stand overnight. The salt formed was dissolved with dilute sulfuric acid, the ether layer was dried and concentrated and the residue distilled through an unpacked column to give 6.79 g. (63.5%) of ethylbenzene-β-*d*, b.p. 57–58° (50 mm.), n^{20}D 1.4960 (mass spectrum,[14] Table V).

(B) **From the Tosylate of Phenethyl Alcohol.**—Phenethyl alcohol (12.2 g., 0.1 mole) was converted to its tosylate with 19 g. (0.1 mole) of *p*-toluenesulfonyl chloride.[32] The product, m.p. 38–40°, lit.[32] m.p. 39–40°, weighed 19.5 g. (70.5%).

The tosylate (11.06 g., 0.04 mole) was reduced with 1.84 g. (0.044 mole) of lithium aluminum deuteride in ethereal slurry in the usual way[33] and upon distillation through an unpacked column gave 2.67 g. (69%) of ethylbenzene-β-*d*, b.p. 59.0° (55 mm.), n^{20}D 1.4952 (mass spectrum,[14] Table V).

Monodeuterated Ethylbenzene from Monodeuterated Phenethyl Alcohol.—Monodeuterated phenethyl alcohol (3.98 g., 0.032 mole) obtained from the lithium aluminum deuteride reduction of 2-chloro-2-phenylethanol was converted to the tosylate (9.4 g., m.p. 35–45°) by 6.15 g. (0.032 mole) of *p*-toluenesulfonyl chloride.[32] The entire product was then reduced with 35 ml. (0.038 mole) of 1.1 *M* lithium aluminum hydride ethereal solution.[33] Distillation of the product through an unpacked column gave 0.36 g. (10.4%) of monodeuterated ethylbenzene, b.p. 59° (55 mm.), n^{20}D 1.4960 (mass spectrum,[14] Table V, last column).

Oxidation of Alcohols.—Monodeuterated isobutyl alcohol (0.75 g., 0.01 mole) was oxidized by a solution of 3.8 g. of potassium permanganate, 0.3 g. of sodium hydroxide and 75 ml. of water, upon standing at room temperature for 2 days. After filtration of the reaction mixture, extraction of the manganese dioxide with hot water, concentration and acidification of the combined filtrate and water extracts and continuous ether extraction of the resulting solution, 0.27 g. (30%) of isobutyric acid (partially deuterated) was obtained by distillation through a Craig column. The mass spectrum of this compound is recorded in Table VI.[14] *Anal.:* D, found, 3.08 atom %.

In a similar manner, 0.75 g. (0.01 mole) of a synthetic mixture of 85.6% isobutyl-1-*d* alcohol and 14.4% isobutyl-2-*d* alcohol was oxidized to give 0.18 g. (20%) of isobutyl acid (partially deuterated, mass spectrum[14] in Table VI), and 1.0 g. (0.013 mole) of monodeuterated *n*-butyl alcohol was oxidized to give 0.29 g. (24%) of monodeuterated *n*-butyric acid. The mass spectrum of this compound is recorded in Table VII.[14]

Anal. Calcd. for $C_4H_7DO_2$: atom % D, 12.5. Found: D, 10.92.

Similar oxidations of isobutyl alcohol in water containing 20% deuterium oxide gave isobutyric acid identical in infrared spectrum with an authentic sample (no band at 8.42 μ).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Mechanism of Halide Reductions with Lithium Aluminum Hydride. V. Reduction of β-, γ-, δ- and ε-Chloroacids and the Corresponding Chlorohydrins

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The reductions of α- and β-chloroacids containing primary, secondary and tertiary halogen to halohydrins and alcohols by means of lithium aluminum hydride are compared. While the primary and secondary halides are reduced to a similar extent in the α- and β-series, the reduction of tertiary halogen in the α-series is much more facile than the reduction of tertiary halogen in the β-series. This is in agreement with the previously proposed hydride shift mechanism for the reduction of 1,2-chlorohydrins containing tertiary halogen. Reduction of haloacids $Cl(CH_2)_nCOOH$ (n = 1–5) and the corresponding halohydrins $Cl(CH_2)_nCH_2OH$ has been studied as a function of n. Reduction of the chlorine function proceeds quite readily when n = 1 or 2 but not when n = 4 or 5. The result is interpreted in terms of a cyclic transition state for the reduction of chlorohydrins with primary halogen.

In the accompanying paper[2] it was shown that the mechanism of reduction of the secondary bromide 2-bromo-1-butanol is different from the major path of the reduction of the tertiary chloride 2-chloro-2-methylpropanol. Reduction of the tertiary halide with lithium aluminum deuteride involves in the main a hydride shift while that of the secondary halide involves direct displacement of halogen by deuterium. Nevertheless, the rather facile reduction[2,3] of 1,2-chloro- as well as bromohydrins with primary or secondary halogen cannot be a simple SN2 process, since ordinary primary and secondary chlorides (including chloroethers in which inductive effects are similar as in chlorohydrins) are not readily reduced with lithium aluminum hydride in ether. Thus it seemed of interest to study a series of 1,3-, 1,4-, 1,5- and 1,6-chlorohydrins and the corresponding chloroacids in order to determine whether these compounds display the same high reducibility as 1,2-chlorohydrins and if not, where the transition comes from the ready reducibility of the 1,2-compounds to the resistance to reduction of the simple halides. The results for the chlorohydrins (primary chloride) are shown in Table I. Since the first member of the series, ethylene chlorohydrin, was not studied, data for the secondary chlorides 2-chloro-1-propanol and 3-chloro-1-butanol are also included, as are some simple halides for purposes of comparison. Table II shows corresponding data for a series of primary chloroacids. Primary, secondary and tertiary α- and β-chloroacids are compared in Table III.

The data in Table III indicate that in comparing

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[1] Taken from the Ph.D. dissertation of J. T. Traxler.

[2] E. L. Eliel and Th. J. Prosser, THIS JOURNAL, **78**, 4045 (1956).

[3] E. L. Eliel, C. Herrmann and J. T. Traxler, *ibid.*, **78**, 1193 (1956).

TABLE I

REDUCTION OF CHLOROHYDRINS

Compound reduced	Alcohol (A) obtained, %	% Chlorohydrin (C) recovered, %	(A)/(C)
$Cl(CH_2)_3OH$	47	32	1.5
$Cl(CH_2)_4OH$	?	>41	Small
$Cl(CH_2)_5OH$	12	62	0.19
$Cl(CH_2)_6OH$	<5	66	< .08
$C_6H_5OCH_2CH_2Cl$[3]	2[b]	89[c]	.02
$C_6H_5O(CH_2)_5Cl$[3]	17[b]	77[c]	.22
$CH_3CHClCH_2OH$[a]	15	63	.24
$CH_3CHClCH_2CH_2OH$	<22	68	< .32

[a] 1.5 moles hydride per mole of chlorohydrin. In all other reactions the ratio was one mole hydride per mole chlorohydrin, see Experimental. [b] Ether. [c] Chloride.

TABLE II

REDUCTION OF CHLOROACIDS $Cl(CH_2)_nCOOH$

n	Alcohol (A) obtained, %	Chlorohydrin (C) obtained, %	(A)/(C)
1[3]	16–38	< 5	Large
2	62	21	3.0
3	<45	>18	<2.5
4	< 5.4	51	<0.11
5	11(?)[a]	66	0.17(?)

[a] This figure may be too high, having been assigned exclusively on the basis of refractive index. No discrete hexyl alcohol fraction was isolated.

TABLE III

REDUCTION OF VARIOUS α- AND β-CHLOROACIDS

Compound reduced	Type	Alcohol (A), %	Chlorohydrin (C), %	(A)/(C)
$ClCH_2COOH$[3]	α, prim.	16–38	<5	Large
$CH_3CHClCOOH$[3]	α, sec.	44	46	1.0
$(CH_3)_2CClCOOH$	α, tert.	72	2	36
$ClCH_2CH_2COOH$	β, prim.	62	21	3.0
$CH_3CHClCH_2COOH$	β, sec.	21	57	0.37
$(CH_3)_2CClCH_2COOH$	β, tert.	*ca.* 6	[a]	Small

[a] The chlorohydrin could not be isolated, but isoprene, probably formed by dehydrohalogenation and dehydration of the halohydrin, was obtained in about 38% yield.

α- with β-chloroacids with respect to ease of reduction of the halogen, one finds a marked difference between compounds in which the halogen is primary or secondary on one hand and those in which it is tertiary on the other. When the halogen is primary or secondary, its ease of reduction is similar for α- and for β-haloacids, though slightly greater in the α-series. When the halogen is tertiary, on the other hand, it is very readily reduced in the α-series but not at all readily in the β-series. This is in agreement with the hydride shift mechanism for tertiary α-chloroacids, since such a shift can take place only if the carboxyl function (or alcohol function derived from it by reduction) is vicinal to the halogen. No such shift is required in the primary α-haloacids, and thus the halogen in other primary (*e.g.*, β-) haloacids may, *a priori*, be reduced readily, even if it is not adjacent to the carboxyl or hydroxymethyl function.

Turning next to the detailed mechanism of reduction of the primary (and presumably secondary) haloacids and halohydrins, one finds (Tables I and II) that the halogen is reduced easily only if it is in the 2- or 3-position relative to the other functional group. Halogen in the 5- or 6-position is barely more reactive than that in simple halides. The situation with halogen in the 4-position (as in 4-chlorobutyric acid or 4-chloro-1-butanol) is not so clear. 4-Chloro-1-butanol (whether recovered or reaction product) tends to cyclize to tetrahydrofuran either during the lithium aluminum hydride reduction or during the hydrolysis or (less likely, in view of the precautions taken) during the distillation of the products. This not only leads to a low estimate of the recovered halohydrin but also impedes the quantitative recovery of butyl alcohol, the completely reduced product. Therefore the results for 4-chloro-1-butanol (Table I) and 4-chlorobutyric acid (Table II) are not very accurate, but they do seem to indicate that these compounds take an intermediate position between the readily reducible 2- and 3-substituted and the rather inert 5- and 6-substituted chloro compounds.

These results would seem to support a cyclic intramolecular reduction mechanism as pictured in Fig. 1.

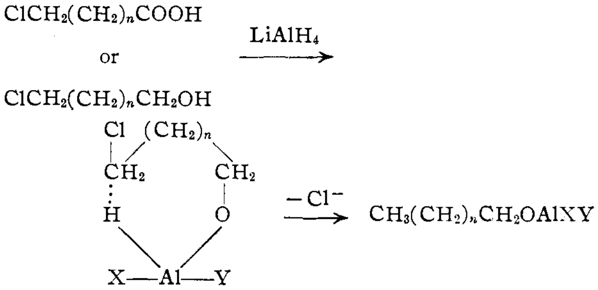

Fig. 1.

This mechanism accounts for facile reduction of the halide function in 1,2-halohydrins ($n = 0$), slightly less facile reduction of 1,3-halohydrins ($n = 1$) and still less facile reduction of 1,4-halohydrins ($n = 2$) or the corresponding halo-acids. In view of what is known about ease of ring closure as a function of ring size,[4] one would expect a five-membered cyclic transition state to be formed somewhat more readily than a six-membered one, which, in turn, ought to be formed more readily than a seven-membered one. The mechanism also accounts for the sluggish reduction of the 1,5- and 1,6-halohydrins and haloacids, since eight- and nine-membered rings do not form at all readily. What little reduction there is in the 1,5- and 1,6-substituted halides is probably due to a straight intermolecular nucleophilic attack by hydride, as observed in simple halides and epoxides.[5]

Reduction of the haloacids to alcohols is assumed to involve the corresponding halohydrins as intermediates, in agreement with results previously reported.[2,3] Yet comparison of Tables I and II indicates that in the 1,3- and 1,4-series haloacids tend to give higher yields of alcohols than the corresponding halohydrins. This is again in agreement with previous results in the 1,2-series[2,3] and is believed to be due to the nature of the groups X and Y in the intermediate shown in Fig. 1. Apparently, when X and Y are oxide or alkoxide, reduction is more facile than when X and Y are hydride

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or halide. Accordingly, reduction of 0.25 mole of 2-chloro-1-propanol with 0.44 mole of hydride in the presence of 0.25 mole of methanol gave propyl alcohol in 23.5% yield along with 47% of recovered chlorohydrin, while in the absence of methanol and with 0.375 mole of reducing agent, the yield was only 15% of propyl alcohol and 63% of chlorohydrin. The addition of water in the reduction of 2-chloro-1-propanol[6] and 2-chloro-2-phenylethanol[2] gave similar improvements in yield. Similar though more clean-cut results have recently been reported[7] in the reduction of acetone with sodium borohydride which is accelerated by water, isopropyl alcohol and triethylamine. In reductions with lithium aluminum hydride, also, there is published evidence that $AlH_{4-n}(OR)_n^-$ is a more effective reducing agent than AlH_4^-. Thus the reduction of 2-butanone in the presence of *d*-camphor gives active *sec*-butyl alcohol,[8] suggesting that the effective reducing agent contains at least one asymmetric O-bornyl group. In the reduction of 3-cyclohexyl-2-butanone, also, the second and subsequent reducing equivalents of the hydride appear to be more available than the first.[9]

In the 1,5- and perhaps also in the 1,6-series, the differences in reducibility of halohydrin and haloacid are not so remarkable. This is in agreement with the observation[6] that the addition of alcohols has no accelerating effect on the lithium aluminum hydride reduction of simple halides.

Experimental

All melting and boiling points are uncorrected. Microanalyses by Micro-Tech Laboratories, Skokie, Ill. Infrared Analyses recorded by Messrs. Anthony Verbiscar and Rolland Ro as well as the authors. All fractional distillations were performed by means of a 20-cm. helix-packed column.

3-Chloroisovaleric Acid.—A solution of 100 g. (1 mole) of 3,3-dimethylacrylic acid (Fairmount) in *ca.* 500 ml. of commercial absolute ether was saturated with hydrogen chloride at 0° and then allowed to come to room temperature in a tightly stoppered flask. After 6 days the flask was again chilled, opened and the excess hydrogen chloride and ether removed by distillation. The residue crystallized on standing. Recrystallization from petroleum ether (b.p. 30–60°) gave 101.7 g., m.p. 55–60°, and 7.5 g., m.p. 56–58°, total yield 80%. The analytical sample melted at 56–58° (lit.[10] 56–57°) and did not depress the melting point of a specimen prepared[10] from β-isovalerolactone.[11]

Anal. Calcd. for $C_5H_9ClO_2$: C, 43.96; H, 6.64. Found: C, 44.01; H, 6.73.

Reductions.—Results of the hydride reductions are summarized in Table IV. "Mole Ratio" in the table is the ratio moles hydride/moles chloride. Where the letter "s" appears a hydride slurry was employed and boiled under reflux for 1 hr. before addition of the halide; in this case the mole ratio is based on an assumed 85% available $LiAlH_4$ in the dry hydride. In all other instances clear, standardized solutions of hydride were employed. In all cases the halide was added to the hydride solution and the reaction mixture boiled with stirring for 1 to 2 hr. Decomposition was effected with sulfuric acid and the products were isolated by continuous extraction with ether.

Identification of Products.—Products were identified by derivatives and in some cases by infrared spectra. Since fractional distillation of the reaction products in many cases did not give complete separation (see Table IV), product composition was calculated in most instances on the basis of refractive index, assuming that each fraction contains only two components and that the refractive index is a linear function of composition.

3-Chloropropionic Acid.—Fraction 1 boiled at 94.5–97° (atm.) and its infrared spectrum was identical with that of propyl alcohol (b.p. 97°). Its 3,5-dinitrobenzoate melted at 75–76° (lit.[12] 74–75°), undepressed by admixture of propyl 3,5-dinitrobenzoate. The infrared spectrum of fraction 3 was identical with that of authentic 3-chloro-1-propanol (b.p. 74–76° (23 mm.)), and the fraction gave a 3,5-dinitrobenzoate melting at 75–78° (lit.[13] 77°) undepressed by admixture of an authentic sample. Since the literature[13,14] reports $n^{20}\mathrm{D}$ 1.3850 for propyl alcohol and 1.4469 for 3-chloro-1-propanol, fraction 1 is essentially pure propyl alcohol, 2 contains about 95% of this alcohol and 3 about 95% of 3-chloro-1-propanol.

3-Chlorobutyric Acid.—The infrared spectrum of the first fraction resembled that of butyl alcohol closely and its 3,5-dinitrobenzoate melted at 62–63° (lit.[15] 64°), undepressed by admixture of butyl 3,5-dinitrobenzoate. Fraction 2 gave an α-naphthylurethan melting at 84–85° after crystallization from petroleum ether.

Anal. Calcd. for $C_{15}H_{16}ClNO_2$: C, 64.84; H, 5.81. Found: C, 64.84; H, 5.66.

The literature[16] reports $n^{20}\mathrm{D}$ 1.3993 for butyl alcohol and 1.4446 for 3-chloro-1-butanol (b.p. 67–68° (15 mm.)). Thus fraction 1 is essentially pure butanol and 2 contains 84% 3-chloro-1-butanol and 16% butyl alcohol.

4-Chlorobutyric Acid.—Fractions 1 and 4 contained butyl alcohol as evidenced by the formation of a phenylurethan melting at 54–56° (lit.[17] 61°) whose melting point was not depressed by admixture of authentic butyl N-phenylcarbamate. Fraction 3 contained butyl alcohol as evidenced by the formation of a 3-nitrophthalate, m.p. 138–140° (lit.[18] 147°), undepressed on admixture of authentic butyl 3-nitrophthalate. Fraction 4 also contained tetrahydrofuran, as evidenced by its infrared spectrum. If fractions 1, 2 and 4 were pure butyl alcohol, the yield of this product would be 45%; the actual yield was obviously less than that. Fraction 2 gave a phenylurethan melting at 58–60° (lit.[19] 54°), undepressed by admixture of the phenylurethan of authentic 4-chloro-1-butanol. The literature[19] reports b.p. 84–85° (16 mm.), $n^{20}\mathrm{D}$ 1.4518, for this compound; thus fraction 2 appears to be pure 4-chloro-1-butanol, isolated in 18% yield. This is a minimum yield since some of the chlorohydrin was transformed into tetrahydrofuran during or after the reduction.

2-Chloro-2-methylpropionic Acid.—The identification of isobutyl alcohol as the major reduction product of this chloroacid already has been documented.[3] The presence of 86% of 2-chloro-2-methyl-1-propanol in fraction 3 was inferred from the boiling point, infrared spectrum and refractive index.[2] Fraction 2 was considered as pure isobutyl alcohol, 1 as a mixture of this alcohol with diethyl ether.

5-Chlorovaleric Acid.—Fraction 1 with phenyl isocyanate gave a small amount of amyl N-phenylcarbamate, m.p. 42–43° (lit.[20] 46°), undepressed by admixture of an authentic sample, in addition to much diphenylurea, suggesting the presence of water. Fraction 2 gave an α-naphthylurethan melting at 69–72° (lit.[13b] 72°) which did not depress the melting point of the α-naphthylurethan of authentic 5-chloro-1-pentanol. If fraction 1 is considered pure amyl alcohol (lit.[21] b.p. 138°, $n^{20}\mathrm{D}$ 1.4099), the yield of this alcohol is 5.4%. Fraction 2 was

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TABLE IV

REDUCTION OF HALOACIDS AND HALOHYDRINS WITH LITHIUM ALUMINUM HYDRIDE

Compound reduced (mole)	Mole ratio LAH/halide	Products				
		Fraction	B.p., °C.	Mm.	$n^{20}D$	g.
$ClCH_2CH_2COOH$[a]	1.0 s	1	62–65	160	1.3838–41[k]	13.6
(0.4)		2	to 84	33	1.3876[k]	0.9
		3	84–86	33	1.4422[k]	8.4
$CH_3CHClCH_2COOH$[b]	1.5	1	35–37	60	1.4002	0.71
(0.2)		2	71–81	30	1.4371	15.2
$ClCH_2CH_2CH_2COOH$[c]	1.5	1	30–32	6–7	1.4011	2.0
(0.2)		2	69–71	6	1.4528	3.95
		3[d]	34–41	70	1.3778	1.72
		4[d]	56–61	70	1.4050	2.92
$(CH_3)_2CClCOOH$[a]	1.5	1	55–66	Atm.	1.3724	1.07
(0.23)		2	95–106,	Atm.	1.4000	
			35–45	22	1.4077	11.64
		3	50–55	22	1.4320	0.62
$Cl(CH_2)_4COOH$[e]	1.5	1[d]	136–150	Atm.	1.3938	0.71
(0.15)		2	33–71	1.4–1.5	1.4516	9.36
$(CH_3)_2CClCH_2COOH$	1.5	1	34–45	Atm.	1.3563	12.56
(0.2)		2	45–88	Atm.	1.4150	11.67
		3	60–73	Atm.	1.4120	3.17
$Cl(CH_2)_5COOH$[f]	1.5 s	1	81–83	2.8	1.4500	10.09
(0.135)		2	83–84	2.8	1.4532	3.37
$CH_3CHClCH_2OH$	1.50	1	35–85	Atm.	1.3569	2.45
(0.25)		2	85–120	Atm.	1.3930	2.11
		3	125–130	Atm.	1.4380	14.63
$CH_3CHClCH_2OH$[g]	1.75[h]	1	35–86	Atm.	1.3559	0.77
(0.25)		2	86–92	Atm.	1.3804	1.96
		3	44–46		1.4300	12.93
$ClCH_2CH_2CH_2OH$[a]	1.0 s	1	44–52	90	1.3797	5.06
(0.2)		2	72–78	25	1.4411	6.65
$CH_3CHClCH_2CH_2OH$[i]	1.1	1	35–70	40	1.3738	1.71
(0.2)		2	87–90	40	1.4402	16.15
$Cl(CH_2)_4OH$[j]	1.0 s	1[d]	84–98	Atm.	1.4091	1.92
(0.2)		2	64–66	5	1.4509	8.77
$Cl(CH_2)_5OH$[e]	1.0	1	50–51	15	1.4197	2.68
(0.2)		2	95–98	15	1.4530	14.59
$Cl(CH_2)_6OH$[i]	1.0 s	1	40–80	2.4	1.4229	0.39
(0.07)		2	80–84	2.4	1.4538	6.21

[a] Commercial. [b] From crotonic acid.[30] [c] From γ-butyrolactone.[31] [d] Redistillation of cold trap residue. From commercial δ-chlorovaleronitrile.[32] [f] From commercial ε-chlorocapronitrile.[32] [g] In the presence of a molar equivalent of methanol. [h] Including the 0.25 mole of hydride required to react with the methanol. [i] From the acid. [j] From tetrahydrofuran.[33] [k] At 23°.

considered pure 5-chloro-1-pentanol, lit.[13b,22] b.p. 114° (16 mm.), $n^{20}D$ 1.4518.

3-Chloro-3-methylbutyric Acid.—The reduction of this compound gave rise to a mixture of compounds from which pure components were isolated only with difficulty. Redistillation of fractions 1 and 2 gave a total of 17.05 g. of material boiling below 65° at atmospheric pressure which from its odor, infrared spectrum and refractive index appeared to be a mixture of diethyl ether and isoprene. The presence of isoprene was confirmed by preparation of a maleic anhydride adduct, m.p. 63–64° (lit.[23] 63–64°), undepressed by admixture of an authentic sample. The literature[24] reports b.p. 34°, $n^{20}D$ 1.4216 for isoprene and, on the basis of refractive index, the yield of isoprene in the reduction was estimated at about 38%. The higher boiling material contained a small amount of isoamyl alcohol, identified by its 3-nitrophthalate, m.p. 163–164° (lit.[18] 163–165°), undepressed by admixture of authentic isoamyl hydrogen 3-nitrophthalate. From distillation and refractive index data the yield of isoamyl alcohol was estimated at about 6%. One fraction, weighing 0.44 g. and boiling at 80–85°, actually had an infrared spectrum resembling that of authentic isoamyl alcohol with additional bands due to water. The presence of water probably accounts for the low boiling point of the alcohol. Treatment of the material boiling above 65° with 2,4-dinitrophenylhydrazine gave a small amount of the 2,4-dinitrophenylhydrazone of methyl isopropyl ketone, m.p. 116–118° (lit.[25] 119–120°) undepressed by admixture of the 2,4-dinitrophenylhydrazone of authentic methyl isopropyl ketone. The amount of the ketone formed appeared to be small (*ca.* 1–2%) and its origin is obscure.

6-Chlorocaproic Acid.—Although no discrete fraction corresponding to hexyl alcohol was obtained, the presence of this material was inferred from the infrared spectrum of fraction 1 which showed a methyl band at 7.22 μ absent in the spectrum of 6-chloro-1-hexanol. The literature[26] reports b.p. 94° (2 mm.), $n^{20}D$ 1.4555, for 6-chloro-1-hexanol and b.p. 155.7° (760 mm.), $n^{20}D$ 1.4178, for hexanol-1. On the basis of refractive index, fraction 1 contained 15% of hexanol, corresponding to 1.5 g. or 11% yield of hexanol-1, but this figure may not be very accurate. The rest of fraction 1 (8.6 g.) and all of fraction 2 was considered 6-chloro-1-hexanol whose yield is thus computed to be 66%. The α-naphthylurethan of the chlorohydrin melted at 49–50°

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after recrystallization from petroleum ether (reported[27] 49–50°).

2-Chloro-1-propanol.—Literature data for propyl alcohol[14] are b.p. 97°, n^{20}D 1.3850, and for 2-chloro-1-propanol[28] b.p. 53° (29 mm.), n^{20}D 1.4390. Thus fraction 3 was pure 2-chloro-1-propanol, fraction 2 contained 15% of the chlorohydrin and 85% propyl alcohol and fraction 1 was assumed to be a mixture of propyl alcohol and ether containing 17% of the former. Thus the total yield of propyl alcohol is 2.2 g. (15%) and that of the chlorohydrin 14.95 g. (63%). In the reduction carried out in the presence of methanol, fraction 1 appeared to be mainly methanol (b.p. 65°, n^{20}D 1.3286), fraction 2 was calculated to contain 85% of propyl alcohol and fraction 3 contained 14% propyl alcohol and 86% 3-chloro-1-propanol. Thus the total yield of the chlorohydrin was 11.1 g. (47%) and that of propyl alcohol 3.5 g. (23.5%).

3-Chloro-1-propanol.—Fraction 1 was derivatized to propyl 3,5-dinitrobenzoate, m.p. 73.5–75°, undepressed by admixture of an authentic sample. Fraction 2 had an infrared spectrum identical to that of the starting material. From the literature data already cited[12–14] 1 appears to be essentially pure propyl alcohol and 2 to contain 91% of 3-chloro-1-propanol and 9% of propanol-1. Thus the yield of the chlorohydrin is 6.0 g. (32%) and that of the alcohol 5.7 g. (47%).

3-Chloro-1-butanol.—Fraction 1 was shown to contain butyl alcohol by preparation of the 3-nitrophthalate, m.p. 137–139°, undepressed by admixture of an authentic sample. Fraction 2 gave an α-naphthylurethan melting at 84–85° which did not depress the melting point of the analytical sample of 3-chloro-1-butyl N-α-naphthylcarbamate previously described. From the refractive index, fraction 2 is calculated to contain 91% chlorohydrin or 14.6 g. (68% recovery). The maximum amount of butyl alcohol isolated is therefore 3.25 g. (22%), the actual amount being probably less, since fraction 1 appeared to contain water.

4-Chloro-1-butanol.—From the data already cited,[19] fraction 2 appears to be pure 4-chloro-1-butanol, recovered in 41% yield.

5-Chloro-1-pentanol.—Fraction 1 contained amyl alcohol as evidenced by the formation of a phenylurethan melting at 44–47°, undepressed by admixture of authentic amyl N-phenylcarbamate. Fraction 2 was recovered 5-chloro-1-pentanol as evidenced by formation of an α-naphthylurethan melting at 70–72°, undepressed by admixture with the same derivative of the authentic chlorohydrin. From the refractive index data fraction 1 appears to contain 77% of pentanol-1 and 23% of pentamethylene chlorohydrin, while fraction 2 is pure chlorohydrin. Thus the yield of alcohol is 2.1 g. (12%) and that of chlorohydrin 15.2 g. (62%).

6-Chloro-1-hexanol.—Fraction 2, from its refractive index, appeared to be pure starting material. The maximum yield of hexanol-1 (assuming all of fraction 1 to be this material) is 5%. Hexanol-1 was proved to be present in this fraction by the preparation of its phenylurethan, m.p. 39–40° (lit.[29] 42°), undepressed by admixture of an authentic sample.

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NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Ethanolysis of 1,1,1-Trifluoro-2,3-epoxybutane and 2-Methyl-1,1,1-trifluoro-2,3-epoxypropane

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The ethanolysis of 1,1,1-trifluoro-2,3-epoxybutane and 2-methyl-1,1,1-trifluoro-2,3-epoxypropane under acidic and basic conditions results in exclusive cleavage of the carbon–oxygen bond not adjacent to the trifluoromethyl group. The $-I_s$ effect of the trifluoromethyl group is more significant in orienting cleavage than steric factors or hyperconjugative stabilization.

Discussion

The acid and base-catalyzed ring cleavage reactions of 1,1,1-trifluoro-2,3-epoxypropane (I) have been shown[2] recently to proceed with exclusive scission of the terminal ether linkage. Although propylene oxide (II) undergoes an essentially analogous cleavage with basic reagents, the reaction with acids[3] and alcohols under acid conditions[4] favors the formation of a primary alcohol.

Analogous ethoxyalcohols are formed by the ethanolysis of 2,3-epoxybutane (III)[5] and isobutylene oxide (IV).[6] Ethanolysis of III can result in only one positional isomer, but IV has been observed to form two positional isomers, predominantly the primary alcohol under acidic conditions[6] and mixtures of primary and tertiary alcohols under neutral conditions.[6b] The reaction of IV with basic reagents such as amines[7] results in exclusively tertiary alcohols while halohydrins containing the primary alcohol grouping predominate in the reactions with hydrogen halides.[8]

A study has been made of the ethanolysis reactions of 1,1,1-trifluoro-2,3-epoxybutane (V) and 2-methyl-1,1,1-trifluoro-2,3-epoxypropane (VI). Whereas exclusive terminal cleavage of I may have arisen in part through the greater accessibility of

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[1] A portion of a thesis submitted by C. E. Hathaway to Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1956.

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