ketones has been condensed with acrylonitrile to give cyanoethylated products. In several cases, mixtures of mono- and dicyanoethylated compounds were produced.

Conditions have been found whereby 5-methyl-2-*n*-butyrylthiophene and 2,5-dimethyl-3-propionylfuran may be condensed with acrylonitrile to give only a monocyanoethylated condensation product.

PITTSBURGH 13, PA. RECEIVED NOVEMBER 21, 1949

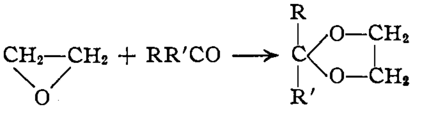
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

Reactions of Ethyleneimine with Aldehydes and Ketones[1]

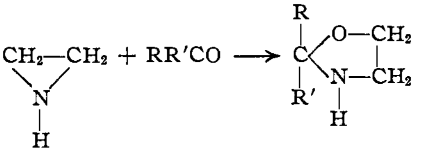
BY J. B. DOUGHTY,[2] C. L. LAZZELL AND A. R. COLLETT

The structure of ethyleneimine, $H_2\overline{C-CH_2-N}H$, and of ethylene oxide, $H_2\overline{C-CH_2-O}$, suggests that they should react similarly. The reactions of ethylene oxide have been more extensively investigated than those of the imine but where comparable data exist their reactions have been shown to be similar. In order to furnish additional data, a series of reactions of the imine with several aldehydes and ketones has been carried out.

Ethylene oxide reacts with aldehydes and ketones to give cyclic acetals[3,4]



Assuming a parallel reaction for ethyleneimine, oxazolidines would be formed.



The possibility of this reaction appeared even more favorable since oxazolidines have been prepared by the reaction of ethanolamines with aldehydes and ketones to give these cyclic compounds.[5-12] These latter reactions appear to proceed by the formation of an intermediate condensation product which loses water to form the five membered cyclic oxazolidine. Since ethyleneimine is prepared by removing water from monoethanolamine it was thought that the imine might add to aldehydes and ketones to give the heterocyclic compounds.

Experimental

Reagents.—The ethyleneimine used in all reactions was prepared by a modification of the procedure of Wenker[13] which was similar to that proposed by Leighton, Perkins and Renquist.[14] The monoethanolamine used was obtained from Carbide and Carbon Chemicals Corporation. All aldehydes and ketones used were obtained from the Eastman Kodak Company and were treated with appropriate reagents before purification by distillation.

General Procedure.—One mole of aldehyde or ketone was mixed with 100 ml. of either ethyl or isopropyl ether in a 500-ml. round-bottomed flask. This solution was cooled to 5–10° in an ice–water-bath. To the cooled solution a mole of ethyleneimine was added dropwise with one and one-half to two hours being required for the addition. When all the ethyleneimine had been added the flask was fitted with a water cooled condenser and placed over a heating unit. The reaction mixture was refluxed for twenty-four hours or longer and then the ether solvent removed by distillation. The liquid oxazolidines were recovered and purified by vacuum distillation.

Oxazolidines.—Six aldehydes and two ketones were treated with ethyleneimine to give oxazolidines. The yields, analyses and some characteristic constants of these oxazolidines are given in Table I.

The oxazolidines of the lower members of the aliphatic series are water-clear liquids having a characteristic amine-like odor. 2-Phenyloxazolidine is a light yellow liquid. 2-Hexyloxazolidine is a white crystalline solid which is completely soluble in isopropyl ether at room temperature. All products hydrolyze easily in water and decompose when distilled at atmospheric pressure.

Since these oxazolidines hydrolyze easily, this procedure was used to check the composition of the products. Ten grams of each product was mixed with 50 ml. of water and kept at room temperature for two days. After standing the mixtures were made acidic with hydrochloric acid. The two layers formed were separated and the water layer extracted with ethyl ether. The insoluble water layer and the ether extracts were combined. The combined liquids were distilled and the aldehyde or ketone recovered. The water layer was evaporated to dryness and the monoethanolamine hydrochloride crystals obtained were washed with alcohol and ether, then dried and weighed. The results are summarized in Table II.

It will be noted by inspection of Table I that the agreement between the experimental and the calculated values of the molar refraction is good. This favors the presence of the ring structure since an open chain compound would possess unsaturation and therefore a higher value for the molar refraction. Again it will be noted from Table II that when these compounds were subjected to gentle hydrolysis the expected products were identified and

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[1] This paper represents a part of the dissertation submitted by J. B. Doughty in partial fulfillment of the requirements for the Ph.D. degree to the Graduate Faculty of West Virginia University.

[2] Development Department, West Virginia Pulp and Paper Company, Charleston, S. C.

[3] Lawrence, Masters Thesis, West Virginia University, 1942.

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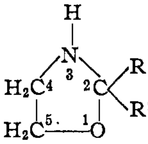
[14] Leighton, Perkins and Renquist, *ibid.*, **69**, 1540 (1947).

TABLE I

2-OXAZOLIDINES 

Aldehyde or ketone reacted	2-Oxazolidine	Yield, %	Boiling point °C.	Mm.	Nitrogen, % Found	Calcd.	$n^{25}{}_D$	$d^{25}{}_4$	Mol. ref. Found	Calcd.
Isobutyraldehyde	Isopropyl	55	37–39	40	11.9	12.3	1.4531	0.9356	33.30	33.11
Acetaldehyde	Methyl	56	85–85.5	740	15.7	16.1	1.4313	.9872	22.85	23.87
Benzaldehyde	Phenyl	10	156–157	24	9.4	9.5	....	....	...	...
Butyraldehyde	Propyl	57	45–45.5	40	11.8	12.3	1.4497	.9307	33.20	33.11
Propionaldehyde	Ethyl	28	87.5–88	740	13.8	13.9	1.4481	.9415	28.80	28.49
Heptaldehyde	Hexyl	95	M. p. 38–39°		8.8	8.9	....	....	...	...
Acetone	Dimethyl	6	53–53.5	45	13.6	13.9	1.4491	.9556	28.68	28.49
Methyl *n*-amyl ketone	Methyl, *n*-amyl	5	88–89	7	9.2	8.9	1.4492	.9053	46.60	46.77

TABLE II

HYDROLYSIS PRODUCTS OF OXAZOLIDINES

2-Oxazolidine	Cubic milliliters of aldehyde or ketone Found	Theo.	Grams of amine hydrochloride Found	Theo.
Isopropyl	6.0	7.8	7.0	8.4
Methyl	...	...	8.4	11.2
Phenyl	6.0	6.7	5.5	6.5
Dimethyl	...	...	9.0	9.6
Propyl	6.2	7.6	7.6	8.4
Ethyl	...	...	7.0	9.6
Hexyl	8.0	8.6	5.7	6.2

recovered in sufficient amounts to indicate that these compounds are readily hydrolyzed, a characteristic property of the oxazolidines.

Attempts to prepare an oxazolidine by treating ethyleneimine with crotonaldehyde were not successful. When using the general procedure of reaction in ether solution the mixture became cherry-red after refluxing for only a few minutes and upon removal of the ether became very viscous and dark red in color. The addition of only 0.5 ml. of the imine to 10 ml. of crotonaldehyde gave a hard plastic mass of deep red color within a day.

Although oxazolidines have been reported[7] as being prepared from *p*-hydroxybenzaldehyde, *m*-hydroxybenzaldehyde and *m*-nitrobenzaldehyde by the reaction of monoethanolamine these aldehydes did not react with ethyleneimine to give the heterocyclic compound under the conditions studied. *p*-Hydroxy- and *m*-hydroxybenzaldehydes reacted with ethyleneimine to give yellowish red plastic materials which softened under 100° without a sharp melting point and were insoluble in hot butyl alcohol. Nitrogen analyses indicated one mole of ethyleneimine had reacted for each mole of aldehyde. In attempts with *m*-nitrobenzaldehyde by the general procedure there appeared to be no reaction and all the imine was recovered unchanged.

Summary

1. A new synthesis for oxazolidines has been suggested.

2. Four new oxazolidines: 2-ethyl, 2-propyl, 2-hexyl and 2,2-dimethyl have been prepared and some of their properties determined.

3. Ethyleneimine reacts with crotonaldehyde, *p*-hydroxybenzaldehyde and *m*-hydroxybenzaldehyde to give plastic products of unknown structure.

MORGANTOWN, WEST VIRGINIA
RECEIVED OCTOBER 19, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

Synthetic Chlorins and Dihydrochlorins[1,2]

BY WALTER SCHLESINGER,[3] ALSOPH H. CORWIN AND LEWIS J. SARGENT

In their examination of synthetic chlorins, Fischer and Helberger[4] noted one sharp contrast in behavior between these substances and the natural chlorins derived from chlorophyll. This was the fact that the natural chlorins all gave active hydrogen determinations corresponding with the presence of two NH bonds in the nucleus while the synthetic chlorins gave zero values in the Zerewitinoff determination. These findings were confirmed by the work of Fischer and Rothemund.[5] While a formulation of a ring with no hydrogens on nitrogen and extra hydrogens on carbons in the beta positions of the porphyrin nucleus is possible, other substances suggesting such a formulation have not been discovered. It is of interest, therefore, to reëxamine the synthetic chlorins with a view to a more precise determination of their structure.

Fischer and his collaborators[6] prepared etiochlorin I by the reduction of etiohemin chloride I with sodium in absolute alcohol and in isoamyl alcohol.[5] Because of the greater availability of etioporphyrin II, our studies have been con-

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[1] Porphyrin Studies. IX. Paper VIII, Andrews, Corwin and Sharp, THIS JOURNAL, **72**, 491 (1950).

[2] A portion of this paper is from the doctoral dissertation of Walter Schlesinger, The Johns Hopkins University, 1940.

[3] William Wrigley, Jr., Co., Chicago, Ill.

[4] Fischer and Helberger, *Ann.*, **471**, 285 (1929).

[5] Fischer and Rothemund, *Ber.*, **64**, 208 (1931).

[6] Fischer, Platz, Helberger and Niemer, *Ann.*, **479**, 40 (1930).