Table I. Heats of Reactions

Reaction	ΔH, Kcal./Mole	Reaction
$\frac{1}{2}V_2O_5(c) + H^+(sol) = VO_2^+(sol) + \frac{1}{2}H_2O(sol)$	−3.94 ± 0.02	(1)
$NH_4VO_3(c) + 2\,H^+(sol) = VO_2^+(sol) + NH_4^+(sol) + H_2O(sol)$	−3.61 ± 0.02	(2)
$NaVO_3(c) + 2\,H^+(sol) = VO_2^+(sol) + Na^+(sol) + H_2O(sol)$	−6.69 ± 0.25	(3)
$NH_4Cl(c) = NH_4^+(sol) + Cl^-(sol)$	+3.41 ± 0.01	(4)
$NaCl(c) = Na^+(sol) + Cl^-(sol)$	+1.02 ± 0.04	(5)
$HCl \cdot 4.395\,H_2O(liq) = H^+(sol) + Cl^-(sol) + 4.395\,H_2O(sol)$	−2.94 ± 0.04	(6)
$4.895\,H_2O(liq) = 4.895\,H_2O(sol)$	+0.03 ± 0.01	(7)

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Displacement Reactions of 3-(2-Chloroethyl)-2-oxazolidinones with Phenoxides and Mercaptides

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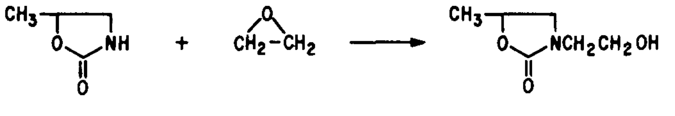
Condensation of 2-oxazolidinones with alkylene oxides at about 130° C. produces 3-(2-hydroxyalkyl)-2-oxazolidinones in excellent yields. The 3-(2-chloroethyl) derivatives react with phenoxides or mercaptides to produce the corresponding ethers or thioethers in fair to excellent yields.

THE REACTION of 3-(2-chloroethyl)-2-oxazolidinone with alkali metal alkoxides (*1, 3, 4*) or hydroxides (*1*) to produce *N*-vinyl-2-oxazolidinone has been reported. As part of a program aimed at preparing and studying derivatives of 2-oxazolidinones, the author investigated several reactions of 3-(2-chloroethyl)-2-oxazolidinones with nucleophiles such as phenoxide, mercaptide, or other divalent sulfur nucleophiles.

The required 3-(2-hydroxyalkyl)-2-oxazolidinones have been prepared by reaction of a dialkanolamine with diethyl carbonate (*6*), ethyl trichloroacetate (*9*), or carbon dioxide (*10*) or by reaction of a dialkanolamine sulfate ester with bicarbonate (*11*).

A convenient synthesis involves the direct condensation of a 2-oxazolidinone with an alkylene oxide at about 100° to 140° C. and 50 to 60 p.s.i. to give the hydroxyalkyl derivatives in excellent yield—e.g.,



Ethylene-, propylene-, or 1,2-butylene oxides all reacted.

Conversion of the *N*-(2-hydroxyalkyl)-derivatives to the chlorides was straightforward (*3, 4*). A variety of phenoxides reacted with the chlorides to give the corresponding phenyl ethers in low to moderate yields. Prolonged refluxing in ethanol (12 to 24 hours) was required. In addition to the displacement product, some dehydrochlorination product, *N*-vinyl-5-methyl-2-oxazolidinone, was obtained. Infrared analysis of the crude product indicated no hydroxyl band, demonstrating the lack of any significant amounts of C-alkylated product (*7, 8*).

Mercaptans and dithiocarbamates reacted readily to give excellent yields of products. In neither case did dehydrochlorination appear to be a factor. All of these sulfur derivatives with two methylene groups between the nitrogen and sulfur had a strong, sharp band at 7.90 to 7.95 microns in the infrared whereas in alkylthio derivatives of the type N—CH—SR this band is shifted to 8.05 microns (*5*).

EXPERIMENTAL

Materials. The phenols used were commercial materials sold by Dow Chemical Co. The thiols and sodium diethyl dithiocarbamate were obtained from Eastman.

3-(2-Hydroxyethyl)-2-oxazolidinone was prepared from diethanolamine and diethyl carbonate by the method of Homeyer (*6*), n_D^{25} 1.4830. It could not be distilled without decomposition, so the product was used without purification.

5-Methyl-2-oxazolidinone was prepared by the method of Close (2), b.p. 121-124° C. (2 mm.); n_D^{25} 1.4595.

3-(2-Hydroxyethyl)-5-methyl-2-oxazolidinone was synthesized as follows: A Pfaudler kettle was charged with 20.2 pounds (0.2 pound mole) of 5-methyl-2-oxazolidinone. The kettle was evacuated twice and pressurized with nitrogen and then heated to 130° C. Ethylene oxide (8.8 pounds., 0.2 pound mole) was fed in at such a rate that the pressure did not exceed 60 p.s.i. The mixture was heated an additional hour at 130° C. Unreacted oxide was vented under reduced pressure. A portion of the crude product was distilled through an 8-inch Vigreux column, b.p. 138-141°/1.5 mm., n_D^{25} 1.4735.

Anal. Calcd. for $C_6H_{11}NO_3$: C, 49.65; H, 7.65. Found: C, 49.73; H, 7.72.

Propylene oxide gave 3-(2-hydroxypropyl)-5-methyl-2-oxazolidinone, b.p. 135° (0.3 mm.), n_D^{25} 1.4664 (lit. b.p. 132°/0.2 mm., n_D^{20} 1.4690) (*10*). Butylene oxide gave 3-(2-hydroxybutyl)-5-methyl-2-oxazolidinone, b.p. 140°/1.2 mm., n_D^{25} 1.4675.

Anal. Calcd. for $C_8H_{15}NO_3$: C, 55.50; H, 8.73. Found: C, 55.75; H, 8.82.

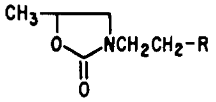
3-(2-Chloroethyl)-2-oxazolidinone was prepared from 3-(2-hydroxyethyl)-2-oxazolidinone by the dropwise addition of 238 grams (2.0 moles) of thionyl chloride to 262 grams (2.0 moles) of the hydroxy compound in 200 ml. of methylene chloride during one-half hour. The temperature rose as high as 37° during the addition. The solution was heated at reflux for 5 hours and then poured onto ice. The solution was neutralized with NaOH and then extracted with 500 ml. of methylene chloride. The CH_2Cl_2 solution was washed twice with water and dried over Drierite. Distillation through an 8-inch Vigreux gave 166 grams (55%) of light yellow liquid boiling at 121-25°/0.9 mm., n_D^{25} 1.4884 (lit. b.p. 100°/0.1 mm., n_D^{25} 1.4900) (*4*).

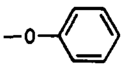
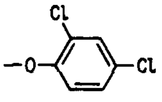
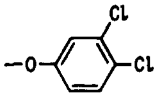
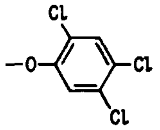
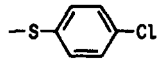
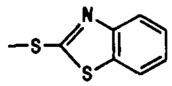
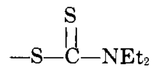
3-(2-Chloroethyl)-5-methyl-2-oxazolidinone was prepared as above, b.p. 119-122°/0.2 mm., n_D^{25} 1.4760.

Anal. Calcd. for $C_6H_{10}ClNO_2$: C, 44.05; H, 6.18. Found: C, 44.32; H, 6.29.

Detailed Study of Sodium Phenoxide with 3-(2-Chloroethyl)-5-methyl-2-oxazolidinone. Sodium phenoxide was prepared by dissolving 6.9 grams (0.3 gram-atoms) of sodium in 150 ml. of 2B absolute ethanol. Phenol (28.2 grams, 0.3 mole, Dow U.S.P.) in 50 ml. of absolute ethanol was added followed by a solution of 49.1 grams (0.3 mole) of 3-(2-chloroethyl)-5-methyl-2-oxazolidinone in 50 ml. of absolute ethanol. The solution was heated at reflux for 18 hours and the salt (12.2 grams, 70%) removed by filtration. The solution was neutralized with anhydrous HCl and the additional salt formed removed by filtration. After removal

Table I. Properties of 3-(Aryloxy)- or 3-(Alkylthio-)-Derivatives



R	B.P., ° C./mm. (M.P., ° C.)	n_D^{25}	Yield, %	Empirical Formula	Calcd., %		Found, %	
					C	H	C	H
	139-143/0.06	1.5255	50	$C_{12}H_{15}NO_3$	65.08	6.83	64.78	6.50
		1.4598	48	$C_{12}H_{13}Cl_2NO_3$	49.65	4.48	49.55	4.28
	188-208/0.03	1.5499	33	$C_{12}H_{13}Cl_2NO_3$	49.65	4.48	49.23	4.35
 [b]	(76-79) 210-215/0.9		13	$C_{12}H_{13}Cl_3NO_3$	44.45	3.73	45.65	3.85
$—S—C_5H_{11}$[c,d]	134-136/0.8	1.4877	80	$C_{10}H_{19}NO_2S$	55.35	8.84	55.08	8.48
$—S—C_5H_{11}$[d]	141-150/0.3	1.4958	76	$C_{11}H_{21}NO_2S$	57.18	9.13	56.95	8.58
$—S—C_{12}H_{25}$[e]	180-200/0.1(33°)		84	$C_{18}H_{35}NO_2S$	50.62	4.25	50.13	4.38
	[a]	1.5857	96	$C_{12}H_{14}ClNO_2S$	53.03	5.19	52.85	5.10
	[a]	1.6188	89	$C_{13}H_{14}N_2O_2S_2$	53.10	4.76	52.91	4.91
 $—S—C(=S)—NEt_2$	[a]	1.5671	90	$C_{11}H_{20}N_2O_2S_2$	48.00	7.34	47.82	7.35

[a] Not distilled. [b] Technical grade 2,4,5-trichlorophenol used. [c] 3-(2-chloroethyl)-2-oxazolidinone used. [d] 3-methyl-1-butanethiol used. [e] Technical grade 1-dodecanethiol used.

of the solvent, the residue was distilled through a flash still: cut A, 5.0 grams, b.p. 48° to 63° C. (0.1 mm.); cut B, 3.0 grams, b.p. 66° to 72° C. (0.08 mm.); cut C, 8.3 grams, b.p. 76–80° C. (0.08 mm.); cut D, 4.3 grams, b.p. 78° to 102° C. (0.10 to 0.15 mm.); cut E, 13 grams, b.p. 111° to 137° C. (0.2 mm.). Cuts B and C and cuts D and E were combined and the cuts analyzed by gas-liquid chromatography. (An F & M Model 500 was employed with a 2-foot × ¼ inch SE 30 on Chromosorb W column and a helium flow of 80 cc. per minute.) The retention times for phenol (Ti = 100°; 15° per minute) was 1.66 minutes; the chloride, 6.3 minutes; *N*-vinyl-5-methyl-2-oxazolidinone, 4.0 minutes, and the phenyl ether, 10.0 minutes. The estimated total weight of phenol was 11.9 grams; the chloride, 14.2 grams; and the vinyl compound, 2.9 grams. The pot residue, which was the phenyl ether, weighed 29.3 grams. Infrared showed essentially no hydroxyl.

The same general procedure was used for the other phenols; however, the amount of dehydrochlorination was not determined in the other reactions.

General Procedure for 3-(Alkylthio-)-Derivatives. The general procedure was carried out as for the phenols. However, precipitation of NaCl began nearly immediately during addition of the chloro compound. The reaction was mildly exothermic during the addition. A reflux period of 4 hours was generally sufficient to give yields of product exceeding 80%. Physical properties and analytical data are included in Table I. The alkylthio compounds were generally colorless to light yellow liquids, while the benzthiozolyl compound was an orange, viscous liquid.

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Densities and Partial Molar Volumes in Some Aqueous Nitrate Melts

Lithium Nitrate–Potassium Nitrate–Water at 119° C. Potassium Nitrate–Calcium Nitrate Tetrahydrate at 100° C.

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The specific volume of mixtures of water with equimolar lithium nitrate–potassium nitrate at 119° C. and at water mole ratios (R_H) between 0.25 and 1.0 mole per mole nitrate is given by v(cc./gram) = 0.5093 + 0.0856 R_H − 0.0087 R_H^2. The specific volume of mixtures of potassium nitrate with calcium nitrate tetrahydrate at 100° C. and with mole fraction (N_{Ca}) of the tetrahydrate between 1 and 0.4 is given by v(cc./gram) = 0.4976 + 0.1551 N_{Ca} − 0.0603 N_{Ca}^2. Partial molal volumes in these systems are calculated and additivity relations are discussed.

PROPERTIES of very concentrated aqueous electrolyte solutions are of interest in relating the behavior of molten salts to that of aqueous electrolyte solutions (*1, 4*). During the course of an investigation of association constants, vapor pressures, and diffusion coefficients in some aqueous nitrate melts, density data were needed for solutions of water in equimolar lithium nitrate-potassium nitrate at 119° C. with water concentrations between 0.25 and 1.0 mole of water per mole of nitrate—i.e., at molalities between 55 and 220 moles of salt per kg. of water—and for mixtures of potassium nitrate with calcium nitrate tetrahydrate at 100° C. and containing between 40 and 100 mole % of calcium nitrate tetrahydrate. These densities, measured by an Archimedean method, are presented in this paper. Some partial molal volumes are calculated and additivity relations are discussed.

EXPERIMENTAL

Materials. Analytical reagent grade lithium nitrate, potassium nitrate, and calcium nitrate tetrahydrate from Mallinckrodt were used. No further purification was done

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