SYNTHESIS OF 2-ALKOXY-3-CHLOROTETRAHYDROFURANS

L. M. Bolotina, N. I. Kutsenko, and P. A. Moshkin

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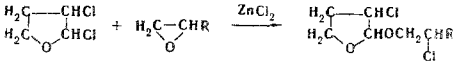
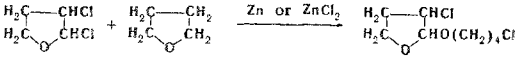
A simple one-stage method for the synthesis of 2-alkoxy-3-chlorotetrahydrofurans has been developed which is based on the chlorination of tetrahydrofuran with sulfuryl chloride at 55–65° C with the subsequent addition of an alcohol (without the isolation of the dichlorinated tetrahydrofurans). Eight compounds of the type mentioned have been synthesized by this method, six of them being previously unknown.

2-Alkoxy-3-chlorotetrahydrofurans were first obtained in yield not exceeding 50% by heating 2,3-dichlorotetrahydrofuran (I) with alcohols [1]. Kratochvil [2] obtained a number of such compounds by extending to I the previously known reaction of epoxides with acyclic α-chloro ethers [3]. In this way 3-chloro-2-(β-chloroalkoxy)tetrahydrofurans were synthesized with yields of 35–80%:

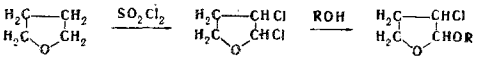


The reaction of I with tetrahydrofuran takes place analogously in the presence of metallic zinc. This reaction was later performed with the use of zinc chloride as catalyst [4]. In both cases, 3-chloro-2-(γ-chlorobutoxy)tetrahydrofuran was obtained:



Compound I, the starting material in the synthesis of 2-alkoxy-3-chlorotetrahydrofurans, is obtained by chlorinating tetrahydrofuran with sulfuryl chloride [5] or with chlorine in the presence of catalysts [1, 6–8]. We have used the chlorination of tetrahydrofuran with sulfuryl chloride and subsequent treatment of the reaction mixture with alcohols and heating, without the isolation of I.

This has enabled us to obtain 2-alkoxy-3-chlorotetrahydrofurans in one stage with fairly high yields by the following route:



R=C_2H_5; n-C_4H_9; n-C_5H_{11}; n-C_6H_{13}; n-C_7H_{15}; n-C_8H_{17}; n-C_9H_{19}; n-$C_{10}H_{21}$.

The constants and analytical data of the substances obtained are given in the table.

EXPERIMENTAL

In a current of nitrogen, 1 mole of sulfuryl chloride was added dropwise with stirring at 65° C over 1–1.5 hr to 2 moles of tetrahydrofuran. After the addition of the whole of the sulfuryl chloride, the temperature of the reaction mixture was raised to 72–75° C and kept there for another 1 hr. Then 0.5 mole of an alcohol was added and the mixture was heated in the boiling water bath for 3 hr. It was cooled to 25–30° C, and 200 ml of 20% sodium chloride solution was added to it. After 10 minutes' stirring, the upper layer was separated off and dried, the excess of tetrahydrofuran was driven off, and the residue was distilled in vacuum.

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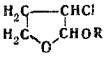
Scientific-Research Institute for Plastics, Moscow

 Alkoxychlorotetrahydrofurans

R	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Empirical formula	Found, % C	Found, % H	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % Cl	Yield, %
C_2H_5	50—51 (7)	1.1050	1.4380	36.01	35.86	$C_6H_{11}ClO_2$	48.4	7.0	23.7	47.9	7.3	23.6	87
n-C_4H_9	92—93 (14)	1.0519	1.4404	44.83	44.99	$C_8H_{15}ClO_2$	53.4	8.4	19.2	53.8	8.4	19.9	89
n-C_5H_{11}*	95 (10)	1.0351	1.4445	49.57	49.71	$C_9H_{17}ClO_2$	56.4	8.9	18.2	56.1	8.8	18.4	83
n-C_6H_{13}*	117 (10)	1.0214	1.4480	54.14	54.33	$C_{10}H_{19}ClO_2$	57.7	9.3	17.0	58.1	9.2	17.2	87
n-C_7H_{15}*	127—129 (13)	1.0147	1.4487	58.25	58.95	$C_{11}H_{21}ClO_2$	59.8	9.2	16.4	59.9	9.5	16.1	84
n-C_8H_{17}*	126—130 (8)	1.0085	1.4496	62.43	63.57	$C_{12}H_{23}ClO_2$	61.0	9.2	14.9	61.4	9.8	15.1	84
n-C_9H_{19}*	134—135 (6)	0.9879	1.4491	67.47	68.18	$C_{13}H_{25}ClO_2$	62.4	9.6	14.2	62.7	10.0	14.3	89
n-$C_{10}H_{21}$*	142 (12)	0.9634	1.4475	72.88	72.80	$C_{14}H_{27}ClO_2$	63.3	9.9	13.5	63.5	10.2	13.4	91

*New compound.