.p. 167–169° from MeOH. (Found: C, 37·21; H, 3·87; Cl, 15·63; N, 12·21. Calc. for $C_{14}H_{16}Cl_2N_4O_9$. C, 36·94; H, 3·54; Cl, 15·58; N, 12·31%).

In a larger run the molar ratio of I to morpholine was 1:3·7 and the yield of the product was 88%. Solvents such as toluene or 1,2-dimethoxyethane also have been used to good advantage in this reaction.[6]

Reaction of 2,4,4,4-*tetrachloro*-1-*butanol with other amines*

The alcohol I (1 mole) was heated with the amine (3·5–5 moles) for 3–6 hr at 100° (27 hr at 86° for diethylamine, 11·5 hr at 100° for 2-hydroxyethylamine). The mixture was then cooled, diluted with benzene, and filtered to obtained ca. 2 moles of the respective amine hydrochloride. The filtrate was distilled to obtain the compounds shown in Table 1. All the compounds showed IR bands at 2·9–3·1 μ (hydroxyl) and at 6·2 μ (CCl_2=).

Hydrogenation of 2-*morpholino*-4,4-*dichloro*-3-*buten*-1-*ol* (II)

To a solution of 19·7 g (0·30 mole) KOH (85% purity) in 75 ml MeOH there was added 22·6 g (0·10 mole) II and 10 ml Raney Ni. The resulting mixture was shaken with H_2 at an initial press. of 50 p.s.i. In 4 hr the mixture absorbed 0·305 mole H_2. The mixture was then filtered and the solid was washed with ether. The filtrate was evaporated, the residue diluted with ether, and the resulting ether solution was washed with water and dried. Distillation gave 5·5 g liquid, b.p. 96–100° (13·0 mm). It was redistilled to obtain 4·5 g liquid, b.p. 99–102° (3·5 mm), n_D^{24} 1·4702, showing a hydroxyl band at 2·90 μ but no absorption between 5 and 6·5 μ. Its gas chromatogram showed about 15% of a lower boiling component.

2-*Morpholino*-1-*butanol picrate* was prepared from 1·59 g of the above hydrogenated product, a yellow solid, m.p. 114–125°, 3·61 g. The analytical sample, m.p. 129–131°, was prepared by several recrystallizations from MeOH. Its IR spectrum was different from that of 1-morpholino-2-butanol picrate (see below). (Found: C, 43·17; H, 5·26; N, 13·85. Calc. for $C_{14}H_{20}N_4O_9$; C, 43·30; H, 5·10; N, 14·43%).

2-*Morpholinobutyl benzoate*, a liquid, b.p. 144–145° (0·5 mm), showed no hydroxyl band, but a strong band at 5·82 μ in the IR. (Found: C, 67·91; H, 7·82; N, 5·72. Calc. for $C_{15}H_{21}NO_3$: C, 68·41; H, 8·04; N, 5·32%).

Reaction of 2-*morpholino*-4,4-*dichloro*-3-*buten*-1-*ol with acetic acid*

Hydrogen chloride was passed for 4 hr through a solution of 22·6 g (0·10 mole) II in 100 ml acetic acid while the temp was kept at 30–35° and until the solution was saturated with HCl. The solution was stirred at room temp for 10 hr, then acetic acid was removed *in vacuo*. The residue was dissolved in a small amount of water and the resulting solution made slightly alkaline by addition of solid $NaHCO_3$. The mixture was then extracted with ether and the ether extract dried. Evaporation of the extract and distillation of the resulting residue gave 22·1 g (82·5%) colourless liquid, b.p. 126° (0·3 mm) to 117° (0·1 mm). Redistillation gave the analytical sample, b.p. 122° (0·1 mm), n_D^{26} 1·4977, showing a very weak band at 2·9 μ, a strong band at 5·76 μ and a medium sharp band at 6·20 μ in the IR. (Found

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[6] In large scale runs (3 moles I) an exothermic reaction set in at 90° and could not be controlled by cooling, although 2 mole runs were carried out on several occasions without incident.

C, 44·93; H, 5·71; Cl, 26·51; N, 5·09. Calc. for $C_{10}H_{15}Cl_2NO_3$: C, 44·79; H, 5·64; Cl, 26·45; N, 5·22%).

Reaction of 4,4,4-*trichloro*-1,2-*epoxybutane* (IV) *and morpholine*

1-*Morpholino*-4,4-*dichloro*-3-*buten*-2-*ol* (V). A mixture of 175·5 g (1·00 mole) IV and 305 g (3·50 mole) morpholine was heated to 100° whereupon a slight exothermic reaction occurred. The mixture was kept at 100° for 5 hr, then cooled and diluted with 100 ml benzene. Filtration, washing with a small amount of benzene and drying gave 83·5 g morpholine hydrochloride, m.p. 173–175°. The filtrate was distilled to obtain, in addition to lower-boiling fractions, 204 g liquid, b.p. 115–135° (0·2 mm). Fractionation of the distillate gave 193 g (85·5%) of V, b.p. 110–114° (0·1 mm), n_D^{26} 1·5092. It was homogeneous in gas chromatography and it proved to be identical with the lower boiling impurity in the reaction of I and morpholine. Its IR spectrum was different from II and showed a band at 2·92 μ and a medium doublet at 6·03 and 6·16 μ. (Found: C, 40·63; H, 5·99; Cl, 32·38; N, 6·04. Calc. for $C_8H_{13}Cl_2NO_2$: C, 42·49; H, 5·79; Cl, 31·36; N, 6·20%).

1-*Morpholino*-4,4-*dichloro*-3-*buten*-2-*yl phenylcarbamate* could not be prepared under the conditions of preparation of the urethane of II. The reaction was not exothermic and no solid could be isolated.

1-*Morpholino*-4,4-*dichloro*-3-*buten*-2-*ol methiodide*, a white solid, m.p. 204–205° (dec), showed bands at 3·10 and 6·17 μ in the IR. (Found: C, 29·30; H, 4·24; Cl, 19·34; I, 34·32; N, 3·72. Calc. for $C_9H_{16}Cl_2INO_2$: C, 29·37; H, 4·38; Cl, 19·27; I, 34·48; N, 3·81%).

1-*Morpholino*-3,4,4-*trichloro*-2-*butanol hydrochloride* was prepared from V by dissolving it in conc HCl, letting it stand overnight, evaporating to dryness and recrystallizing from acetone containing a small amount of MeOH. It was obtained as a white solid, m.p. 174–175°, showing a strong band at 3·08, broad absorption at 3·7 to 4·0 μ, but no absorption between 4·5 and 6·5 μ in the IR. (Found: C, 32·23; H, 5·23; H, 5·22; Cl, 45·22; N, 4·60. Calc. for $C_8H_{15}Cl_4NO_2$: C, 32·13; H, 32·13; H, 5·06; Cl, 47·43; N, 4·68%).

Reaction of 4,4,4-*trichloro*-1,2-*epoxybutane* (IV) *and morpholine at room temperature*

1-*Morpholino*-4,4,4-*trichloro*-2-*butanol* (VII). A mixture of 26·4 g (0·15 mole) IV and 13·1 g (0·15 mole) morpholine was allowed to stand at room temp for 12 days. After this, 30 ml benzene was added and 0·05 g morpholine hydrochloride (m.p. and IR spectrum) was filtered off. The filtrate was evaporated to give 39·5 g yellow viscous oil. Distillation of this gave 35·0 g (88%) yellowish oil, b.p. 110–115° (0·1 mm) which turned red on standing. Its IR spectrum showed a strong band at 2·92 μ but it was transparent from 3·6 to 6·9 μ (band around 6·2 μ absent). The analytical sample, obtained by redistillation, was a colourless viscous liquid, b.p. 102–105° (0·15 mm). (Found: C, 36·68; H, 5·19; Cl, 40·82; N, 5·40. Calc. for $C_8H_{14}Cl_3NO_2$: C, 36·59; H, 5·37; Cl, 40·51; N, 5·34%

The attempted preparation of the methiodide of VII gave instead, as the only isolable compound, the methiodide of V, identical in the m.p. and IR spectrum with the authentic compound.

Dehydrochlorination of VII

1-*Morpholino*-4,4-*dichloro*-3-*buten*-2-*ol* (V). A mixture of 14·5 g (0·055 mole) VII, 3·65 g (0·055 mole) 85% KOH and 50 ml MeOH was heated under reflux and stirred for 3 hr, and then cooled. Nearly all the MeOH was removed in a stream of air, the residue diluted with ether and the resulting ether solution was washed with water. After drying, the ether was evaporated and the residue distilled to obtain 6·91 g V, b.p. 99–101° (0·15 mm), n_D^{25} 1·5092, identical in its IR spectrum with that of the authentic V. Its methiodide, prepared in the usual manner, was identical in its m.p. and IR spectrum with the authentic methiodide of V.

Reaction of 1,1-*dichloro*-3,4-*epoxy*-1-*butene* (VI) *and morpholine*

A mixture of 13·9 g (0·10 mole) VI and 9·0 g (0·104 mole) morpholine was heated at 100° for 5 hr, then cooled and filtered to remove a small amount of solid. Distillation gave 15·5 g liquid, b.p. 95–98° (0·4 mm), which was redistilled to obtain 12·8 g V, b.p. 93–95° (0·4 mm), $n_D^{25.5}$ 1·5110. Its IR spectrum was indistinguishable from the butenol V obtained from morpholine and IV.

Reaction of 4,4,4-*trichloro*-1,2-*epoxybutane and piperidine*

1-*Piperidino*-4,4-*dichloro*-3-*buten*-2-*ol* (X). A mixture of 52·6 g (0·30 mole) V and 89·5 g (1·05 mole) piperidine was heated to 80°. An exothermic reaction occurred and the temp was kept below 100°. After the reaction had subsided, the mixture was heated at 100° for 5 hr, then cooled and diluted with

50 ml benzene. Filtration, washing with a small amount of benzene and drying gave 38·9 g piperidine hydrochloride, m.p. 240–241°. The filtrate was freed of benzene and the residue was distilled to obtain 56·8 g (84·5%) X, b.p. 79–80° (0·2 mm), n_D^{26} 1·5072, showing a medium band at 2·95 and a strong band at 6·16 μ in the IR. It was homogeneous in gas chromatography. (Found: C, 47·95; H, 6·87; Cl, 31·52; N, 6·13. Calc. for $C_9H_{15}Cl_2NO$: C, 48·23; H, 6·75; Cl, 31·63; N, 6·25%).

1-*Piperidino-4,4-dichloro-3-buten-2-ol methiodide*, m.p. 155–157° (acetone and MeOH), showed a strong band at 3·11, a medium band at 6·17 μ, but no bands between 3·6 to 6·1 μ in the IR. (Found: C, 32·94; H, 5·02; Cl, 18·87; I, 34·12; N, 3·58. Calc. for $C_{10}H_{18}Cl_2INO$: C, 32·81; H, 4·96; Cl 19·37; I, 34·67; N, 3·83%).

1-*Piperidino-4,4-dichloro-3-buten-2-ol hydrochloride*, a white solid, m.p. 160–162° (mixture of MeOH, acetone and ether), showed a medium band at 3·16, a mulliplet at 3·8, and a medium band at 6·18 μ in the IR. (Found: C, 41·33; H, 6·10; Cl, 40·56; N, 5·18. Calc. for $C_9H_{16}Cl_3NO$: C, 41·48; H, 6·19; Cl, 40·82; N, 5·38%).

Hydrogenation of 1-*morpholino-4,4-dichloro-3-buten-2-ol* (V)

A solution of 22·6 g (0·10 mole) V in 100 ml MeOH was shaken with 1·0 g 5% Pd–C and H_2 at an initial press. of 50 p.s.i. The mixture absorbed 0·158 mole H_2 in about 4 hr whereupon absorption stopped. The mixture was evaporated on the steam bath and the residue diluted with acetone and ether and allowed to crystallize. Filtration and recrystallization of the resulting solid from a mixture of MeOH, acetone and ether gave 9·1 g white solid, m.p. 125–135°. Several recrystallizations from the same mixture of solvents gave slightly impure 1-morpholino-2-butanol hydrochloride, m.p. 165–166·5° showing medium absorption at 3·12 μ but none from 4·2 to 6·8 μ in the IR. Its m.p. on admixture of authentic VIII hydrochloride (see below) was 166–169°, and the two samples showed identical IR spectra.

The filtrate obtained in the initial filtration of the solid was evaporated to dryness *in vacuo*, then was treated with K_2CO_3 aq. The resulting mixture was extracted thoroughly with ether, the extract dried and evaporated *in vacuo*. Distillation of the residue gave 9·0 g liquid, b.p. 56–113° (0·1 mm), n_D^{26} 1·4811, showing a medium hydroxyl band at 2·95 and a weak band at 6·18 μ ($Cl_2C{=}$) in the IR. The material showed Cl_2 (Beilstein) and a small amount of a high boiling impurity. Fractionation through a simple unpacked column gave, in addition to higher-boiling fractions, 3·1 g liquid, b.p. 46–52° (0·01 mm), n_D^{26} 1·4618, slightly contaminated with a Cl_2-containing impurity. (Found: C, 59·35; H, 10·59; N, 8·57. Calc. for $C_8H_{17}NO_2$: C, 60·34; H, 10·76; N, 8·80%).

The *hydrochloride* was a white solid, m.p. 171–172°, mixed m.p. with VIII hydrochloride, 170–173°. Its IR spectrum was indistinguishable from that of the authentic hydrochloride of VIII.

Hydrogenation of 1-*piperidino-4,4-dichloro-3-buten-2-ol* (X)

A solution of 22·4 g (0·10 mole) X in 100 ml MeOH was shaken with 1·0 g 10% Pd–C and H_2 at an initial press. of 50 p.s.i. The mixture absorbed 0·195 mole H_2 in 3 hr and then the absorption stopped. The mixture was filtered and the filtrate was evaporated on the steam bath. The residue was dissolved in acetone and ether and allowed to crystallize. Filtration gave 4·0 g white solid, m.p. 195–197°. Several recrystallizations from a mixture of acetone and MeOH gave the analytical sample, m.p. 199–200°, showing a strong band at 3·04, broad absorption at 3·6–4·0 and no bands at 4·5 to 6·5 μ in the IR. Its m.p. was undepressed on admixture of the authentic 1-piperidino-2-butanol hydrochloride (see below) and the IR spectra of the two compounds were indistinguishable from each other. (Found: C, 55·82; H, 10·35; Cl, 18·33; N, 7·27. Calc. for $c_9H_{20}ClNO$: C, 55·80; H, 10·41; Cl, 18·30; N, 7·23%).

Working up the filtrate as in the hydrogenation of V gave 10·4 g impure liquid (gas chromatography), b.p. 50–94° (0·2 mm), n_D^{27} 1·4865, showing Cl_2 by Beilstein test.

Reaction of 1,2-*epoxybutane* (IX) *and morpholine*

1-*Morpholino-2-butanol* (VIII). A mixture of 27·0 g (0·31 mole) morpholine and 21·6 g (0·30 mole) IX was heated at reflux (77°). After about 4 hr, the temp rose to 100° and the reaction mixture was stirred at this temp for an additional 2 hr. Distillation gave 32·2 g (67·5%) butanol, b.p. 86·89° (4 mm). Redistillation gave 29·4 g colourless liquid, b.p. 97–98° (7 mm), n_D^{25} 1·4621. It showed a band at 2·90 μ, but had no absorption between 5 and 6·5 μ in the IR. It was homogeneous in gas chromatography. (Found: C, 60·33; H, 10·32; N, 9·17. Calc. for $C_8H_{17}NO_2$: C, 60·34; H, 10·76; N, 8·80%).

1-*Morpholino-2-butanol hydrochloride*, from VIII and conc HCl, was recrystallized from acetone containing a small amount of MeOH. The analytical sample, m.p. 172–173°, showed a strong sharp band at 3·08 μ, broad bands at 3·70 to 4·0 μ, but was transparent in the region from 4·0 to 6·75 μ in the IR. (Found: C, 49·21; H, 9·25; Cl, 18·22; N, 7·15. Calc. for $C_8H_{18}ClNO_2$: C, 49·10; H, 9·27; Cl, 18·12; N, 7·16%).

1-*Morpholino-2-butanol picrate*, a yellow solid m.p. 116–117° crystallized from MeOH. It showed strong absorption at 3·1–3·3 μ and at 6·1–6·5 μ, but was transparent from 4·0 to 6·0 μ in the IR. (Found: C, 43·08; H, 5·21; N, 14·70. Calc. for $C_{14}H_{20}N_4O_9$: C, 43·30; H, 5·19; N, 14·43%).

Reaction of 1,2-*epoxybutane and piperidine*

1-*Piperidino*-2-*butanol* (XI), To 26·4 g (0·31 mole) piperidine which had been heated at 95° there was added dropwise over a period of 3 hr, 21·6 g (0·30 mole) IX and the resulting mixture was heated for an additional 7 hr at 95°. Distillation gave 42·0 g (89%) XI, b.p. 40–43° (0·05 mm). The analytical sample was obtained by redistillation, 39·6 g b.p. 80–81° (7·3 mm), n_D^{25} 1·4593. It showed one peak in gas chromatography and, in the IR spectrum, strong bands at 2·89, 3·40, 3·49 and 3·56 μ, but was transparent at 4·0 to 6·75 μ. (Found: C, 70·17; H, 12·61; N, 8·96. Calc. for $C_9H_{19}NO$: C, 68·73; H, 12·18; N, 8·91%).

1-*Piperidino-2-butanol hydrochloride* was prepared from the above alcohol and conc. HCl, m.p. 199–200° from MeOH and acetone. (Found: C, 55·76; H, 10·25; Cl, 18·32; N, 7·09. Calc. for $C_9H_{20}ClNO$: C, 55·80; H, 10·41; Cl, 18·30; N, 7·23%).

1-*Piperidino-2-butanol picrate*, m.p. 106–108° (MeOH), showed bands at 3·1 and 3·15 μ and a strong doublet at 6·12 and 6·20 μ in the IR. (Found: C, 46·60; H, 5·86; N, 14·27. Calc. for $C_{15}H_{22}N_4O_8$: C, 46·63; H, 5·74; N, 14·50%).

2,4,4,4-*Tetrachloro*-1-*butanol* (I). A mixture of 580 g (10·0 moles) allyl alcohol, 1500 ml CCl_4, 500 ml butanol and 50 g $FeCl_3 6H_2O$ was stirred and heated under reflux (72°). After about 2 hr, the colour changed from brown to green. After 14·5 hr heating the solvent was distilled to head temp. 71° and the residue cooled and washed several times with water. The organic layer was dried ($MgSO_4$), filtered, and the filtrate evaporated on a steam bath *in vacuo*. The residue was distilled to obtain 1070 g liquid, b,p. 45–85° (0·1 mm) and 157·6 g higher boiling residue. The liquid was redistilled at 0·1 mm to obtain these fractions: 32–58°, 54·6 g; 58–74°, n_D^{24} 1·4497, 14·6 g; 74–77°, n_D^{24} 1·5068, 990 g (49%). The last fraction was 2,4,4,4-tetrachloro-1-butanol. Its gas chromatogram showed a low-boiling impurity (1 ft column, 200°, neopentyl glycol succinate). In one of the first runs, 2,4,4,4-tetrachloro-1-butanol, b.p. 112° (13 mm), n_D^{24} 1·5075, was analyzed. (Found: C, 22·65; H, 2·92; Cl, 67·01. Calc. for $C_4H_6Cl_4O$: C, 22·69; H, 2·85; Cl, 66·93%).

2,4,4,4-*Tetrachlorobutyl benzoate*, white leaflets, m.p. 79·5–80·5° (from MeOH) had a strong band at 5·86 μ, a weak doublet at 6·29 and 6·35 μ in the IR. (Found: C, 41·72; H, 3·27; Cl, 44·89. Calc. for $C_{11}H_{10}Cl_4O_2$: C, 41·80; H, 3·19; Cl, 44·88%).

2,4,4,4-*Tetrachlorobutyl* p-*toluenesulfonate* was a white solid, m.p. 64–65°, showing no absorption at 3 μ, a weak sharp band at 6·28 μ and a strong band at 7·40 μ (sulfonate). (Found: C, 36·12; H, 3·24; Cl, 38·86; S, 8·85. Calc. for $C_{11}H_{12}Cl_4O_3S$: C, 36·09; H, 3·30; Cl, 38·74; S, 8·76%).

4,4,4-*Trichloro*-1,2-*epoxybutane* (IV). To a solution of 252 g (6·3 moles) NaOH in 1800 ml water there was added in one portion 1270 g (6·00 moles) I. The resulting mixture was then stirrred and heated to 75° and held at this temp. for 1 hr whereupon the pH dropped to about 7. It was then steam distilled until no more oil distilled with steam. The distillate was extracted with ether, the resulting extract dried ($MgSO_4$) and distilled at atm. press. to remove most of the ether. The residue was then distilled *in vacuo* to obtain 735 g (69·5%) 4,4,4-trichloro-1,2-epoxybutane, b.p. 109–130° (75 mm), n_D^{26} 1·4792, about 98% pure by gas chromatography (2 ft column of UCON Polar 50 HB 5100). Distillation of the higher-boiling material gave 135 g liquid, b.p. 95–100° (3·5 mm), n_D^{26} 1·5065, containing unused I and a lower-boiling impurity in a ratio of about 7:3. The analytical sample of IV was obtained by redistillation, b.p. 110° (100 mm), n_D^{26} 1·4794. (Found: C, 27·35; H, 2·94; Cl, 60·76.) Calc. for $C_4H_5Cl_3O$: C, 27·38; H, 2·87; Cl, 60·63%).

In one of the runs the lower-boiling material was fractionated several times to obtain 1,1-dichloro-3,4-epoxy-1-butene, b.p. 89–91° (80 mm), n_D^{25} 1·4908, showing a strong band at 6·13 μ (= CCl_2) in the IR, but no hydroxyl band. Gas chromatography showed about 10% of a higher-boiling compound. (Found: C, 32·51; H, 2·90; Cl, 52·20. Calc. for $C_4H_4Cl_2O$: C, 34·56; H, 2·90; Cl, 51·02%).

If only one equiv. NaOH was used at 100° the resulting IV was contaminated with unused I and other products. Epoxide IV was obtainable using 2 equiv. NaOH aq at room temp, but this was a less desirable synthesis than the one given above.

4,4,4-*Trichloro*-1,2-*butanediol dibenzoate* was prepared from IV and benzoic anhydride in the following manner. A mixture of 4·88 g (0·040 mole) benzoic acid and 5·63 g (0·040 mole) benzoyl chloride was heated to gentle reflux for 20 min, then evacuated (30 mm) for 5 min. To the resulting material there was then added 5·27 g (0·030 mole) IV and 0·50 g sodium benzoate. The mixture was heated to reflux for 15 min at the end of which it became brown and nearly homogeneous. The resulting solid was washed with $NaHCO_3$ aq and water, and then dissolved in MeOH, filtered with charcoal and allowed to crystallize. Filtration and drying gave 8·1 g nearly white solid, m.p. 85–91°. Several recrystallizations from MeOH gave the dibenzoate as white resettes, m.p. 92·5–93·5°, showing a sharp strong band at 5·84 μ and a doublet at 6·25 and 6·36 μ in the IR. (Found: C, 54·08; H, 3·86; Cl, 26·32. Calc. for $C_{18}H_{15}Cl_3O_4$: C, 53·82; H, 3·76; Cl, 26·48%).

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