

water, and the suspension heated on the steam bath for 1 hr., then filtered. The filtrate was evaporated to small volume and acidified to precipitate impure nicotinic acid. This was washed successively with boiling water and boiling ethanol and air-dried. It yielded an amide, m.p. 155–156° which showed no depression in mixed melt with an authentic specimen.<sup>15</sup>

*Hydrogenation of I. (a) Dihydroderivative.* A solution of I (17.1 g., 0.13 mole) in 50 ml. of anhydrous methanol was hydrogenated at 22° and 30 p.s.i. in presence of 50 mg. of Adams catalyst,<sup>16</sup> and absorbed 0.13 mole of hydrogen in 0.5

hr. The mixture was filtered, the methanol was removed and the product distilled, b.p. 65–66°/12 mm.;  $n_D^{25}$  1.4532;  $n_D^{20}$  1.4392; m.p. 160–161°. (b) Tetrahydroderivative. A solution of I (6.5 g., 0.043 mole) in glacial acetic acid (100 ml.) absorbed 0.086 mole of hydrogen at 23° and 40 p.s.i., in presence of 45 mg. of Adams catalyst. The mixture was filtered, diluted with 200 ml. of water, neutralized, and saturated with potassium hydroxide. Ether extraction followed by drying, removal of ether, and distillation yielded the product (5.8 g.) as a colorless oil with irritating odor, b.p. 58–59°/9 mm.;  $n_D^{25}$  1.4392; phenylthiourea, m.p. 108–109°.

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NEW YORK 3, N. Y.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, JEFFERSON CHEMICAL CO., INC.]

## Preparation of Substituted 2-Oxazolidones from 1,2-Epoxides and Isocyanates

GEORGE P. SPERANZA AND W. J. PEPPEL

Received June 30, 1958

Quaternary ammonium halides have been found to be efficient catalysts for the addition of isocyanates to 1,2-epoxides. Substituted 2-oxazolidones are obtained in good yields.

Many basic substances, including tertiary amines, are known to catalyze the polymerization of isocyanates to cyclic dimers or to isocyanurates.<sup>1,2</sup> In reported attempts to prepare substituted 2-oxazolidones from 1,2-epoxides and isocyanates using basic catalysts, only polymerization of the isocyanate has been observed.<sup>3,4</sup>

We have found that quaternary ammonium halides are highly efficient catalysts for the addition of isocyanates to 1,2-epoxides, and substituted 2-oxazolidones are obtained in good yields. An inorganic halide, potassium iodide, selected for its solubility in the reaction mixture, was also found to be a good catalyst. The ability of quaternary ammonium halides to catalyze opening of the oxirane ring has been disclosed in connection with the preparation of alkylene carbonates from alkylene oxides and carbon dioxide.<sup>5</sup>

When ethylene oxide and phenyl isocyanate were heated with a small amount of tetraethylammonium bromide in an autoclave at 200° for one hour, 3-phenyl-2-oxazolidone was obtained in 92% yield. When triethylamine was substituted as the catalyst, triphenyl isocyanurate was observed to be the principal product and 3-phenyl-2-oxazolidone was isolated with difficulty in small amount. Since

Jones and Savill found that phenyl isocyanate alone slowly polymerized at room temperature in the presence of cetyl pyridinium chloride, neither type of catalyst is entirely specific.<sup>4</sup>

The preparation of a variety of substituted 2-oxazolidones is summarized in Table I. The reactions with ethylene and propylene oxides were carried out in a rocking autoclave under the autogenous pressure. No attempts were made to determine optimum reaction conditions or to select a preferred inert solvent, several being used mainly to facilitate recovery of the products. Vinylcyclohexene diepoxide and a commercial epoxy resin were used along with 2,4-toluenediisocyanate to obtain polymeric products which were found to have no well defined softening or melting points but otherwise were not characterized further.

The product isolated in 64% yield from the reaction of the unsymmetrical propylene oxide with phenyl isocyanate was shown to be 3-phenyl-5-methyl-2-oxazolidone (I) by comparison with a sample prepared by the method of Homeyer.<sup>6</sup> The intermediate, *N*-2-hydroxypropylaniline, was prepared from aniline and propylene oxide and is known to have the structure shown.<sup>7</sup> Identity of the oxazolidones was confirmed by a mixed melting point determination and the similarity of the infrared spectra.

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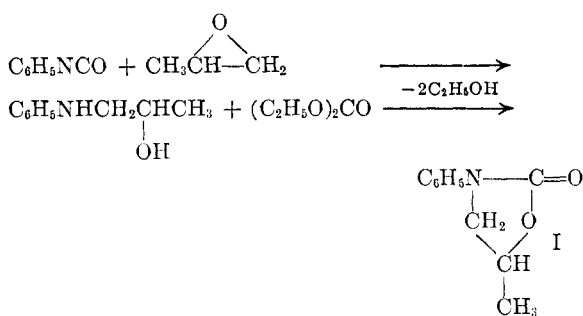
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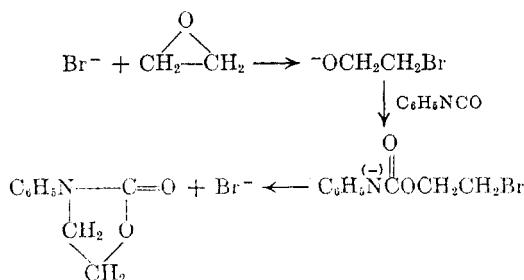
TABLE I  
 PREPARATION OF OXAZOLIDONES FROM 1,2-EPOXIDES AND ISOCYANATES

Epoxide	Isocyanate	Catalyst	Solvent	Reaction Conditions, Hr., °C.	2-Oxazolidone	M.P., °C.	Yield, %
Ethylene	Phenyl	TEAB <sup>a</sup>	Dioxane	1, 200	3-Phenyl	120	92
Propylene	Phenyl	TEAB	Dioxane	1, 200	3-Phenyl-5-methyl	81.5	64
Ethylene	2,4-Toluene di-	TEAB	DMF <sup>b</sup>	1, 200-225	2,4-Bis-3-oxazolidonyl toluene	137.5	53
Ethylene	Ethyl	TEAB	Acetonitrile	1.5, 200	3-Ethyl	B.p. 129/10 m.	26
Dodecylene	Phenyl	TEAB	DMF	3, 160	3-Phenyl-5-decyl	69.7	25
Vinylcyclohexene di- <sup>c</sup>	2,4-Toluene di-	TEAB	DMF	4, 155	Resin	>300	100
Ethylene	Phenyl	Potassium iodide	Acetonitrile	2, 160	3-Phenyl	119	74
Ethylene	Phenyl	Triethylamine	Acetonitrile	2, 160	3-Phenyl	117	Very low
Epon 828 <sup>d</sup>	2,4-Toluene di-	TMAI <sup>e</sup>	None	4, 165	Resin	>300	100

<sup>a</sup> Tetraethylammonium bromide. <sup>b</sup> Dimethylformamide. <sup>c</sup> Union Carbide Chemicals Co. <sup>d</sup> Shell Chemical Corp. <sup>e</sup> Tetramethylammonium iodide.



Opening of the epoxide ring by anions such as the halide ions has been observed and interpreted in other connections.<sup>8</sup> It is postulated from the present work that opening of the epoxide ring by the quaternary halide precedes addition of the isocyanate and the following over-all mechanism is accordingly suggested.



#### EXPERIMENTAL<sup>9</sup>

**3-Phenyl-2-oxazolidone.** To a 1400-ml. rocking autoclave was added 100 g. (0.84 mole) of phenyl isocyanate, 300 ml. of dioxane, 3 g. of tetraethylammonium bromide, and 50 g. (1.1 moles) of ethylene oxide. The reaction mixture was heated to 200° and held at this temperature for 1 hr. (190

p.s.i.g.). After opening the autoclave, 100 g. of 3-phenyl-2-oxazolidone was filtered from the reaction mixture. On evaporating the dioxane, an additional 26 g. of product was obtained (total yield 92%). The product was further purified by recrystallization from dioxane. The product had a melting point of 119.8–120.2°. A mixed melting point with authentic 3-phenyl-2-oxazolidone (prepared by the method of Homeyer<sup>6</sup> from *N*-phenylethanolamine and diethyl carbonate) showed no depression. The infrared spectra of the two samples were identical.

**3-Phenyl-5-methyl-2-oxazolidone.** To a 1400-ml. rocking autoclave was added 100 g. (0.84 mole) of phenyl isocyanate, 75 g. (1.3 moles) of propylene oxide, 3 g. of tetraethylammonium bromide, and 300 ml. of dioxane. After 1 hr. at 200° the contents were removed from the autoclave, and the solvent and unreacted propylene oxide removed by distillation at 40-mm. pressure. A brown oil (154 g.) which solidified to a yellow-brown solid was obtained. After three recrystallizations from ethanol, 95 g. (64% yield) of 3-phenyl-5-methyl-2-oxazolidone was collected which melted at 79.5–81.5°. The mixed melting point with authentic 3-phenyl-5-methyl-2-oxazolidone (prepared from aniline, propylene oxide and diethyl carbonate<sup>6</sup>) was 79.5–81.5°. The infrared spectra of the two samples were identical.

*Anal.* Calcd. for C<sub>10</sub>H<sub>11</sub>O<sub>2</sub>N: C, 67.78; H, 6.26. Found: C, 67.72; H, 6.15.

**2,4-Bis(3-oxazolidonyl)toluene.** To a 1400-ml. rocking autoclave was added 124 g. (0.78 mole) of 2,4-toluene-diisocyanate, 88 g. (2.0 moles) of ethylene oxide, 300 ml. of dimethyl formamide, and 3 g. of tetraethylammonium bromide. The reactants were heated to 200° and held at 200–225° for 50 min. After removal of the solvent and unreacted oxide a black oil (203 g.) was obtained. This oil was added to boiling benzene and that portion of the oil which dissolved was decanted. Yellow-brown crystals were obtained from the benzene extract. After repeatedly dissolving a portion of the oil in boiling benzene a total of 101 g. (53% yield) of product was obtained. A sample was purified further by recrystallizing the product from ethanol and a final recrystallization from benzene, m.p. 136.5–137.5°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>O<sub>4</sub>N<sub>2</sub>: C, 59.53; H, 5.38. Found: C, 59.50; H, 5.25.

**3-Phenyl-5-*n*-decyl-2-oxazolidone.** To a 300-ml. 3-necked flask equipped with a stirrer, thermometer, condenser, and calcium chloride drying tube was added 50 ml. of dimethyl

(8) W. C. J. Ross, *J. Chem. Soc.*, 2257 (1950).

(9) All melting points and boiling points are uncorrected.

formamide, 18.4 g. (0.1 mole) of 1,2-dodecylene oxide,<sup>10</sup> 11.9 g. (0.1 mole) of phenyl isocyanate, and 0.2 g. of tetraethylammonium bromide. The reaction mixture was heated for 4 hr. at 160°. The solvent was removed by distillation at 10-mm. pressure, and the reaction products cooled. The product was recrystallized from 250 ml. of petroleum ether (b.p. 30–60°). The product (7.2 g., 25% yield) melted at 68.5–68.7°. A mixed melting point with authentic 3-phenyl-5-*n*-decyl-2-oxazolidone (preparation described below) showed no depression.

*3-Phenyl-5-n-decyl-2-oxazolidone (method of Homeyer<sup>9</sup>).* Aniline (56 g.) and 57 g. of 1,2-dodecylene oxide were heated for 2 hr. at 185° in a flask equipped as in the experiment described above. After removing the unreacted starting materials by distillation at 20-mm. pressure the alkanolamine was allowed to solidify (64 g.). Then, 30 g. of diethyl carbonate, 0.2 g. of sodium, and 100 ml. of xylene were added, and a

(10) Becco Chemicals Division (Food Machinery & Chemicals Corp.), Station B, Buffalo 7, N. Y.

column packed with 2 × 20 cm. of stainless steel protruded packing was attached to the reaction flask. The mixture was heated and distillation continued until 20 ml. of ethanol was collected. The solid that separated on cooling the flask contents was recrystallized from petroleum ether. This sample of 3-phenyl-5-*n*-decyl-2-oxazolidone melted 68.5–69.7°.

*Resin from Epon 828<sup>11</sup> and toluene diisocyanate.* To a 3-necked 300-ml. round-bottom flask equipped with a stirrer, nitrogen inlet tube, thermometer, condenser, and drying tube was added 20 g. of Epon 828, 17.4 g. of 2,4-toluene-diisocyanate, and 0.4 g. of tetramethylammonium iodide. The reaction mixture was heated for 4 hr. at 165°. A yellow resin (37 g.) was obtained which showed no tendency to melt up to 300°.

AUSTIN, TEXAS

(11) Shell Chemical Corp., 50 W. 50 St., New York 20, N. Y. [A polyepoxide from 2,2-bis(4-hydroxyphenyl)propane and epichlorohydrin.]

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

## Catalytic Synthesis of Heterocycles.<sup>1</sup> X. Dehydrocyclization of 4-Ethyl-3-pyridinethiol to 6-Azathianaphthene

CORWIN HANSCH, WAYNE CARPENTER, AND JAMES TODD

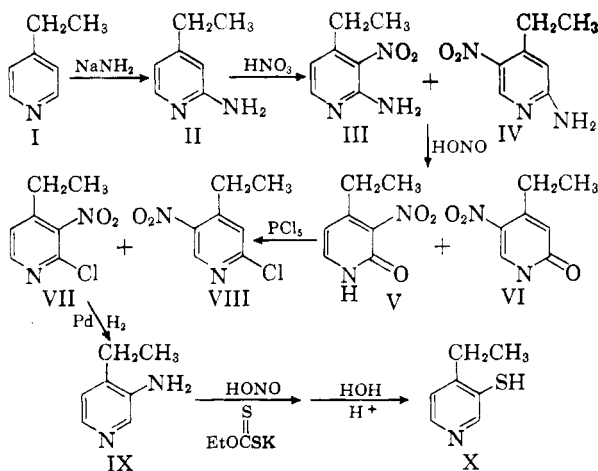
Received June 16, 1958

A procedure for the synthesis of 4-ethyl-3-pyridinethiol from 4-ethylpyridine has been developed. The dehydrogenation of this *o*-ethylthiol to 6-azathianaphthene is discussed.

In the previous paper in this series<sup>2</sup> it was shown that the thiophene ring could be formed on the pyridine nucleus by the dehydrocyclization of 2-methyl-5-ethyl-4-pyridinethiol to 6-methyl-5-azathianaphthene. The conversion to azathianaphthene was not high, being of the order of 20–25%. The low yield was due principally to hydrogenolysis of the C—S bond. The low yield in the above reaction was not unexpected since it was recognized that the

4-pyridinethiol would be in equilibrium with the thione form which would be much more likely to undergo hydrogenolysis. For this reason it was decided to investigate the dehydrogenation of a 3-thiol in which the possibility of the thione form would be absent. The scheme shown for the synthesis of 4-ethyl-3-pyridinethiol was worked out.

4-Ethylpyridine (purchased from the Reilly Tar and Chemical Co.) was converted in 60% yield to 2-amino-4-ethylpyridine (II). This material was nitrated in concentrated sulfuric acid according to the procedure of Seide<sup>3</sup> to give 90% yield of a mixture of 3- and 5-nitro-2-amino-4-ethylpyridine. About three times as much 3 isomer formed as 5. It was not necessary to separate the isomers at this point and the crude mixture was simply converted with nitrous acid<sup>4</sup> to a mixture of the pyridones V and VI in 70 to 75% yield. The mixed pyridones, V and VI, were then converted to the mixed chloropyridines, VII and VIII, by means of phosphorus pentachloride according to Phillips.<sup>5</sup> The yield of the mixed chloropyridines was 75%. The mixed chlorides were then smoothly converted to the single substance, 3-amino-4-ethylpyridine, by catalytic hydrogenation using palladium-on-calcium carbonate.<sup>6</sup> Yields of



(1) This research was supported in part by the Office of Naval Research under contract N9onr 676(00) and in part by a grant from the National Science Foundation.

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