SYNTHESIS AND SOME REACTIONS OF OXAZOLIDINES CONTAINING FUNCTIONAL GROUPS

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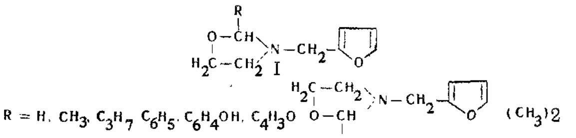
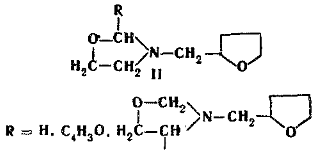
A number of hitherto unknown 2-substituted 3-furfuryloxazolidines and 2-substituted 3-tetrahydrofurfuryloxazolidines are synthesized. The reaction of hydroxyethyloxazolidine with esters, and of 5-(phenylaminomethyl)-3-phenyloxazolidine with ethylene chlorohydrin are investigated.

In recent years a number of papers have shown that it is possible to use oxazolidines [1–7], including those with functional groups [8–10], to prepare polymeric materials. For that purpose we have synthesized oxazolidines containing furfuryl and tetrahydrofurfuryl rings as well as oxazolidines containing the hydroxyethyl group.

2-Substituted 3-furfuryloxazolidines (I) were prepared by condensing furfurylaminoethanol with aldehydes and acetone. Reaction was effected using axeotropic distillation with benzene to remove the water. Yields of oxazolidines were 60–90%. Under the same conditions, reaction of tetrahydrofurfurylaminoethanol with paraformaldehyde, furfural, and glyoxal, gave 2-substituted 3-tetrahydrofurfuryloxazolidines (II).



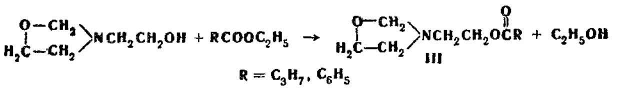
R = H, CH_3, C_3H_7, C_6H_5, C_6H_4OH, C_4H_3O $(CH_3)_2$



R = H, C_4H_3O,

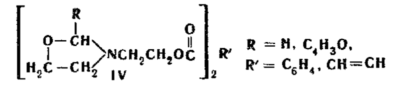
The oxazolidines I and II are transparent liquids or oils, soluble in water, ethanol, ether, and dioxane. Oxazolidines containing the hydroxyethyl group were used to prepare 2-propyl-3-(β-hydroxyethyl) oxazolidine, 2, 2-dimethyl-3-(β-hydroxyethyl)-oxazolidine*, and 2-(2-furyl)-3-(β-hydroxyethyl) oxazolidine. Hydroxy-ethyloxazolidines were prepared similarly to I and II by reacting diethanolamine with aldehydes in benzene solution. 2-Furyl-3-(β-hydroxyethyl) oxazolidines were prepared in the presence of potassium carbonate catalyst.

Oxazolidines containing a hydroxyethyl group, were reacted further. Reaction of 3-(β-hydroxyethyl) oxazolidine [11, 12] with ethyl butyrate and ethyl benzoate, in the presence of the alkoxide of the starting 3-(B-hydroxyethyl) oxazolidine gave compounds containing both an ester group and an oxazolidine ring (III) [13]:



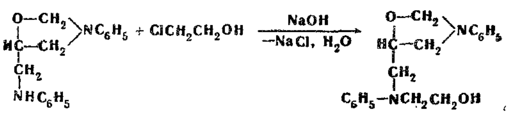
$R = C_3H_7, C_6H_5$

Thus, starting from 3-(β-hydroxyethyl) oxazolidine, diethyl maleate, and dimethyl terephthalate, and also from 2-(2-furyl)-3-(β-hydroxyethyl) oxazolidine and the same esters, dioxazolidines of general formula IV were obtained.



R = H, C_4H_3O, R′ = C_6H_4, CH=CH

Moreover, the condensation of 1,3-di(phenylamino)-2-propanol [14] with paraformaldehyde, taken in equivalent amount, gave 5-phenylaminomethyl-3-phenyloxazolidine. The preparation of this substance from formaldehyde and 1,3-di(phenylamino)-2-propanol has been reported previously [15], but its constants were not given. The product that we obtained was characterized by its boiling point, specific gravity, and refractive index. On standing it crystallized. By reaction with ethylene chlorohydrin it was converted into 5-(β-hydroxyethylphenylaminomethyl)-3-phenyloxazolidine [16].



EXPERIMENTAL

Preparation of oxazolidines (Table 1). The starting furfurylaminoethanol or tetrahydrofurfurylaminoethanol* plus the benzene were placed in a 3-necked flask, fitted with a thermometer, reflux condenser, water separator, and dropping funnel. The mixture was stirred, heated on a boiling water bath, and the

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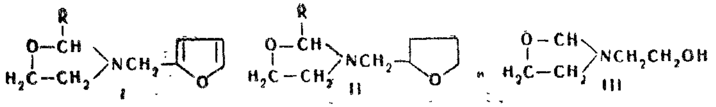
*A patent [10] describes the condensation of diethanolamine with an aliphatic aldehyde and acetone, to give 2-propyl-3-(β-hydroxyethyl)-oxazolidine and 2, 2-dimethyl-3-(β-hydroxyethyl) oxazolidine, but constants and analyses for the condensation products are not given.

*The furfurylaminoethanol and tetrahydrofurfurylaminoethanol [17] used in the present work, were synthesized in Prof. A. A. Ponomarev's laboratory at Saratov State University.

Table 1


Oxazolidines

Aldehyde or ketone	Taken, g		R	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR		Formula	N, %		Yield
	Furfurylaminoethanol	Aldehyde					Found	Calculated		Found	Calculated	
Oxazolidines* 1												
Paraformaldehyde	14.1	3.0	H	90—91 (1)	1.0913	1.5005	41.4	41.03	$C_8H_{11}NO_2$	9.37; 9.41	9.15	85.6
Acetaldehyde	14.1	6.4	CH_3	101—103 (1)	1.0848	1.5052	45.47	45.65	$C_9H_{13}NO_2$	8.23; 8.51	8.38	70.65
Butyraldehyde	14.1	8.64	C_3H_7	87—91 (2)	1.0272	1.4828	54.10	54.89	$C_{11}H_{17}NO_2$	6.60; 6.69	7.17	61.3
Benzaldehyde	7.05	6.36	C_6H_5	138—142 (2)	1.1327	1.5526	64.84	65.14	$C_{14}H_{15}NO_2$	6.14; 6.54	6.11	87.3
Salicylaldehyde	7.05	6.71	C_6H_4OH	170—175 (4)	1.1956	1.5645	66.92	66.66	$C_{14}H_{15}NO_3$	5.98; 6.02	5.71	69.1
Furfural	14.1	10.52	C_4H_3O	136—140 (6)	1.1621	1.5268	58.01	57.91	$C_{12}H_{13}NO_3$	6.51; 6.51	6.39	94.5
Glyoxal	14.1	4.74	$C_8H_{10}NO_2$	170—175 (3)	1.1879	1.5309	79.18	79.87	$C_{16}H_{20}N_2O_4$	9.32; 9.11	9.21	72.36
Acetone	14.1	6.96	$(CH_3)_2$	98—103 (5)	1.0639	1.5009	50.28	50.27	$C_{10}H_{15}NO_2$	8.03; 7.97	7.75	65.7
Oxazolidines II												
	Tetrahydrofurfurylaminoethanol											
Paraformaldehyde	30.45	6	H	98—100 (5)	1.0489	1.4770	42.10	41.97	$C_8H_{15}NO_2$	8.89; 9,03	9.15	84.0
Furfural	14.6	9.6	C_4H_3O	131—136 (3)	1.1228	1.5092	59.18	58.95	$C_{12}H_{17}NO_3$	6.50; 6,53	6.27	82.35
Glyoxal	14.5	4.74	$C_8H_{14}NO_2$	200—205 (4)	1.1426	1.5059	81.18	81.74	$C_{16}H_{28}N_2O_4$	9.06; 9,13	8.94	63.2
Oxazolidines III												
	Diethanolamine											
Butyraldehyde	105	72	C_3H_7	103—105 (4)	1.0146	1.4699	43.69	44.05	$C_8H_{17}NO_2$	8.61; 8.82	8.80	60.9
Acetone	52.5	29	C_2H_5	79—83 (4)	1.0350	1.4679	38.75	39.43	$C_{17}H_{15}NO_3$	9.95; 9.54	9.58	73.4
Furfural	21.0	21.12	C_4H_3O	142—144 (4)	1.2435	1.5165	44.4	43.71	$C_9H_{13}NO_3$	7.85; 7.79	7.65	90.4

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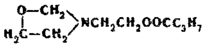
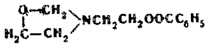
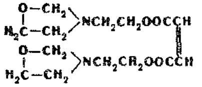
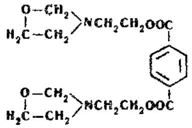
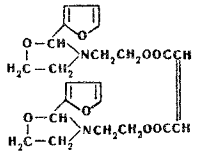
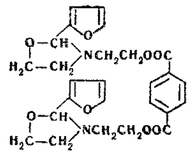
*With acetone both hydrogen at position 2 of the oxazolidine ring are replaced by methyl.

**Here 2 g K_2CO_3 was used as the catalyst.

Table 2

3-Alkoxyethyl(aryloxyethyl)oxazolidines

Taken, g		Compound formed	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	*MR*		Formula	Element	Found %	Calculated %	Yield, %
Oxazolidine	Na acylate					Found	Calculated					
38.1	34.8		150—155 (2)	1.1102	1.4875	48.37	48.79	$C_9H_{17}NO_3$	C H	58.35 9.09	57.75 9.45	60.36
40.1	45.0		172—177 (2)	1.1537	1.5368	59.51	59.05	$C_{12}H_{15}NO_3$	C H	64.4 7.7	65.15 7.69	59.88
63.5	43.0		Dark brown viscous oil					$C_{14}H_{22}N_2O_6$	N	9.09; 8.99	8.90	Quantitative
51.4	38.8		Dark brown viscous oil					$C_{18}H_{24}N_2O_6$	N	7.85; 7.71	7.70	Quantitative
40.24	17.2		Dark brown material, solidified on standing to a brittle mass.					$C_{22}H_{26}N_2O_8$	N	6.01; 6.35	6.25	Quantitative
36.6	19.4		Dark brown material, solidified on standing to a brittle mass.					$C_{26}H_{28}N_2O_8$	N	5.65; 6.49	5.65	Quantitative

aldehyde or acetone added dropwise. The water formed in the reaction was trapped in the separator. At the end of the process the benzene was distilled off from the reaction products, and the residue vacuum-fractionated.

5-Phenylaminomethyl-3-phenyloxazolidine was prepared similarly from 1, 3-diphenylaminopropan-2-ol and paraformaldehyde, yield 59.3%. Pale yellow transparent oily liquid, 220–223° (2 mm), d_4^{20} 1.1668, n_D^{20} 1.6258. Found: N 11.16; 11.11%; MR_D 77.00. Calculated for $C_{16}H_{18}NO_2$: N 11.023%; MR_D 77.20.

3-Acyloxyethyl(aryloxyethyl)oxazolidines (Table 2). A round bottom flask was fitted with a rod and disk column and thermometer, and equimolecular amounts of hydroxyethyloxazolidine and appropriate ester introduced into the flask, while 0.03–0.05 Na metal was first dissolved in the hydroxyethyloxazolidine. The reaction mixture was heated on an oil bath. The alcohol formed during the reaction was distilled off, first at ordinary pressure, and at the end of the reaction under slight vacuum. The end of the reaction was checked by the amount of alcohol which had been formed.

5-(β-Hydroxyethylphenylaminomethyl)-3-phenyloxazolidine. A 3-necked flask was fitted with stirrer, reflux condenser, thermomenter, and dropping funnel, and 0.11 mole ethylene chlorohydrin and 0.1 mole 5-(phenylaminomethyl)-3-phenyloxazolidine were added. The mixture was heated to 100° in an oil bath. Then 4.4 g KOH in 15.5 g water was added over a period of 1 hr 30 min–2 hr from the dropping funnel, and the reaction mixture heated to 100–110° for 2 hr. At the end of the reaction, the product was separated from the water layer, dissolved in BuOH, and washed with water till the reaction for the chlorine ion was negative. The residue was a dark brown oil, yield quantitative. Found: N 10.29; 10.7%. Calculated for $C_{19}H_{26}N_2O$: N 9.39%.

REFERENCES

1. K. D. Petrov and O. K. Bosteva, Author's Certificate 92618; Byull. izobr., no. 11, 13, 1951.
2. K. D. Petrov and O. K. Gosteva, ZhOKh, **23**, 1940, 1953.
3. K. D. Petrov, O. K. Gosteva, and V. I. Pukhova, Author's Certificate 93771; Byull. izobr. no. 6, 16, 1952.
4. K. D. Petrov, O. K. Gosteva, and V. I. Pukhova, ZhOKh, 27, 3218, 1957.
5. O. K. Gosteva, Khim. Prom., no. 8, 463, 1958.
6. K. D. Petrov, M. D. Nikolaev, and N. Z. Strashun, Plastmassy, 2, 56, 1959.
7. K. D. Petrov, E. S. Lagucheva, E. A. Soldatova, and L. V. Sal'nikova, Author's Certificate 157490; Byull. izobr., no. 18, 1963.
8. K. D. Petrov and S. R. Tulyaganov, ZhOKh, **32**, 2932, 1962; Author's Certificate, 151, 804.
9. K. Rosenbush, Das Leder, **6**, 80, 1955.
10. E. M. Hankuns, W. D. Emmous, U. S. Patent no. 3037006, 1962; C. A. 57, 12495, 1962.
11. H. Ulrich and K. Saurwein, German Patent no. 564787, 1932; Zbl, 11, 609, 1933.
12. T. D. Stewart and W. E. Bradley, J. Am. Chem. Soc., **54**, 4177, 1932.
13. K. D. Petrov, E. S. Lagucheva, and V. I. Pukhova, ZhOKh, **30**, 3015, 1960.
14. Ad. Fauconnier, C. r., **107**, 250, 1888.
15. J. W. Groxall and S. Melamed, U.S. Patent no. 271 563, 1955; C.A. **50**, 8742, 1956.
16. K. D. Petrov, E. S. Lagucheva, and V. I. Pukhova, ZhOKh, **24**, 1603, 1954.
17. A. Ponomarev, V. Pletneva, V. Sedavkina, and L. Barskaya, ZhOKh, **24**, 718, 1954.

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