ADDITION OF SOME α-HALO ETHERS TO UNSATURATED COMPOUNDS

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The addition of α-halo ethers to olefins and to diolefins has formed the subject of numerous investigations. As halo ethers, alkyl chloromethyl ethers have been used, and as olefins, isobutene, 2-methyl-2-butene, styrene, cyclohexene, and others [1, 2]. The addition of α-halo ethers to conjugated bonds has been studied for butadiene [1, 3-8], isoprene [9], chloroprene [10], cyclopentadiene [1], and butenyne [11]. Later, Azerbaidzhan chemists used the simple olefins ethylene, propene, and butene in the reaction [12]. Mamedov and Khydyrov have recently synthesized γ-chloro ethers of the aromatic series by this method [13]. Investigations have been reported recently also on the addition of α-halo ethers to an acetylenic bond [14-16]. In almost all these investigations α-chloro ethers have been added to ethylenic and acetylenic hydrocarbons. Only quite recently have data appeared on the addition of α-halo ethers to unsaturated halogen compounds, namely vinyl chloride [17], allyl chloride [18], and chloroethylenes [19].

TABLE 1. Addition of $CH_3COOCH_2CH_2OCH_2Cl$

Unsaturated compound	B.p., °C (p, mm)	n_D^{20}	d_4^{20}	MR		Cl, %		Yield, %
				found	calculated	found	calculated	
Isobutene	71-75 (1)	1.4420	1.0497	52.60	51.93	17.14 16.99	17.11	19
Allyl chloride	124-127 (10)	1.4640	1.2117	52.17	52.17	30.80 31.18	30.95	10.6
Allyl acetate	112-115 (1)	1.4492	1.1663	58.36	58.20	14.02 14.06	13.98	7.8
Styrene	120-130 (1)	1.5100	1.1339	67.46	66.80	13.50	13.81	10.2
Ethyl cinnamate	150-152 (1)	1.5078	1.1640	84.00	82.30	9.65	10.7	16
Butadiene	87-89 (2)	1.4621	1.0926	51.94	51.46	17.22 17.01	17.16	40
	73-74 (2)	1.4530	1.0830	51.58	51.46	17.15	17.16	

The present paper describes addition products formed by olefins and diolefins with α-halo ethers containing functional groups, namely 2-acetoxyethyl chloromethyl ether [2-(chloromethoxy)ethyl acetate] and 2-chloroethyl chloromethyl ether. The first ether was prepared by the action of acetyl chloride on 1,3-dioxolane [20], and the second by the chloromethylation of 2-chloroethanol. Data on the addition products of 2-acetoxyethyl chloromethyl ether are presented in Table 1, and data on the addition products of 2-chloroethyl chloromethyl ether in Table 2.

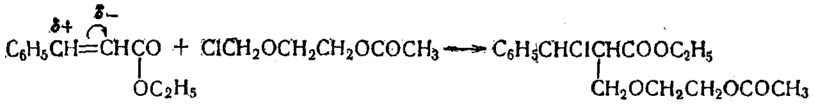
In the reactions with isobutene, styrene, and ethyl cinnamate we used mercuric chloride as catalyst, and in the remaining cases we used zinc chloride. In the reactions with allyl chloride and allyl acetate we used zinc chloride as its complex with nitrobenzene. The products of the addition of chloro ethers to isobutene and to styrene are thermally unstable and, even when vacuum-distilled, partially eliminate hydrogen chloride with resulting contamination of the product with unsaturated compound. When the product of the addition of 2-chloroethyl chloromethyl ether to styrene is distilled at 6 mm, above 100° vigorous liberation of hydrogen chloride occurs and the unsaturated compound formed polymerizes rapidly in the flask. With the product of the addition of 2-acetoxyethyl chloromethyl ether to styrene, still more profound decomposition occurs at 10 mm, and a mixture of substances is obtained. In the addition of 2-acetoxyethyl chloromethyl ether to butadiene two isomeric products are obtained (see Table 1). On analogy with products of the addition of the simplest α-halo ethers to butadiene, to the low-boiling product of b.p. 73-74° (2 mm) we must assign the structure

$$CH_3-CO-O-CH_2-CH_2-O-CH_2-CH_2-CHCl-CH=CH_2$$

and to the product of b.p. 87-89° (2 mm) we must assign the structure

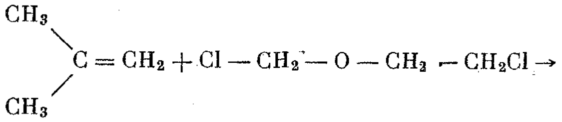
$$CH_3COO-CH_2-CH_2-O-CH_2-CH_2-CH=CH-CH_2Cl$$

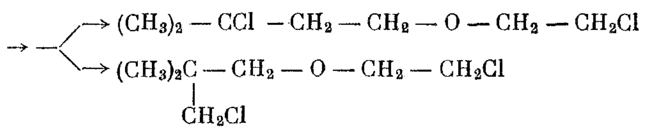
It must be supposed that the addition of 2-acetoxyethyl chloromethyl ether to ethyl cinnamate goes in accordance with the polarization of the unsaturated ester:



$$\overset{\delta+}{C_6H_5CH}{=}\overset{\delta-}{CH}\underset{OC_2H_5}{CO} + ClCH_2OCH_2CH_2OCOCH_3 \rightarrow C_6H_5CHCl\underset{CH_2OCH_2CH_2OCOCH_3}{CH}COOC_2H_5$$

The addition of α-chloro ethers to isobutene could occur in two ways:





$$\rightarrow (CH_3)_2-CCl-CH_2-CH_2-O-CH_2-CH_2Cl \quad (I)$$

$$\rightarrow (CH_3)_2\underset{CH_2Cl}{C}-CH_2-O-CH_2-CH_2Cl \quad (II)$$

To resolve the question of the structure of the reaction product for the case of reaction with 2-chloroethyl chloromethyl ether, the product was treated with solid potassium hydroxide. The unsaturated ether then obtained in low yield had an infrared spectrum having a well marked peak at 1645 cm^{-1}, which indicates the presence of an unsymmetrically disubstituted ethylenic bond $RR'C=CH_2$. The formation of the unsaturated product is evidence in favor of the structure (I) for the product of the addition of 2-chloroethyl chloromethyl ether to isobutene. The addition of α-chloro ethers to styrene proceeds in accordance with Markovnikov's rule, as will be shown in the next communication.

TABLE 2. Addition of $ClCH_2OCH_2CH_2Cl$

Unsaturated compound	B.p., °C (p, mm)	n_D^{20}	d_4^{20}	MR found	MR calculated	Cl, % found	Cl, % calculated	Yield, %
Styrene	120-122 (1)	1.5276	1.1701	61.33	60.77	29.95	30.41	21
Isobutene*	96 (10)	1.4542	1.1074	45.23	45.90	38.35	38.38	61.5
Allyl chloride	124 (8)	1.4792	1.2681	45.97	46.14	51.60 52.20	51.75	43
Allyl acetate	145-147 (10)	1.4590	1.2025	52.08	52.17	30.60	30.95	11

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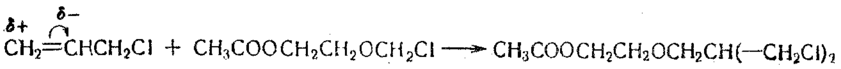
*While this article was being prepared for publication there appeared a paper by Mamedov and Agaev [21], in which a description was given of 2-chloroethyl 3-chloro-3-methylbutyl ether, which we have prepared in the present investigation. Its constants were [21]: b.p. n_D^{20} 1.4542; d_4^{20} 1.1024; yield 48%; found, MR 45.44; found Cl 39.00 and 38.82%.

The direction in which α-chloro ethers add to allyl chloride was shown in work by Pishnamazzade and Gasanova [18]. Hence, it may be supposed that the products of the addition of 2-acetoxyethyl chloromethyl ether and of 2-chloroethyl chloromethyl ether to allyl chloride have the structures (III) and (IV) respectively



$$\overset{\delta+}{CH_2}\overset{\delta-}{=}CHCH_2Cl + CH_3COOCH_2CH_2OCH_2Cl \longrightarrow CH_3COOCH_2CH_2OCH_2CH(-CH_2Cl)_2$$

(III)

and $(CH_2Cl)_2-CHCH_2OCH_2CH_2Cl$.

(IV)

We did not determine the exact structures of the compounds obtained by the addition of α-chloro ethers to allyl acetate.

EXPERIMENTAL

Addition of 2-Acetoxyethyl Chloromethyl Ether to Isobutene. A dark-colored thick-walled bottle containing 78 g of 2-ethoxyethyl chloromethyl ether of b.p. 82-84° (10 mm) and 2 g of mercuric chloride was placed in a cooling mixture and closed with a stopper having two openings. A glass tube, reaching to the bottom of the bottle, was inserted in one of the openings, and through this tube isobutene was passed. A short glass tube connected to a calcium chloride tube was inserted in the other opening. Isobutene was prepared by the dehydration of t-butyl alcohol, of which 45 g was taken for reaction. Isobutene was passed through the chloro ether for one hour. The bottle was then closed tightly with a rubber stopper and left in the cooling mixture for three hours. It was then allowed to stand at room temperature for 18 hours, after which 150 ml of diethyl ether was added to the contents of the bottle. The ether layer was washed three times with water and dried with calcium chloride. The ether was distilled off at room temperature under the vacuum of a water pump. The first fractionation of this from an Arbuzov flask gave 27.4 g of a fraction of b.p. 83-106° (1 mm) and 9 g of resinous residue. On refractionation of this fraction we isolated 21 g of a substance of b.p. 71-75° (1 mm).

Addition of 2-Acetoxyethyl Chloromethyl Ether to Allyl Chloride. A mixture of 37 g of 2-acetoxyethyl chloromethyl ether, 3 g of freshly fused zinc chloride that had been ground to a powder, and 0.5 ml of nitrobenzene was prepared in a three-necked flask fitted with mechanical stirrer, reflux condenser, and dropping funnel and surrounded by a cooling mixture. In the course of 30 minutes 18.5 g of allyl chloride was added dropwise from the dropping funnel, and the contents were then allowed to stand for 18 hours at room temperature with periodic stirring. The reaction mixture was then heated in an oil bath at 50-60° for one hour. The reaction mixture was cooled, 100 ml of ether was added into the flask, and the ethereal solution was washed three times with water and dried over calcium chloride. After two distillations we isolated 5.9 g of a substance of b.p. 124-127° (10 mm).

Addition of 2-Acetoxyethyl Chloromethyl Ether to Allyl Acetate. For reaction we took 35 g of allyl acetate, 53.4 g of 2-acetoxyethyl chloromethyl ether, 2 g of zinc chloride, and 0.5 ml of nitrobenzene. The synthesis and all operations in the treatment of the reaction mixture were similar to those for the addition of the same chloro ether to allyl chloride. The ether layer was dried with sodium sulfate. In the first distillation we collected 10.3 g of a fraction having b.p. 110-145° (6 mm). After the second fractionation we isolated 6.85 g of a substance of b.p. 112-115° (6 mm).

Addition of 2-Acetoxyethyl Chloromethyl Ether to Styrene. A dark-colored bottle surrounded by a cooling mixture was charged with 36.7 g of 2-acetoxyethyl chloromethyl ether, 25 g of styrene, and 2 g of mercuric chloride. The bottle was left at room temperature for four days. When the reaction was complete, the reaction mixture was treated as in the preceding syntheses. In the first fractionation we collected 12.6 g of a fraction of b.p. 132-140° (1 mm). Refractionation gave 6.3 g of addition product, b.p. 120-130° (1 mm).

Addition of 2-Acetoxyethyl Chloromethyl Ether to Ethyl Cinnamate. A mixture of 18 g of 2-acetoxyethyl chloromethyl ether, 20.8 g of ethyl cinnamate, and 1.3 g of mercuric chloride was prepared in a 50 ml pear-shaped flask fitted with reflux condenser. After one day the reaction mixture was heated in an oil bath at 100-120° for 90 minutes. The contents of the flask were cooled to room temperature and treated as in the preceding syntheses. In the fractionation we isolated 6.2 g of a substance of b.p. 150-152° (1 mm).

Addition of 2-Acetoxyethyl Chloromethyl Ether to Butadiene. 300 g of 2-acetoxyethyl chloromethyl ether was cooled to − 18° and added to 118 g of butadiene in a thick-walled bottle surrounded by a cooling mixture; 7.5 g of ground freshly fused zinc chloride was added. The bottle was closed with a stopper through which passed a glass tube that terminated in a sealed capillary. The bottle was kept in the cooling mixture for about 10-12 hours and was then allowed to stand at room temperature for 2.5 days. At the end of the reaction the capillary was broken off, unchanged butadiene was removed, and the reaction mixture was diluted with 300 ml of ether and washed three times with water. The ether layer was dried with calcium chloride, ether was distilled off at 10 mm, and the residue was vacuum-fractionated. We obtained: Fraction I (44.2 g), b.p. 30-82° (10 mm); Fraction II (134.2 g), b.p. 82-140° (10 mm);

Fraction III (56.7 g), b.p. 108-140° (1 mm); Fraction IV (17.3 g), b.p. 140-147° (1 mm); residue (63.7 g). When fractionated from a flask with a Widmer column, Fractions II and III gave 45 g of one isomer of b.p. 73-74° (2 mm) and 117 g of another isomer, b.p. 87-89° (2 mm).

Preparation of 2-Chloroethyl Chloromethyl Ether, and Syntheses Carried out with It. A mixture of 165 g of 2-chloroethanol and 67 g of paraform was cooled (from − 5° to 0°) and stirred while being saturated with hydrogen chloride over a period of one hour. The organic layer was dried and fractionated. We obtained 178 g (78%) of 2-chloroethyl chloromethyl ether; b.p. 48° (10 mm); n_D^{20} 1.4565; d_4^{20} 1.2813; found, MR 27.41; calculated, MR 27.43. The literature [21] gives: b.p. 153-155°; d_4^{20} 1.2881; n_D^{20} 1.4571; found, MR 27.28.

The addition of 2-chloroethyl chloromethyl ether to isobutene, to styrene, to allyl chloride, and to allyl acetate was carried out in a similar way to the syntheses described above. The elimination of hydrogen chloride from the γ-chloro ether obtained by the addition of 2-chloroethyl chloromethyl ether to isobutene was carried out in a vacuum-distillation apparatus. An Arbuzov flask fitted with thermometer and dropping funnel was charged with 11 g of potassium hydroxide powder. The flask was immersed in an oil bath that had been heated beforehand to 90°, and 35 g of the γ-chloro ether was added gradually dropwise. The substance that distilled over was collected in one receiver. This operation was repeated twice. In the third distillation we obtained 4 g of a substance having the following constants: b.p. 64-67° (24 mm) d_4^{20} 0.9765; n_D^{20} 1.4470. Found: C 56.58; 56.75; H 8.78; 8.90; Cl 23.90%; MR 40.68. $C_7H_{13}OCl$. Calculated: C 56.64; H 8.81; Cl 23.87%, MR 40.57.

SUMMARY

The addition was carried out of 2-acetoxyethyl chloromethyl ether and of 2-chloroethyl chloromethyl ether to isobutene, to allyl chloride, to styrene, and to allyl acetate and also of 2-acetoxyethyl chloromethyl ether to butadiene and to ethyl cinnamate.

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