[Contribution from the Central Research Department, Monsanto Chemical Company]

ALKOXYCHLOROALKENES

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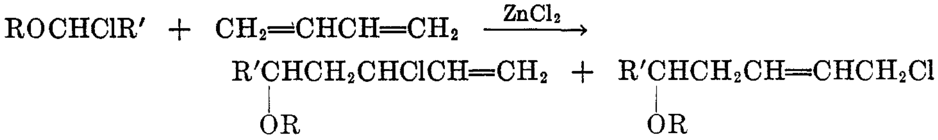
Straus and Thiel (1) showed that in the presence of mercuric chloride methyl α-chlorobenzyl ether added to butadiene to give 65% of 1-phenyl-1-methoxy-5-chloro-3-pentene and that in the presence of zinc chloride, methyl chloromethyl ether added to butadiene to give 70% of a mixture of 5-methoxy-3-chloro-1-pentene and 5-methoxy-1-chloro-2-pentene. For the latter reaction stannic chloride was as good a catalyst as zinc chloride, antimony pentachloride much better, and mercuric chloride poorer. The same type of addition was effected with methyl α-bromobenzyl ether and with bromomethyl ether.

We have found this reaction to be general for butadiene and α-chloroethers. We have effected the addition of twelve α-chloroethers to butadiene in the presence of zinc chloride and in each case have obtained a mixture of the 5-alkoxy-3-chloro-1-alkene and the 5-alkoxy-1-chloro-2-alkene in yields of 61–86%. The isomers were separated by fractional distillation at reduced pressure, since they isomerized when heated at atmospheric pressure.

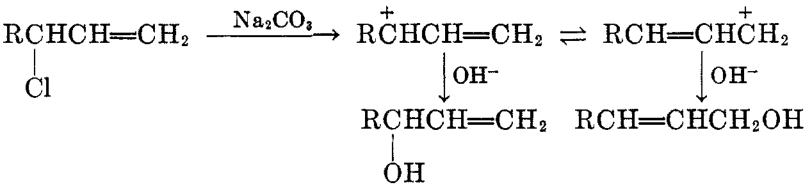


$$\mathrm{ROCHClR'} + \mathrm{CH_2{=}CHCH{=}CH_2} \xrightarrow{\mathrm{ZnCl_2}} \underset{\displaystyle \mathrm{OR}}{\mathrm{R'CH}}\mathrm{CH_2CHClCH{=}CH_2} + \underset{\displaystyle \mathrm{OR}}{\mathrm{R'CH}}\mathrm{CH_2CH{=}CHCH_2Cl}$$

As shown in Table I the higher-boiling isomer has been postulated as the 1,4-adduct. This postulation is based on boiling point and on the fact that the alcohols (predominantly primary) prepared therefrom are much more readily esterified than those (largely secondary) prepared from the lower boiling isomers.

In the presence of zinc chloride either of these compounds rearranges into a mixture of the two isomers (2).

Treatment of seven of these chlorides with boiling aqueous sodium carbonate gave unsaturated alcohols in 52–91% yields. In some cases both isomers were isolated. Since these hydrolyses were conducted in aqueous emulsion, this probably was a rearrangement of the intermediate carbonium ion before it could add an hydroxyl ion. At the temperature employed (100°) neither the chlorides nor the alcohols rearrange by themselves. Hydrogenation of nine of the unsaturated alcohols in ethanol solution in the presence of Raney nickel gave the corresponding saturated alcohols in 73–92% yields.



$$\begin{array}{ccccc} \underset{\displaystyle \mathrm{Cl}}{\mathrm{RCH}}\mathrm{CH{=}CH_2} & \xrightarrow{\mathrm{Na_2CO_3}} & \mathrm{R\overset{+}{C}HCH{=}CH_2} & \rightleftharpoons & \mathrm{RCH{=}CH\overset{+}{C}H_2} \\ & & \downarrow \mathrm{OH^-} & & \downarrow \mathrm{OH^-} \\ & & \underset{\displaystyle \mathrm{OH}}{\mathrm{RCH}}\mathrm{CH{=}CH_2} & & \mathrm{RCH{=}CHCH_2OH} \end{array}$$

TABLE I

ALKOXYCHLOROPENTENES AND ALKOXYCHLOROHEXENES

COMPOUND	B.P., °C./MM.	n_D^{25}	d_{25}^{25}	% YIELD	CALC'D		FOUND	
					C	H	C	H
5-Methoxy-3-chloro-1-pentene[a]	49/19	1.4345(20°)	0.973($\frac{20}{20}$)	66	53.5	8.18	54.3	8.05
5-Methoxy-1-chloro-2-pentene[b]	71/20	1.4512	.998		53.5	8.18	54.2	8.05
5-Ethoxy-3-chloro-1-pentene	65/21	1.4370	.959	61	56.6	8.75	56.6	8.96
5-Ethoxy-1-chloro-2-pentene	77/19	1.4460	.971		56.6	8.75	57.3	9.03
5-*n*-Propoxy-3-chloro-1-pentene	77.5/19	1.4380	.946	85	59.0	9.22	59.3	9.30
5-*n*-Propoxy-1-chloro-2-pentene	90/19	1.4445	.951		59.0	9.22	59.7	9.11
5-*n*-Butoxy-3-chloro-1-pentene	60/1	1.4400	.931	77	61.2	9.62	62.0	9.72
5-*n*-Butoxy-1-chloro-2-pentene	74/1	1.4485	.943		61.2	9.62	62.4	9.66
5-*n*-Pentyloxy-3-chloro-1-pentene	70.5–71.0/2	1.4367	.908	77	63.0	10.0	64.0	10.4
5-*n*-Pentyloxy-1-chloro-2-pentene	85/2	1.4517	.937		63.0	10.0	62.8	10.0
5-(3-Methylbutoxy)-3-chloro-1-pentene	92/3	1.4440	.929	84.3	62.9	9.99	63.4	9.79
5-(3-Methylbutoxy)-1-chloro-2-pentene	109/5	1.4485	.935		62.9	9.99	63.8	9.97
5-(2-Ethylhexoxy)-3-chloro-1-pentene	93/1	1.4478	.912	76	67.0	10.75	67.5	10.75
5-(2-Ethylhexoxy)-1-chloro-2-pentene	108/1(dec.)	1.4467	.896		67.0	10.75	—	—
5-Cyclohexoxy-3-chloro-1-pentene	85/3	1.4700	.986	77.5	65.4	9.40	67.2	9.85
5-Cyclohexoxy-1-chloro-2-pentene	90/3	1.4725	.987		65.4	9.40	66.6	9.63
5-(2-Chloroethoxy)-3-chloro-1-pentene	75/2	1.4660	1.128	82	45.9	6.56	45.6	6.60
5-(2-Chloroethoxy)-1-chloro-2-pentene	84/2	1.4735	1.130		45.9	6.56	46.1	6.60
5-Ethoxy-3-chloro-1-hexene	62/16	1.4315	0.921	86	59.0	9.2	59.1	9.5
5-Ethoxy-1-chloro-2-hexene	77.5–78.5/14	1.4489	.964		59.0	9.2	59.0	9.2
5-*n*-Butoxy-3-chloro-1-hexene	67.5/3	1.4386	.917	75	63.0	10.0	63.0	10.1
5-*n*-Butoxy-1-chloro-2-hexene	83/3	1.4490	.931		63.0	10.0	63.2	10.1
5-Isobutoxy-3-chloro-1-hexene	44/1	1.4321	.900	66	63.0	10.0	63.5	10.3
5-Isobutoxy-1-chloro-2-hexene	56/1	1.4449	.922		63.0	10.0	63.1	9.7

[a] Pudovik (2) gives b.p. 34–35°/11 mm., n_D^{20} 1.4364, d_4^{20} 0.969.

[b] Pudovik (2) gives b.p. 58–59°/13 mm., n_D^{20} 1.4540, d_4^{20} 1.001.

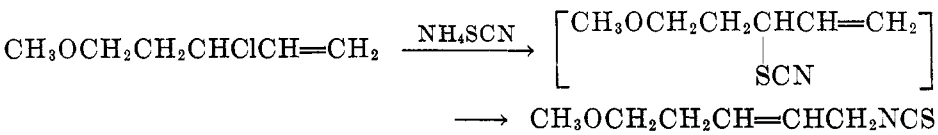
5-*n*-Butoxy-1-chloro-2-pentene reacted with sodium acetate in boiling acetamide to give 5-*n*-butoxy-2-penten-1-yl acetate in 73% conversion and 88% yield. In boiling glacial acetic acid the conversion was 64% and the yield 77%. With sodium acetate in acetic acid solution 5-isobutoxy-1-chloro-2-hexene gave the acetate in 58% yield, which was hydrogenated in the presence of Raney nickel to give 75% of 5-isobutoxy-1-hexyl acetate.

When 5-*n*-butoxy-1-chloro-2-pentene and sodium adipate were heated at 160–170° in the presence of triethylamine, a 61% yield of 5-*n*-butoxy-2-penten-1-yl adipate was obtained. Hydrogenation in the presence of Raney nickel gave 32% of the corresponding saturated adipate.

Five other saturated esters of dibasic acids were prepared by heating the corresponding alcohol and dibasic acid (or its anhydride) while the evolved water was removed as its azeotrope with toluene. The yields were 72–92%. 5-Isobutoxy-1-hexyl 4-ketopimelate was prepared in 49% yield by transesterification of the ethyl ester in the presence of a *p*-toluenesulfonic acid catalyst.

5-Ethoxy-3-chloro-1-pentene, 5-ethoxy-1-chloro-2-pentene, the mixture of 5-*n*-butoxy-3-chloro-1-pentene and 5-*n*-butoxy-1-chloro-2-pentene, and the mixture of 5-isobutoxy-3-chloro-1-hexene and 5-isobutoxy-1-chloro-2-hexene all reacted with *n*-butylamine to give 65–78% of the corresponding secondary amines. Hydrogenation in the presence of Raney nickel of *n*-butyl-5-ethoxy-2-pentenyl-1-amine, the mixed *n*-butyl-*n*-butoxypentenylamines, and the mixed *n*-butyl-isobutoxyhexenylamines gave the corresponding saturated secondary amines. The benzamide of the *n*-butyl-*n*-butoxypentylamines and the benzenesulfonamide of the *n*-butyl-isobutoxyhexylamines were prepared by the Schotten-Bauman method.

5-Methoxy-1-chloro-2-pentene, 5-methoxy-3-chloro-1-pentene, 5-*n*-butoxy-1-chloro-2-pentene, and 5-*n*-butoxy-3-chloro-1-pentene reacted with ammonium thiocyanate in boiling ethanol to give isothiocyanates in 58–86% yield. Since in each case the low-boiling chloride gave the high-boiling isothiocyanate, predominately, and *vice versa*, an allylic type rearrangement probably was involved. All four products gave a strong test for the isothiocyanate group and a negative test for the thiocyanate group. Both crotyl thiocyanate and β-ethylallyl thiocyanate undergo such a rearrangement on distillation (3). Mumm and Richter postulated a cyclic intermediate for this particular allyl rearrangement.



$$\mathrm{CH_3OCH_2CH_2CHClCH{=}CH_2} \xrightarrow{\mathrm{NH_4SCN}} \left[\mathrm{CH_3OCH_2CH_2}\underset{\substack{|\\ \mathrm{SCN}}}{\mathrm{C}}\mathrm{HCH{=}CH_2}\right] \longrightarrow \mathrm{CH_3OCH_2CH_2CH{=}CHCH_2NCS}$$

EXPERIMENTAL[1]

α-Chloroethers. The chloromethyl ethers were prepared by the method described for monochloromethyl ether (4). *n*-Butyl and *n*-pentyl chloromethyl ethers also were pre-

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[1] All analyses are microanalyses performed by the Oakwold Laboratories, Alexandria, Virginia and the Micro-Tech Laboratories, 800 Lincoln Ave., Skokie, Illinois.

pared in 87–90% yields by saturating a cold solution of trioxane in the appropriate alcohol with hydrogen chloride (5). The α-chloroethyl ethers were prepared by a modification of the Reppe and Baur synthesis (6). The vinyl ether was added to a saturated solution of hydrogen chloride in the reaction product.

Alkoxychloropentenes and alkoxychlorohexenes. A mixture of five moles of the appropriate α-chloroalkyl ether and 20 g. of fused zinc chloride was placed in a 1-liter, three-necked flask equipped with a rubber-sealed stirrer, thermometer, and gas inlet tube. Butadiene was introduced into the mixture while the temperature was held at 0–20°. When the solution was saturated, the stirring was continued while aqueous sodium carbonate was introduced to wash out the catalyst and destroy any excess chloroether. The layers were separated and the organic portion, diluted with benzene, was washed several times with water, dried over Drierite, and distilled. In each case the 5-alkoxy-3-chloro-1-pentene and the 5-alkoxy-1-chloro-2-pentene were separated by careful fractional distillation. The properties of these compounds are summarized in Table I.

Alkoxypentenols and alkoxyhexenols. A typical preparation is that of 5-*n*-butoxy-1-hexen-3-ol and 5-*n*-butoxy-2-hexen-1-ol.

A mixture of 130 g. of sodium carbonate, 1250 cc. of water, and 190.5 g. of mixed *n*-butoxychlorohexenes was heated with stirring at 100° for seventeen and one-half hours. Upon cooling, the reaction mixture was twice extracted with 200-cc. portions of benzene. Distillation of the combined extracts yielded 154 g. (89%) of mixed *n*-butoxyhexenols, b.p. 110–138°/19 mm.

In other experiments acetone, activated copper powder or a wetting agent was added, without appreciably improving the yield. The properties of the compounds prepared are shown in Table II.

In some of these hydrolyses both isomeric alkenols were isolated. In the 5-*n*-pentyloxy-1-chloro-2-pentene hydrolysis the 126 g. (91%) of crude product was carefully distilled through a Lecky-Ewell column to give 26 g. (19%) of 5-*n*-pentyloxy-1-penten-3-ol, b.p. 116–122°/20 mm.; 12 g. (9%) of intermediate, b.p. 122–142°/20 mm.; and 66 g. (48%) of 5-*n*-pentyloxy-2-penten-1-ol, b.p. 142–143°/20 mm. With 5-ethoxy-3-chloro-1-hexene considerably more rearrangement occurred. Distillation of the 132 g. (91%) of crude product yielded 28 g. (19%) of 5-ethoxy-1-hexen-3-ol, b.p. 80–83°/14 mm., n_D^{25} 1.4320–1.4318; 7 g. (5%) of intermediate, b.p. 83–107°/14–15 mm.; and 69 g. (48%) of 5-ethoxy-2-hexen-1-ol b.p. 107–110°/15 mm., n_D^{25} 1.4467–1.4457. The 12 g. residue, n_D^{25} 1.4460, represented an additional 8% of 5-ethoxy-2-hexen-1-ol. In the 5-ethoxy-1-chloro-2-hexene hydrolysis the 117 g. (86%) of crude product was separated into 11 g. (8%) of 5-ethoxy-1-hexen-3-ol, b.p. 83–85°/20 mm.; 5 g. (4%) of intermediate, b.p. 85°/20 mm.–98°/12 mm.; and 77 g. (56%) of 5-ethoxy-2-hexen-1-ol, b.p. 98–103°/12 mm. In the hydrolysis of 232 g. of 5-*n*-butoxy-1-chloro-2-pentene the product consisted of 42 g. (20%) of 5-*n*-butoxy-1-penten-3-ol, b.p. 99–104°/13 mm., n_D^{25} 1.4408; 8 g. (4%) of intermediate; and 126 g. (61%) of 5-*n*-butoxy-2-penten-1-ol, b.p. 123–125°/13 mm., n_D^{25} 1.4483. With 5-*n*-butoxy-3-chloro-1-pentene the results were similar. From 188 g. of the chloro compound were obtained 54.5 g. (32%) of 5-*n*-butoxy-1-penten-3-ol, b.p. 98–103.5°/13 mm., n_D^{25} 1.4395–1.4375; 6 g. (4%) of intermediate, b.p. 103.5–123°/13 mm.; and 77 g. (46%) of 5-*n*-butoxy-2-penten-1-ol, b.p. 123–125°/13 mm., n_D^{25} 1.4479.

Alkoxypentanols and alkoxyhexanols. These compounds were prepared by hydrogenating the corresponding alkoxypentenols and alkoxyhexenols at 75–100° in the presence of 10% of Raney nickel and at about 1000 lbs. hydrogen pressure. The unsaturated alcohol always was diluted with an equal volume of ethanol. The properties of these compounds are summarized in Table II.

Esters. A few esters were prepared by treating the unsaturated chlorides with the sodium salts of the corresponding acids. These reactions are described in detail below.

5-n-Butoxy-2-penten-1-yl acetate. A mixture of 116 g. of acetamide, 31 g. of sodium acetate, and 59 g. of 5-*n*-butoxy-1-chloro-2-pentene was boiled under reflux for two and one-half hours. Upon cooling, the product was treated with 200 cc. of water and the aqueous

TABLE II

ALKOXYALKENOLS AND ALKOXYALKANOLS

COMPOUND	B.P., °C/MM.	n_D^{25}	d_{25}^{25}	% YIELD	CALC'D		FOUND	
					C	H	C	H
5-Methoxy-2-penten-1-ol	96–98/19	1.4480	0.966	52	62.1	10.3	62.2	10.7
5-*n*-Butoxy-1-penten-3-ol	98–99/14	1.4375	0.894	85	68.4	11.4	68.5	11.1
5-*n*-Butoxy-2-penten-1-ol	121–122/13	1.4466	0.909		68.4	11.4	67.9	12.0
5-*n*-Pentyloxy-1-penten-3-ol	120–121/20	1.4426	0.905	91	69.8	11.6	68.0	11.2
5-*n*-Pentyloxy-2-penten-1-ol	143/20	1.4498	0.901		69.8	11.6	68.8	11.5
5-Ethoxy-1-hexen-3-ol	82–83/14	1.4318	0.896	91	66.7	11.1	66.8	11.1
5-Ethoxy-2-hexen-1-ol	101–103/12	1.4477	0.923		66.7	11.1	65.6	11.2
n-Butoxyhexenols	110–138/19			89				
Isobutoxyhexenols	90–95/2.5	1.4414		72	69.8	11.6	69.6	11.6
5-Isobutoxy-2-hexen-1-ol	106/2.6–90/1.5	1.4435	0.899	70	69.8	11.6	68.7	11.3
1-*n*-Butoxy-3-pentanol	98–99/14	1.4290	0.891	—	67.5	12.5	66.7	12.5
5-*n*-Butoxy-1-pentanol	90–94/2	1.4334	0.891	92	67.5	12.5	67.6	12.7
5-*n*-Pentyloxy-1-pentanol	139–141/20	1.4357	0.884	87	69.1	12.7	68.2	12.8
2-Ethoxy-4-hexanol	79–80/15	1.4190	0.879	—	65.8	12.3	65.8	12.6
5-Ethoxy-1-hexanol	99–101/12	1.4318	0.903	87	65.8	12.3	64.8	12.4
2-*n*-Butoxy-4-hexanol	103.5–104.5/15	1.4270	0.870	—	69.1	12.7	69.3	13.2
5-*n*-Butoxy-1-hexanol	127.5/15	1.4335	0.882	—	69.1	12.7	68.9	12.8
2-Isobutoxy-4-hexanol	98–99/14	1.4317	0.895	—	69.0	12.6	68.5	12.7
5-Isobutoxy-1-hexanol	120–121/15	1.4305	0.875	73	69.0	12.6	68.9	12.6

layer separated. The organic portion was diluted with 120 cc. of ether and then washed twice with 4% hydrochloric acid and twice with water. After the ether had been distilled, there was obtained 6 g. (10% recovery) of 5-*n*-butoxy-1-chloro-2-pentene, b.p. to 92°/2.3 mm. and 49 g. (73% conversion and 88% yield) of 5-*n*-butoxy-2-penten-1-yl acetate, b.p. 92–97°/2.3 mm., n_D^{25} 1.4390. An analytical sample boiled at 96–97°/2.3 mm., n_D^{25} 1.4392, d_{25}^{25} 0.937.

Anal. Calc'd for $C_{11}H_{20}O_3$: C, 66.0; H, 10.0
Found: C, 66.2; H, 10.1.

When 5-*n*-butoxy-1-chloro-2-pentene and sodium acetate were boiled for eight hours in glacial acetic acid solution, 5-*n*-butoxy-2-penten-1-yl acetate was obtained in 64% conversion and 77% yield.

5-Isobutoxy-2-hexen-1-yl acetate. A solution of 150 g. of sodium acetate and 191 g. of 5-isobutoxy-1-chloro-2-hexene in 425 g. of glacial acetic acid was boiled under reflux for seven hours. After cooling, the mixture was diluted with 200 cc. of water and extracted twice with benzene. The combined benzene extracts were washed once with water and distilled to give 125 g. (58%) of 5-isobutoxy-2-hexen-1-yl acetate, b.p. 92–94°/2 mm., n_D^{25} 1.4327.

Anal. Calc'd for $C_{12}H_{22}O_3$: C, 67.3; H, 10.3.
Found: C, 67.1; H, 10.1.

5-Isobutoxy-1-hexyl acetate. A 125-g. sample of 5-isobutoxy-2-hexen-1-yl acetate containing 5 g. of Raney nickel was shaken with hydrogen for three hours at 60° and 1000 lbs. pressure. After the nickel had been separated by filtration, the product was distilled to give 94 g. (75%) of 5-isobutoxy-1-hexyl acetate, b.p. 100–102°/4 mm., n_D^{25} 1.4210, d_{25}^{25} 0.901.

Anal. Calc'd for $C_{12}H_{24}O_3$: C, 66.7; H, 11.1.
Found: C, 66.5; H. 10.8.

5-n-Butoxy-2-penten-1-yl adipate was prepared by heating 176.5 g. of 5-*n*-butoxy-1-chloro-2-pentene with 96 g. of powdered sodium adipate for four hours at 160–170° in the presence of 3 cc. of triethylamine. After cooling, the mixture was diluted with a large excess of benzene and filtered. The filtrate was distilled at 0.7 mm. to a pot temperature of 200°. After it had been transferred to a Hickman still (7) the residue was distilled at 2×10^{-4}–10^{-5} mm. to give 130 g. (61%) of 5-*n*-butoxy-2-penten-1-yl adipate, n_D^{25} 1.4604, d_{25}^{25} 0.983.

Anal. Calc'd for $C_{24}H_{42}O_6$: C, 67.6; H, 9.85.
Found: C, 66.4; H, 10.2.

5-n-Butoxy-1-pentyl adipate was prepared by shaking 130 g. of 5-*n*-butoxy-2-penten-1-yl adipate and 25 g. of Raney nickel in 50 cc. of ethanol for seventy minutes with hydrogen at 90–110° and 800–1200 lbs. pressure. Upon cooling, the mixture was filtered free of catalyst and then distilled at 30 mm. to a pot temperature of 210°. The residue was taken up in ether and washed with aqueous sodium carbonate. After the ether was distilled, the 5-*n*-butoxy-1-pentyl adipate was distilled in a Hickman still at 10^{-4} mm. The yield was 42 g. (32%), n_D^{25} 1.4466, d_{25}^{25} 0.969.

Anal. Calc'd for $C_{24}H_{46}O_6$: C, 66.9; H, 10.7.
Found: C, 66.9; H, 11.1.

All but one of the remaining esters were prepared from the saturated alcohols and the corresponding acids. A typical example is the preparation of 5-*n*-butoxy-1-hexyl adipate shown below.

5-n-Butoxy-1-hexyl adipate. A mixture of 58 g. of 5-*n*-butoxy-1-hexanol, 25 g. of adipic acid, and 30 cc. of toluene was heated at 175–200° for fifteen and one-half hours while the evolved water was collected continuously in a Dean and Stark trap. Upon cooling, the reaction mixture was diluted with 200 cc. of benzene, washed with a solution of 10 g. of sodium hydroxide in 100 cc. of water and dried over potassium carbonate. Distillation yielded 61 g. (81%) of 5-*n*-butoxy-1-hexyl adipate, b.p. 214–218°/0.5 mm., n_D^{25} 1.4460, d_{25}^{25} 0.950.

Anal. Calc'd for $C_{26}H_{50}O_6$: C, 68.1; H, 10.9.
Found: C, 68.1; H, 11.7.

The 5-isobutoxy-1-hexyl 4-ketopimelate was prepared by transesterification of the ethyl ester in the presence of a *p*-toluenesulfonic acid catalyst.

The properties of all of these esters are summarized in Table III.

AMINES AND ISOTHIOCYANATES

n-Butyl-5-ethoxy-1-pentenyl-3-amine. A mixture of 149 g. of 5-ethoxy-3-chloro-1-pentene and 438 g. of *n*-butylamine was boiled under reflux for eight hours. Upon cooling, the product was shaken with a solution of 50 g. of sodium hydroxide in 250 cc. of water, the layers were separated and the organic portion was distilled to give 135 g. (72%) of *n*-butyl-5-ethoxy-1-pentenyl-3-amine, b.p. 92–115°/12 mm. An analytical sample boiled at 101°/15 mm., n_D^{25} 1.4341. d_{25}^{25} 0.837.

Anal. Calc'd for $C_{11}H_{23}NO$: Neut. equiv., 185; Found: Neut. equiv., 187.

n-Butyl-5-ethoxy-2-pentenyl-1-amine was prepared in the same way as the preceding amine. When the temperature reached 50°, the reaction became so vigorous that cooling was necessary. The yield of *n*-butyl-5-ethoxy-2-pentenyl-1-amine was 146 g. (78%), b.p. 106–116°/12 mm. An analytical sample boiled at 114–116°/12 mm., n_D^{25} 1.4434, d_{25}^{25} 0.846.

Anal. Calc'd for $C_{11}H_{23}NO$: Neut. equiv., 185; unsat. equiv., 185:
Found: Neut. equiv., 187; Unsat. equiv., 187[2].

n-Butyl-5-ethoxy-1-pentylamine. A small sample of *n*-butyl-5-ethoxy-2-pentenyl-1-amine was dissolved in ethanol and treated with hydrogen at 800 lbs. and 75° in the presence of Raney nickel. The pure *n*-butyl-5-ethoxy-1-pentylamine, obtained from this reaction, boiled at 130–131°/24 mm., n_D^{25} 1.4299, d_{25}^{25} 0.832.

Anal. Calc'd for $C_{11}H_{25}NO$: Neut. equiv., 187. Found: Neut. equiv., 189.

Mixed n-butyl-n-butoxypentylamines. A mixture of 438 g. of *n*-butylamine and 176.5 g. of 5-*n*-butoxy-1-chloro-2-pentene and 5-*n*-butoxy-3-chloro-1-pentene was warmed under reflux. When the reaction started, cooling was necessary. Subsequently the reaction was boiled under reflux for three and one-half hours. Upon cooling, the mixture was washed with a solution of 60 g. of sodium hydroxide in 350 cc. of water, then with a solution of 10 g. of sodium hydroxide in 50 cc. of water, and finally dried over potassium hydroxide. This crude product was shaken for five and one-half hours with hydrogen in the presence of 36 g. of Raney nickel at 160° and 1400–1500 lbs. pressure. After separating the catalyst, unreacted butylamine was distilled. The residue was washed with 100 cc. of 10% sodium hydroxide, dried over potassium hydroxide and distilled to give 101 g. of mixed *n*-butyl-*n*-butoxypentylamines, b.p. 92–98°/1 mm. An analytical sample boiled at 97–98°/1 mm.

Anal. Calc'd for $C_{13}H_{29}NO$: C, 72.5; H, 12.5.
Found: C, 72.4; H, 13.0.

Careful fractionation of the amine mixture gave *n*-butyl-1-*n*-butoxy-3-pentylamine, b.p. 125–128°/15 mm., n_D^{25} 1.4330, d_{25}^{25} 0.840,

Anal. Calc'd for $C_{13}H_{29}NO$: Neut. equiv., 217. Found: Neut. Equiv., 207.

and *n*-butyl-1-*n*-butoxy-5-pentylamine, b.p. 145°/15 mm., n_D^{25} 1.4339, d_{25}^{25} 0.832.

Anal. Calc'd for $C_{13}H_{29}NO$: Neut. equiv., 217. Found: Neut. Equiv., 216.

The *benzamide* was prepared by treating 39 g. of the mixed amines with 40 g. of sodium hydroxide in 200 cc. of water and with 50 cc. of benzoyl chloride according to the Schotten-Bauman method. The yield of amide was 33 g. (57%), b.p. 182–187°/2 mm., n_D^{25} 1.4980.

Anal. Calc'd for $C_{20}H_{33}NO_2$: N, 4.40. Found: N, 4.47.

Mixed n-butylisobutoxyhexenylamines. A mixture of 450 g. of *n*-butylamine and 210 g. of mixed isobutoxychlorohexenes was boiled under reflux for twenty-three hours. Upon cooling, the product was treated with a solution of 60 g. of sodium hydroxide in 300 cc. of water, dried over potassium hydroxide and distilled to give 163 g. (65%) of crude *n*-butylisobutoxyhexenylamines, b.p. 119–145°/13 mm. This product was redistilled to give 45 g.

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[2] These were determined by the bromide–bromate method. See Mulliken and Wakeman, *Ind. Eng. Chem., Anal. Ed.*, **7**, 59 (1935).

TABLE III

ESTERS

COMPOUND	B.P., °C/MM.	n_D^{25}	d_{25}^{25}	% YIELD	CALC'D		FOUND	
					C	H	C	H
5-*n*-Butoxy-2-penten-1-yl acetate	96–97/2.3	1.4392	0.937	88	66.0	10.0	66.2	10.1
5-Isobutoxy-2-hexen-1-yl acetate	92–94/2	1.4327		58	67.3	10.3	67.1	10.1
5-Isobutoxy-1-hexyl acetate	100–102/4	1.4210	0.901	75	66.7	11.1	66.5	10.8
5-*n*-Butoxy-2-penten-1-yl adipate	—	1.4604	0.983	61	67.6	9.85	66.4	10.2
5-*n*-Butoxy-1-pentyl adipate	182–190/0.10	1.4466	0.969	32	66.9	10.7	66.9	11.1
5-*n*-Butoxy-1-pentyl terephthalate	230–238/0.35	1.4836	1.008	72	69.3	9.3	69.4	9.3
5-*n*-Pentyloxy-1-pentyl adipate	202–204/0.15	1.4474	0.952	92	68.2	10.9	68.1	11.1
5-Ethoxy-1-hexyl phthalate	197–201/0.2	1.4829	1.032	73	68.3	9.0	67.8	8.8
5-*n*-Butoxy-1-hexyl adipate	214–218/0.5	1.4460	0.950	81	68.1	10.9	68.1	11.7
5-Isobutoxy-1-hexyl adipate	205–215/0.8	1.4433	0.947	81	68.1	10.9	67.4	10.6
5-Isobutoxy-1-hexyl 4-ketopimelate	229–235/0.3	1.4480	0.974	49	66.7	10.3	67.2	9.7

of forerun, b.p. 110–132°/13 mm., and then 113 g. of *n*-butylisobutoxyhexylamine, b.p. 132–140°/13 mm., n_D^{25} 1.4410.

Anal. Calc'd for $C_{14}H_{29}NO$: C, 74.1; H, 12.8.
Found: C, 73.5; H, 12.2.

Mixed n-butylisobutoxyhexylamines. The above 113 g. of *n*-butylisobutoxyhexenylamines was charged to a rocking-autoclave with 10 g. of Raney nickel and 120 cc. of ethanol and shaken with hydrogen for two hours at 70° under 1000 lbs. pressure. The mixture was filtered and distilled to give 98 g. (86%) of *n*-butylisobutoxyhexylamines, b.p. 98–100°/0.3 mm., n_D^{25} 1.4317.

Anal. Calc'd for $C_{14}H_{31}NO$: C, 73.3; H, 13.5.
Found: C, 72.9; H, 12.9.

The *benzenesulfonamide* was prepared by treating the above 98 g. with a solution of 30 g. of sodium hydroxide in 300 cc. of water and with 100 g. of benzenesulfonyl chloride, according to the Schotten-Bauman method. The product was 144 g. (95%) of an undistillable yellow oil, n_D^{25} 1.4905, which was purified by treatment successively with aqueous hydrochloric acid, aqueous sodium hydroxide, decolorizing carbon, and activated alumina.

Anal. Calc'd for $C_{20}H_{35}NO_3S$: S, 8.7. Found: S, 8.8.

5-Methoxy-1-pentenyl-3-isothiocyanate was prepared by refluxing for two hours a mixture of 100 g. of ammonium thiocyanate, 300 cc. of ethanol, and 134 g. of 5-methoxy-1-chloro-2-pentene. After the alcohol was distilled, the residue was cooled, diluted with 100 cc. of ether and filtered. Distillation of the ethereal filtrate gave 107 g. (68%) of 5-methoxy-1-pentenyl-3-isothiocyanate, b.p. 85–90°/5 mm. An analytical sample boiled at 87–88°/5 mm., n_D^{25} 1.5020, d_{25}^{25} 1.016.

Anal. Calc'd for $C_7H_{11}NOS$: S, 21.0. Found: S, 21.1.

5-Methoxy-2-pentenyl-1-isothiocyanate. A mixture of 100 g. of ammonium thiocyanate, 300 cc. of ethanol, and 134 g. of 5-methoxy-2-chloro-1-pentene was boiled under reflux for two hours. After the alcohol was distilled, the residue was cooled, diluted with 100 cc. of ether and filtered. Distillation of the ether solution yielded 91 g. (58%) of crude methoxypentenylisothiocyanates, b.p. 93–110°/16 mm. From this mixture there was obtained by careful refractionation 15 g. of 5-methoxy-1-pentenyl-3-isothiocyanate, b.p. 86–89°/5 mm., n_D^{25} 1.5021 and 25 g. of 5-methoxy-2-pentenyl-1-isothiocyanate, b.p. 105–107°/5 mm., n_D^{25} 1.5154, d_{25}^{25} 1.031.

Anal. Calc'd for $C_7H_{11}NOS$: S, 21.0. Found: S, 20.7.

5-n-Butoxy-1-pentenyl-3-isothiocyanate was prepared by the same procedure using 88.5 g. of 5-*n*-butoxy-1-chloro-2-pentene, 51 g. of ammonium thiocyanate, and 200 cc. of ethanol. The crude yield was 85 g. (86%), b.p. 90–114°/2 mm. An analytical sample boiled at 118–119°/5 mm., n_D^{25} 1.4880, d_{25}^{25} 0.960.

Anal. Calc'd for $C_{10}H_{17}NOS$: S, 16.5. Found: S, 17.0.

5-n-Butoxy-2-pentenyl-1-isothiocyanate was prepared by the same method from 88.5 g. of 5-*n*-butoxy-3-chloro-1-pentene. The yield was 69 g. (69%), b.p. 94–126°/2–2.5 mm. An analytical sample boiled at 136–140°/5 mm., n_D^{25} 1.4985, d_{25}^{25} 0.976.

Anal. Calc'd for $C_{10}H_{17}NOS$: S, 16.5. Found: S, 16.4.

All four of these isothiocyanates gave a strong positive test for the isothiocyanate group (8) and a negative test for the thiocyanate group (9).

SUMMARY

Twelve α-chloroethers have been added to butadiene in the presence of zinc chloride to give 61–86% yields of mixtures of the corresponding 5-alkoxy-3-chloro-1-alkenes and the 5-alkoxy-1-chloro-2-alkenes. The preparation of esters, alcohols, amines, and isothiocyanates from these compounds is described.

DAYTON 7, OHIO

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