CYCLIC ETHERS AND ACETALS

III. 2,6-Derivatives of 1,4-Dioxane*

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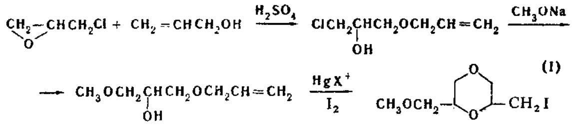
The reactions of 2-iodomethyl-6-methyl-1,4-dioxane, 2-hydroxymethyl-6-iodomethyl-1,4-dioxane, and 2-iodomethyl-6-methoxymethyl-1,4-dioxane with secondary amines have given the corresponding derivatives.

Continuing our previously started investigations [1], we have synthesized a number of ammonium derivatives of 1,4-dioxane containing substituents in position 2. The initial 2-iodomethyl-6-methyl-1,4-dioxane [2] and cis- and trans-2-hydroxymethyl-6-iodomethyl-1,4-dioxanes [3] have been described previously. 2-Iodomethyl-6-methoxymethyl-1,4-dioxane was synthesized in the following manner.



The halogenomethyl derivatives of 1,4-dioxane were treated with dimethylamine, diethylamine, and piperidine. The resulting tertiary amines were converted into the corresponding alkyl iodide derivatives (see table) by treatment with methyl and ethyl iodides. After two recrystallizations from ethanol, the quaternary ammonium salts were chromatographed on paper in the butanol–acetic acid–water (4 : 1 : 5) system. The spots were revealed with Dragendorff's reagent. In all cases only one spot was found. Remembering that in the chromatography of stereoisomeric methiodides of VIII the values of R_f differ fairly substantially, we assume that the tertiary amines that we synthesized consist of a single stereoisomer, the low-boiling one. This conclusion does not contradict the Auwers-Skita rule and is in harmony with the results that we obtained previously [3].

EXPERIMENTAL

1-Allyloxy-3-chloropropan-2-ol. A mixture of 92 g (1 mole) of epichlorohydrin, 400 ml (6 mole) of allyl alcohol, and 0.5 ml of conc H_2SO_4 was heated with stirring for 6 hr. Excess allyl alcohol was driven off and the residue was distilled in vacuo. This gave 80.5 g (53.5%) of product with bp 86.5° C (9 mm); n_D^{20} 1.4635; d_4^{20} 1.120. Literature data [4]: bp 71° C (3 mm); n_D^{20} 1.4625.

1-Allyloxy-3-methoxypropan-2-ol. With stirring, a solution of sodium ethoxide in methanol [from 16.2 g (0.7 g-at.) of sodium in 250 ml of methanol] was added to 105.4 g (0.7 mole) of 1-allyloxy-3-chloropropan-2-ol. The mixture was kept at 60° C for 1 hr, the precipitate was filtered off, and the reaction mixture was distilled. Yield 66.7 g (68%) of a product with bp 80–84° C (8 mm); n_D^{20} 1.4460; d_4^{20} 1.1011. Found, %: C 57.4; H 9.6. MR_D 38.4. Calculated for $C_7H_{14}O_3$, %: C 57.5; H 9.6. MR_D 38.8

2-Iodomethyl-6-methoxymethyl-1,4-dioxane (I). To a mixture of 97.5 g (0.45 mole) of mercuric oxide, 400 ml of water, and 50.3 g of 56% HNO_3 was added 66.3 g (0.46 mole) of 1-allyloxy-3-methoxypropan-2-ol. The solution was filtered and treated with a saturated aqueous solution of potassium iodide. The aqueous solution was decanted off, and the residue was treated with a mixture of water and chloroform (1 : 4) in a total volume of about 1 *l*. The solution was stirred at the boil and iodine was added in portions until it ceased to be decolorized. After cooling, the mercuric iodide was filtered off and washed with an aqueous solution of sodium sulfite until it was decolorized. The chloroform layer was separated off and dried with magnesium sulfate. The chloroform was evaporated off and the residue was distilled in vacuo. Yield 73 g.

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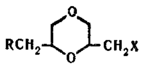
*For part II, see [5].

2,6-Derivatives of 1,4-Dioxane 

Compound	R	X	Bp, ° C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D		Mp, ° C		Emprical formula*	Found, %				Calculated, %				Yield, %
						found	calculated	methiodide	ethiodide		C	H	N	I	C	H	N	I	
I	CH_3O	I	120—125 (6)	1,6600	1,5220	49,9	50,3	—	—	$C_7H_{13}IO_3$	31,4	4,7	—	45,5	30,8	4,7	—	46,6	60
II	CH_3O	$N(CH_3)_2$	91—95 (6)	1,0047	1,4480	50,3	50,3	108	110	$C_{10}H_{22}INO_3$	36,2	6,8	4,5	38,8	36,2	6,6	4,2	38,4	44
III	CH_3O	$N(C_2H_5)_2$	119—120 (8)	0,9855	1,4500	59,1	59,5	118,5	121	$C_{12}H_{26}INO_3$	40,8	7,2	4,0	35,5	40,1	7,2	3,9	35,4	44
IV	CH_3O	NC_5H_{10}**	128—130 (6)	1,0500	1,4820	62,1	62,1	120	115	$C_{13}H_{26}INO_3$	42,2	7,1	3,6	34,4	42,0	7,0	3,7	34,2	46
V	H	$N(CH_3)_2$	116 (100)	1,0285	1,4740	43,2	44,0	202,5	145	$C_9H_{20}INO_2$	36,5	6,5	4,5	42,3	35,8	6,6	4,6	42,2	50
VI	H	$N(C_2H_5)_2$	120 (50)	1,0276	1,4802	52,6	53,3	180	165	$C_{11}H_{24}INO_2$	40,8	7,4	4,2	38,8	40,1	7,3	4,2	38,6	42
VII	H	NC_5H_{10}**	118—120 (20)	1,0205	1,5010	56,6	55,8	146	—	$C_{12}H_{24}INO_2$	42,6	7,4	4,1	37,5	42,2	7,1	4,1	37,3	35
VIII***	HO	$N(CH_3)_2$	132 (8)	1,0680	1,4660	45,6	45,6	165	120	$C_9H_{20}INO_3$	34,2	6,4	4,5	39,8	34,0	6,3	4,4	40,0	70
IX	HO	$N(C_2H_5)_2$	135—140 (6)	1,0360	1,4690	54,6	54,9	104	162	$C_{11}H_{24}INO_3$	38,0	6,9	4,0	37,2	38,2	6,9	4,0	36,8	30
X	HO	NC_5H_{10}**	140—142 (6)	1,2000	1,5500	57,0	57,4	204	170	$C_{13}H_{26}INO_3$	42,5	7,2	4,0	35,1	42,0	7,0	3,8	34,2	42

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*The analytical data and the empirical formulas relate to the methiodides of compounds II-IX and to the ethiodides of X.

** 1-Piperidine.

***For the cis isomer R_f is 0.33; and for the trans isomer R_f is 0.14, bp 150-155° C (3 mm); d_4^{20} 1.0660; n_D^{20} 1.4690; found, MR_D–: 45.7; calculated, MR_D: 45.6.

The tertiary amines II–X and their alkyl iodide derivatives were obtained similarly [1].

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