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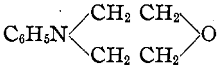
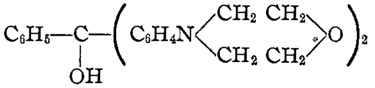
N-Phenyl-tetrahydro-*p*-oxazine (I), also known as phenylmorpholine, has been prepared by dehydrating di-β-hydroxyethyl-aniline with sulfuric acid or phosphorus pentoxide, and also by the condensation of β,β'-dichloro-ethyl ether with aniline.[1]



$C_6H_5N\left<\begin{matrix}CH_2\ CH_2\\ CH_2\ CH_2\end{matrix}\right>O$

I



$C_6H_5-\underset{OH}{C}-\left(C_6H_4N\left<\begin{matrix}CH_2\ CH_2\\ CH_2\ CH_2\end{matrix}\right>O\right)_2$

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).

Calcium carbonate also gives a very clear product, but the removal of the calcium chloride is rather difficult since it forms an addition compound with the di-β-hydroxyethyl-aniline, and the calcium must be removed as sulfate. The use of "Natur Kupfer C" in the condensation was disadvantageous as it resulted in greater formation of tar.

Miss Catherine Fletcher, using sulfuric acid, found that the best yield was obtained by using 5 parts of 70% sulfuric acid with 1 part of the di-β-hydroxyethyl-aniline. Recently 27 g. of the oxazine has been obtained from 100 g. of aniline and 235 g. of ethylene chlorohydrin. Miss Kathryn Boehmer and Miss Madeline Hancock found that the dehydration could be advantageously carried out without sulfuric acid by heating the hydroxyethyl-aniline at a pressure of 190 to 250 mm. at 200° for eight hours. By this method 135 g. of the oxazine has been obtained from 200 g. of aniline and 470 g. of ethylene chlorohydrin, using sodium carbonate in the formation of the hydroxyethylaniline. When a 10% solution of sodium hydroxide was substituted for the sodium carbonate in the first step, 90 g. of the oxazine was obtained from 200 g. of ethylene chlorohydrin and 94 g. of aniline. These various modifications have increased the yield of oxazine from 11 to 45% on the basis of the chlorohydrin and from 15 to 55% on the basis of aniline.

Kamm and Waldo's method involving the formation of β,β'-dichloro-ethyl ether and its condensation with aniline resulted in the formation of 70 g. of the oxazine from the condensation of 72 g. of the ether with 47 g. of aniline. The 72 g. of the ether was obtained from 200 g. of ethylene chlorohydrin, 50 g. of which was, however, recovered.[2] This is a much higher yield in terms of aniline than that noted in the preceding paragraph, but is about the same if the amount of ethylene chlorohydrin is considered. Both methods require about the same amount of time and attention.

N-Phenyl-tetrahydro-*p*-oxazine was condensed with benzaldehyde in the presence of hydrochloric acid to give a substituted triphenylmethane analogous to the leuco base of Malachite Green. This was oxidized with the formation of the corresponding substituted triphenylcarbinol (II) which rearranged in an acid solution to give a green dye. This new dye, "Phenylmorpholine Green," does not form such an insoluble oxalate or picrate as Malachite Green. The new dye has slightly less tinctorial value and gives a slightly lighter shade than does Malachite Green.

Phenylmorpholine Green.—The color base (II) was prepared according to the laboratory method used for the color base of Malachite Green.[3] Sixty g. of the oxazine was heated on a steam cone for 24 hours with 20 g. of benzaldehyde and 29 g. of hydrochloric acid (d., 1.19). After steam distillation, the 60 g. of crude leuco base was dissolved in 49 g. of hydrochloric acid (d., 1.19), 35 g. of acetic acid and 17 cc. of water. After the mixture had been cooled to 0° and 170 g. of finely chipped ice added, a paste containing 50 g. of lead peroxide was added with rapid stirring during 15 minutes. The mixture was then stirred for an hour at 60° with 20 g. of sodium sulfate (decahydrate) in 35 cc. of water. After filtering, the filtrate was added with rapid agitation to 30 g. of sodium hydroxide in 170 cc. of

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[2] The yields noted in this paper have been selected as representative from the results of numerous trials of each method and its modifications.

[3] Adkins and McElvain, "Practice of Organic Chemistry," McGraw-Hill Book Co., New York, **1925**, p. 126.

water held at 40°, 10 g. of the crude color base being obtained. This was dissolved in alcohol and thes mall amount of contaminating, inorganic salts filtered off. The pure compound recovered by the evaporation of the alcohol was used for analysis and also converted to the dye by solution in acids.

Anal. Calcd. for $C_{27}H_{30}N_2O_3$: N, 6.51. Found: 6.47, 6.45.

Summary

N-Phenyl-tetrahydro-*p*-oxazine has been prepared in considerable quantities through modifications of the Knorr, and the Kamm and Waldo methods. The advantages of each of these methods have been demonstrated. An improved method for the condensation of ethylene chlorohydrin and aniline has been described. It has been found advantageous to dehydrate di-β-hydroxyethyl-aniline by heating under reduced pressure rather than to do so by the use of sulfuric acid. The oxazine has been condensed with benzaldehyde to give a new triphenylmethane dye. Some of the properties of the new dye have been noted.

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

SOME SUBSTITUTED AMMONIUM MOLYBDATES AND TUNGSTATES

BY A. C. KRAUSE[1] AND FRANCIS C. KRAUSKOPF

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Introduction

Relatively few compounds of molybdic acid with organic bases have been made.

In 1856 Sonnenschein[2] prepared an ethylammonium molybdate from a solution of molybdic acid in ethylamine. Classen[3] in a like manner formed a tetramethylammonium molybdate. By the use of pyridine sulfate and sodium molybdate Pincussohn[4] prepared a pyridinium molybdate. Similarly, Ditte[5] made phenylammonium molybdate.

The compounds of organic nitrogen bases with tungstic acids are more numerous. Their method of preparation has been generally the same as that of the molybdic salts of the organic bases.

Kohn[6] precipitated a hydrated guanidinium tungstate from a solution of guanidinium carbonate. Knorre[7] prepared benzidinium tungstate from sodium paratungstate.

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[1] The material presented here is a portion of that used by A. C. Krause in his dissertation presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] Sonnenschein, *J. prakt. Chem.*, **67**, 151 (1856).

[3] Classen, *ibid.*, **93**, 448 (1864).

[4] Pincussohn, *Z. anorg. Chem.*, **14**, 379 (1897).

[5] Ditte, *Compt. rend.*, **105**, 813 (1887).

[6] Kohn, *Ber.*, **38**, 783 (1905).

[7] Knorre, *Ber.*, **38**, 783 (1905).