SYNTHESIS OF 2-SUBSTITUTED 1,4-DIOXANES FROM 1,2-EPOXY-3-(2-CHLOROETHOXY)PROPANE

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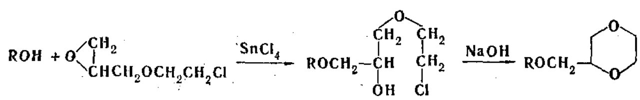
UDC 547.841.07

A number of 2-substituted 1,4-dioxanes were synthesized from β-chloroethyl glycidyl ether, the appropriate alcohols, and diethylamine.

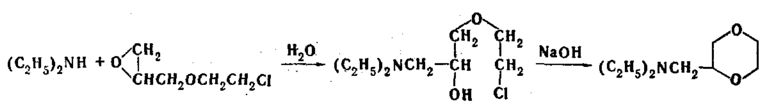
Cyclic diethers (dioxane, for example) are good solvents for resins, fats, and cellulose esters [1], and some of their derivatives display biological and pharmacological activity [2]. Dioxane and its derivatives are obtained by various methods [3, 4]. However, these methods are somewhat unusual and do not enable one to obtain 1,4-dioxanes that contain different substituents.

We have synthesized a number of representatives of 2-substituted 1,4-dioxanes (see Table 1) by the reaction of various hydroxyl-containing compounds and diethylamine with β-chloroethyl glycidyl ether and subsequent dehydrohalogenation.

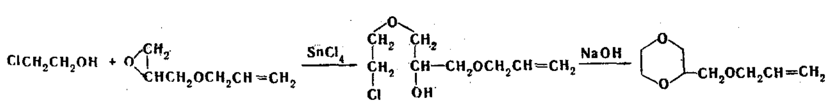


The yield decreases as the molecular weight of the alcohol decreases; this is apparently a consequence of the reaction of the initially formed secondary hydroxyl groups with β-chloroethyl glycidyl ether, i.e., the tendency for telomerization increases as the molecular weight of the alcohol decreases.

When secondary amines are used in place of alcohol, 2-dialkylaminomethyl-1,4-dioxanes are formed:



Alternative synthesis was used in the case of 2-allyloxymethyl-1,4-dioxane in order to establish the structures of the compounds obtained. The IR spectrum of this preparation contains a band characteristic for the 1,4-dioxane ring (1126 cm^{-1}) and a whole set of absorption bands caused by the skeletal vibrations of the ring and the methylene groups [5]. The band at 1644 cm^{-1} indicates the presence of a vinyl group.

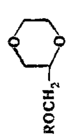


EXPERIMENTAL

2-Allyloxymethyl-1,4-dioxane (XIII). A. A 20-g (0.15 mole) sample of 1,2-epoxy-3-(2-chloroethoxy)-propane was added by drops with stirring in the course of 1 h at 35-40° to a mixture of 43.5 g (0.75 mole)

Sumgait Branch, Academician Yu. G. Mamedaliev Institute of Petrochemical Processes, Academy of Sciences of the Azerbaidzhan SSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 161-163, February, 1973. Original article submitted November 30, 1971.

TABLE 1



Comp.	R	bp, °C (mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Empirical formula	Found, % C	Found, % H	Calc., % C	Calc., % H	Yield, %
I	CH_3	69—70 (20)	1,0545	1,4320	32,51	32,63	$C_6H_{12}O_3$	54,4	8,9	54,5	9,1	57
II	C_2H_5	81—82 (22)	1,0191	1,4330	37,27	37,25	$C_7H_{14}O_3$	57,4	9,7	57,5	9,6	56
III	n-C_3H_7	86—87 (15)	1,0070	1,4350	41,50	41,87	$C_8H_{16}O_3$	60,0	10,1	59,9	10,0	68
IV	i-C_3H_7	83—84 (17)	0,9917	1,4300	41,72	41,87	$C_8H_{16}O_3$	60,1	9,9	59,9	10,0	63
V	n-C_4H_9	60—62 (1)	0,9810	1,4360	46,44	46,49	$C_9H_{18}O_3$	61,9	10,6	62,0	10,4	68
VI	t-C_4H_9	89—90 (15)	0,9946	1,4355	45,81	46,49	$C_9H_{18}O_3$	61,9	10,5	62,0	10,4	62
VII	$Cl(CH_2)_2$	71—72 (1)	1,1820	1,4640	42,17	42,12	$C_7H_{13}ClO_3$[a]	46,2	7,4	46,5	7,2	69
VIII	$Cl(CH_2)_4$	87—89 (1)	1,1218	1,4630	51,23	51,35	$C_9H_{17}ClO_3$[b]	51,6	8,1	51,8	8,2	67
IX	C_5H_9	79—80 (1)	1,0425	1,4650	49,37	48,90	$C_{10}H_{18}O_3$	64,3	9,8	64,5	9,7	65
X	C_6H_{11}	99—100 (1)	1,0370	1,4660	53,49	53,52	$C_{11}H_{20}O_3$	66,1	10,1	65,9	10,1	61
XI	C_5H_9O[c]	100—101 (1)	1,0994	1,4640	50,75	50,55	$C_{10}H_{18}O_4$	59,1	8,9	59,4	8,9	55
XII	C_5H_5O[d]	98—100 (1)	1,1501	1,4835	49,22	49,61	$C_{10}H_{14}O_4$	60,6	7,1	60,6	7,1	56
XIII	$CH_2{=}CHCH_2$	90—91 (15)	1,0294	1,4510	41,38	41,40	$C_8H_{14}O_3$	60,2	8,9	60,7	8,9	70
XIV	$CH_2BrCHBrCH_2$	135—136 (1)	1,6623	1,5140	57,60	57,40	$C_8H_{14}Br_2O_3$[e]	30,4	4,5	30,2	4,4	93
XV	$C_6H_5OCH_2CH_2$	155—158 (1)	1,1515	1,5170	62,59	63,00	$C_{13}H_{18}O_4$	65,4	7,7	65,5	7,6	81
XVI	$C_6H_5O(CH_2)_4$	163—165 (1)	1,0866	1,5070	72,90	72,24	$C_{15}H_{22}O_4$	67,6	8,3	67,6	8,3	73
XVII	i-$C_3H_7OCH_2CH_2$	93—94 (1)	1,0122	1,4390	53,05	52,75	$C_{10}H_{20}O_4$	58,9	9,8	58,8	9,9	89

[a] Found,%: Cl 19.2. Calculated,%: 19.6. [b] Found,%: Cl 17.1. Calculated,%: Cl 16.9. [c] Tetrahydrofurfuryl. [d] Furfuryl.
[e] Found,%: Br 50.0. Calculated,%: Br 50.3.

of allyl alcohol and 0.4 ml of $SnCl_4$, after which stirring was continued for another 2 h. The excess alcohol was removed by distillation, and the residue was added from a dropping funnel to a flask containing 15 g of powdered NaOH and 65 ml of ether. The mixture was stirred at the boiling point of the ether for 3-4 h, after which the ether was decanted, and the resulting salt was dissolved in water. The aqueous solution was extracted twice with 30-ml portions of ether, and the combined ether extracts were washed with 5% aqueous acetic acid solution. The ether solution was dried with calcium chloride, the solvent was removed, and the residue was distilled to give 16.5 g (70%) of 2-allyloxymethyl-1,4-dioxane (see Table 1).

Dioxanes I-XII and XVII (see Table 1) were similarly synthesized.

B. A 17.1-g (0.15 mole) sample of 1,2-epoxy-3-allyloxypropane was added with stirring at 35-40° in the course of 1.5 h to a mixture of 60.3 g (0.75 mole) of ethylene chlorohydrin and 0.3 ml of $SnCl_4$, after which stirring was continued for 2 h. The excess alcohol was removed by distillation, and the residue was dehydrohalogenated and worked up as described above. Distillation gave 15.7 g (66%) of XIII with bp 79-80° (10 mm), d_4^{20} 1.0310 and n_D^{20} 1.4515. Found,%: C 60.3; H 8.8. MR_D 41.31. $C_8H_{14}O_3$. Calculated,%: C 60.7; H 8.9. MR_D 41.40.

2-(2,3-Dibromopropoxy)methyl-1,4-dioxane (XIV). A 17.5-g (0.11 mole) sample of bromine was added from a dropping funnel with stirring to a cooled (from −10 to −14°) mixture of 17.3 g (0.11 mole) of dioxane XIII and 50 ml of chloroform, after which stirring was continued for 10-15 min. The mixture was then neutralized with $NaHCO_3$ solution, and the aqueous portion was extracted twice with ether. The combined extracts were dried with $CaCl_2$ and distilled to give 32.6 g (93%) of XIV (see Table 1).

2-(2-Phenoxyethoxy)methyl-1,4-dioxane (XV). A solution of 5.2 g (0.13 mole) of NaOH in 7 ml of water was added to 12.3 g (0.13 mole) of freshly distilled phenol, after which the mixture was stirred at 90-95° for 35 min and 21.6 g (0.12 mole) of dioxane VII was added by drops. The mixture was then diluted with ether and neutralized, and the aqueous portion was extracted with ether. The combined ether extracts were dried with $CaCl_2$ and distilled to give 23 g (81%) of XV.

2-(4-Phenoxybutoxy)methyl-1,4-dioxane (XVI). This compound was similarly obtained (see Table 1).

2-Diethylaminomethyl-1,4-dioxane (XVIII). A mixture of 8 g (0.11 mole) of diethylamine, 15 g (0.11 mole) of β-chloroethyl glycidyl ether, and two to three drops of water were stirred at 60-70° for 5 h, after which it was added to a flask containing 9 g of powdered NaOH and 40 ml of diethyl ether. The mixture was stirred at the boiling point of the ether for 3-4 h and worked up by the usual method (see method A in the synthesis of dioxane XIII) to give 15.6 g (82%) of XVIII with bp 93-94° (1 mm), d_4^{20} 0.9520 and n_D^{20} 1.4470. Found,%: C 62.1; H 11.1; N 7.9. MR_D 48.62. $C_9H_{19}NO_2$. Calculated,%: C 62.3; H 11.0; N 8.1. MR_D 48.78.

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