[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI]

SOME NEW ALKYL DERIVATIVES OF HYDROXYURETHAN AND OF HYDROXYLAMINE

BY LEONORA NEUFFER AND ANNA LOUISE HOFFMAN[1]

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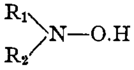
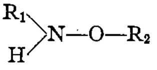
Historical accounts of the alkyl derivatives of hydroxylamine and discussions of their importance have been presented in articles by Jones,[1a] Hecker,[2] and Jones and Neuffer.[3] It is evident that by the substitution of two different groups for hydrogen in hydroxylamine three isomeric compounds are possible. These may be represented by the following formulas.



I



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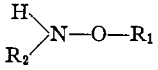

III

Compounds of the β,β type, I, have been prepared by Bewad[4] and by Dunstan and Goulding.[5] Jones and Neuffer[3] have described compounds of the α,β types, II and III, in which the substituting groups are ethyl and *sec*-butyl. The present article describes the preparation of alkyl hydroxyurethans and corresponding alkyl hydroxylamines in which the substituting groups are ethyl and *n*-butyl.

The various alkyl substituted hydroxylamines prepared up to the present time, particularly isomeric compounds, will be used as a basis for a study of relationships between chemical constitution and physical properties in an article which is now in preparation.

The hydroxyurethan and ethyl hydroxyurethan used in the following work were prepared according to the method of Jones.[6] The *n*-butyl hydroxyurethans and hydroxylamines were made by methods described by Jones,[1a] Hecker[2] and Jones and Neuffer.[3]

Experimental Part

General methods are given for the preparation of three classes of substances.

Alkyl Hydroxyurethans. *Alpha.*—An alcoholic solution containing equivalent quantities of an alkyl halide, hydroxyurethan and potassium

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[1] Abstract of a thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Anna Louise Hoffman in partial fulfilment of the requirements for the degree of Master of Arts.

[1a] Jones, *Am. Chem. J.*, **38**, 256 (1907).

[2] Hecker, *ibid.*, **50**, 444 (1913).

[3] Jones and Neuffer, THIS JOURNAL, **36**, 2202 (1914).

[4] Bewad, *J. Russ. Phys. Chem. Soc.*, **32**, 420 and 455 (1900).

[5] Dunstan and Goulding, *J. Chem. Soc.*, **75**, 799, 1004 (1899).

[6] Jones, *Am. Chem. J.*, **20**, 41 (1898).

hydroxide was heated for three hours at a temperature below 100°. The alkyl hydroxyurethan formed was extracted with ether and the potassium salt prepared by extraction with potassium hydroxide solution. Upon acidifying with 10% sulfuric acid solution, extracting with ether, and fractionating under diminished pressure, the alkyl hydroxyurethan was obtained.

Beta.—An alcoholic solution containing a mixture of equivalent quantities of sodium ethylate, an alkyl halide, and an α-hydroxyurethan was heated for several hours at about 60°. After removing sodium iodide and alcohol, an ethereal solution of the α,β-hydroxyurethan was obtained by extraction, dried with anhydrous sodium sulfate, and fractionated under diminished pressure.

α- or α,β-Alkyl Hydroxylammonium Chlorides.—A water solution containing an α-alkyl or an α,β-alkyl hydroxyurethan and twice the calculated amount of potassium hydroxide was heated in a sealed tube just below 100° for about 36 hours, or until the oily hydroxyurethan layer had almost entirely disappeared. By distilling into dil. hydrochloric acid solution and evaporating to dryness, the alkyl hydroxylammonium chloride was obtained as a white crystalline solid. This was recrystallized from absolute alcohol and dry ether. Its chloroplatinate was prepared in alcoholic solution by means of platinic chloride and precipitated by ether as a yellow, crystalline solid.

α- or α,β-Alkyl Hydroxylamines.—A mixture of an α-alkyl or an

Table I

Substances and Properties

Substance	Description	M. p. °C.	B. p. °C.	% N obtained	% Pt obtained from chloroplatinate
α-*n*-Butyl-hydroxyurethan	Colorless oil	.....	98–102 (18 mm.)	8.75	...
α,β-Di-*n*-butyl-hydroxyurethan	Colorless liquid	.....	77–83 (17 mm.)	6.79	...
α-Ethyl-β-*n*-butyl-hydroxyurethan	Colorless liquid	.....	86–90 (20 mm.)	7.62	...
α-*n*-Butyl-β-ethyl-hydroxyurethan	Colorless oil	.....	89–92 (18 mm.)	7.62	...
α-*n*-Butyl-hydroxylammonium chloride	Colorless plates	152–153	...	...	33.0
α,β-Di-*n*-butyl-hydroxylammonium chloride	White crystals	143–144	...	...	...
α-Ethyl-β-*n*-butyl-hydroxylammonium chloride	White crystals	120–121	...	...	30.22
α-*n*-Butyl-β-ethyl-hydroxylammonium chloride	Colorless plates	152–153	...	...	30.42
α-*n*-Butyl-hydroxylamine	Colorless liquid, ammoniacal odor	.....	89	15.67	...
α,β-Di-*n*-butyl-hydroxylamine	Colorless liquid, ammoniacal odor	.....	88	9.39	...
α-Ethyl-β-*n*-butyl-hydroxylamine	Colorless liquid, ammoniacal odor	.....	92–93.5	...	11.88
α-*n*-Butyl-β-ethyl-hydroxylamine	Colorless liquid, ammoniacal odor	.....	91	...	12.32

α,β-alkyl hydroxylammonium chloride and twice the molecular equivalent of potassium hydroxide was heated in a distilling flask. The alkyl hydroxylamine was obtained as a distillate.

Summary

Methods of preparation and properties are described for twelve new *n*-butyl-hydroxyurethans, hydroxylammonium chlorides and hydroxylamines.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

N-PHENYL-TETRAHYDRO-PARA-OXAZINE AND A NEW TRIPHENYLMETHANE DYE

BY HOMER ADKINS AND R. M. SIMINGTON

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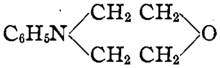
N-Phenyl-tetrahydro-*p*-oxazine (I), also known as phenylmorpholine, has been prepared by dehydrating di-β-hydroxyethyl-aniline with sulfuric acid or phosphorus pentoxide, and also by the condensation of β,β′-dichloro-ethyl ether with aniline.[1]



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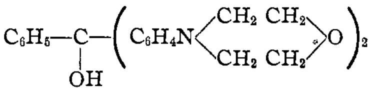

II

The best procedure for the preparation of the oxazine from ethylene chlorohydrin was to reflux 93 g. of aniline and 200 g. of the chlorohydrin for four hours while 800 cc. of a 10% solution of sodium hydroxide was slowly added. The oil was then separated, the water layer extracted with ether, and the ethereal solution added to the oil. After the evaporation of the ether, the crude dihydroxyethyl-aniline was heated for eight or ten hours under 200–300 mm. pressure at a temperature just below 200°. The oxazine was then distilled between 160° and 215° under 50–70 mm. pressure. A pure product may then be obtained by steam distillation.

The use of sodium carbonate to neutralize the hydrochloric acid produced by the condensation of the ethylene chlorohydrin and aniline is unsatisfactory because there is likely to be a considerable loss of ethylene chlorohydrin due to the rapid escape of carbon dioxide. More important, however, is the fact that sodium carbonate causes the formation of a considerable amount of tar. It is better to neutralize the acid formed by the gradual introduction of a 10% solution of sodium hydroxide. If solid sodium carbonate is used the reaction mixture must be fractionally distilled, but with sodium hydroxide the reaction product is of such a quality that it may be used directly for the next step.

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[1] Knorr, *Ber.*, **22**, 2095 (1889). Rindfusz and Harnack, THIS JOURNAL, **42**, 1720 (1920). Kamm and Waldo, *ibid.*, **43**, 2225 (1921). Cretcher and Pittenger, *ibid.*, **47**, 163 (1925).