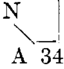
TABLE I

DIALKYLAMINOALKYLPHENOXAZINE-10-CARBOXYLATES (II. R = H)

$(CH_2)_nNR_2'$	M.P.° Dec. of Salt	Formula	Nitrogen Calcd.	Nitrogen Found
$CH_2CH_2N(CH_3)_2$	196–197	$C_{17}H_{18}N_2O_3 \cdot HCl$	8.36	8.21
$CH_2CH_2N(C_2H_5)_2$	132–134	$C_{19}H_{22}N_2O_3 \cdot HCl$	7.72	7.74
CH_2CH_2N 	170–172	$C_{19}H_{20}N_2O_3 \cdot HCl$	7.76	7.71
$CH_2CH_2CH_2N(CH_3)_2$	215–216	$C_{18}H_{21}N_2O_3 \cdot HCl$	8.03	8.23
$CH_2CH_2CH_2N(C_2H_5)_2$	184–186	$C_{20}H_{24}N_2O_3 \cdot HCl$	7.43	7.30

After cooling, the precipitate was filtered off and dried, 7.2 g., m.p. 198–200° dec. By recrystallization in absolute ethanol 6.30 g. (60%) of white crystals, m.p. 215–216° dec. was obtained.

2-Ethyl-10-(3'-N-pyrrolidinopropyl)phenoxazine hydrochloride (III. R = C_2H_5; NR'_2 = N  ; n = 3). (a) *2-Ethylphenoxazine-10-carbonyl chloride.* A 34% (w./w.) solution (20 ml.) of phosgene in toluene was heated in a closed reaction vessel with 6.76 g. (0.032 mole) of 2-ethylphenoxazine in 10 ml. of toluene at 75° for 3.5 hr. The solution was evaporated to dryness and the oil (8.75 g., 100%) did not solidify after being kept in a refrigerator for several days.

(b) *Preparation and decarboxylation of 2-ethylphenoxazine-10-carboxylic acid 3'-N-pyrrolidinopropyl ester.* A solution of 8.75 g. (0.032 mole) of 2-ethylphenoxazine-10-carbonyl chloride and of 9.1 g. (0.070 mole) of 2-pyrrolidinopropanol in 30 ml. of dry benzene was heated on the steam bath for 5.5 hr. After cooling, the mixture was diluted with the same volume of ether and extracted with 60 ml. of 5% hydrochloric acid. After separation the aqueous phase was made alkaline and again extracted with ether. After evaporation of the ether, the residue was decarboxylated by heating in oil bath at 220–230° under reduced pressure (20–40 mm.). When the evolution of carbon dioxide subsided, the product was distilled *in vacuo* to give 7.3 g. (70%) of an oil, b.p. 215°/0.8 mm. The base was dissolved in a solution of hydrochloric acid in absolute ethanol and yielded 6.45 g. of III, m.p. 174–175°, identical with the same product prepared by other methods.[3]

10-(3'-Dimethylaminopropyl)phenoxazine hydrochloride (III R = H, $NR_2' = N(CH_3)_2$; $n = 3$) The hydrochloride of the carboxylate (6.25 g.) described above was dissolved in water and extracted with ether, after having been made alkaline. The residue obtained after evaporation of the ether was decarboxylated at a temperature of 215° under reduced pressure (35–45 mm.). The residual oil was distilled *in vacuo* (173°/0.3 mm.) and transformed into the hydrochloride to give 2.73 g. of white crystals, m.p. 132–134°, identical with the product prepared by another method.[3]

REGA INSTITUTE
UNIVERSITY OF LOUVAIN
LOUVAIN, BELGIUM

Reaction of Chlorinated Urea Products with Ammonia and Ethylamine

CORNELIUS S. GROVE, JR., GERALD F. GRILLOT, AND RICHARD C. CHANG

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As *p*-urazine was needed in studies initiated in this laboratory[1] its synthesis was attempted by a procedure essentially similar to a method described by Chattaway[2] in which a chlorinated urea product is treated with aqueous ammonia. Many repeated attempts to prepare *p*-urazine by this method produced a substance that appears to be biurea,[3] as it exhibited properties identical to a sample obtained from Eastman Kodak Co. and one prepared by the action of urea on hydrazine hydrate,[4] and unlike a sample of *p*-urazine prepared by the method of Curtius and Heidenreich[4] in which the ethyl ester of hydrazinedicarboxylic acid is heated with hydrazine hydrate. Like biurea, the aqueous solution of the product obtained by ammoniating the chlorourea product was neutral. It gave no color with ferric chloride but gave an immediate positive test with Fehling's solution. *p*-Urazine dissolves in water to give an acid solution, gives a red color with ferric chloride, and is supposed to give a positive test with Fehling's solution only upon extended heating. Authentic biurea and the ammoniated chlorourea product melted at 246–258°, whereas *p*-urazine is listed as melting at 260°.[4] The ammoniated chlorourea product gave no noticeable depression of the melting point when mixed with an authentic sample of biurea but gave a definite depression when mixed with an authentic sample of *p*-urazine.

An X-ray examination of biurea and *p*-urazine was performed by Dr. Virginia Russell of the Chemistry Department at Syracuse University.[5] A well formed crystal of biurea was mounted and x-ray pictures were taken on a Weissenberg camera. The crystal was examined with the rotation axis parallel to a diagonal (not 90° apart).

Rotation patterns of an authentic biurea sample and the ammoniated chlorourea product showed two-fold rotation in each. A Weissenberg picture of a zero layer indicates two axes which were found at an angle of 62° to each other. From this evi-

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(1) The support of these studies by W. R. Grace & Co., Clarksville, Md., is gratefully acknowledged.

(2) F. D. Chattaway, *J. Chem. Soc.*, **95**, 235 (1909).

(3) Biurea is also known as hydrazodicarbonamide, carbaminyl hydrazide, hydrazine-*N,N'*-dicarboxylic acid amide, and hydrazoformamide.

(4) T. Curtius and K. Heidenreich, *J. prakt. Chemie*, (2) **52**, 454 (1895).

(5) Present address: Genreal Electric Co., Electronics Park, Syracuse 1, N. Y.

dence it may be surmised that biurea forms a triclinic crystal.

X-ray pictures of *p*-urazine were also prepared by Dr. Russell. A rotation picture and a zero layer picture of this substance seems to indicate an orthorhombic crystal with the following cell dimensions: $a_0 = 5.58$ Å; $b_0 = 5.39$ Å; $c_0 = 6.63$ Å.

On microscopic examination biurea appears as diamond-shaped crystals and shows inclined extinction, whereas *p*-urazine appears as rectangular-shaped crystals and these exhibit parallel extinction.

In the reaction of ammonia with the chlorinated urea product, ammonia may be acting as a dehydrohalogenating agent, exclusively, or may play a more important role in the reaction. If the former is the true situation, ethylamine should also produce biurea when it is treated with the chlorinated urea product. In the latter reaction a white solid was obtained that melted at 247–250° and gave a mixed melting point of 239–244° with biurea. Its properties and analysis indicates that it is diethylbiurea, $C_2H_5NHCONHNHCONHC_2H_5$.[6]

The above results would make one suspect that some intermediate product, such as oxycyanogen (O═C═N—N═C═O) is formed in a Hofmann type rearrangement. The latter product then reacts with ammonia and amines to form biurea and the dialkylbiurea, respectively.

We were unable to isolate either biurea or *p*-urazine from the solution resulting from the reaction of concentrated ammonium hydroxide with monochlorourea prepared by the method of Chalsty and Israelstam.[7] From these latter results one might suspect that monochlorourea is not the reactive species present in the chlorinated urea product.

EXPERIMENTAL

Preparation of the chlorourea products. The method of Chattaway[3] was employed to prepare a product corresponding closely in composition to monochlorourea.

Sixty grams (1 mole) of urea was dissolved in a minimum amount of water. To the resulting solution was added 120 g. (1.5 moles) of zinc oxide.[8] Chlorine gas was then slowly bubbled into the stirred reaction mixture. The temperature was maintained at or very nearly 0° during the addition of the chlorine. As chlorine was added the reaction mixture became momentarily clear. Then a white precipitate began to form and the reaction vessel became filled with a thick mass of crystals. The addition of chlorine was then stopped, but the agitation was continued a while longer to allow the dissolved chlorine to react with the unchanged urea. The white flake-like precipitate was then removed by filtration. Various samples prepared by the above procedure showed from 20 to 35% available chlorine (determined by an addition of excess potassium iodide-starch reagent and titration with standard thiosulfate). Calcd. for monochlorourea (CH_3ON_2Cl): Cl, 37.4. Maximum yield obtained: about 65%.

A product corresponding closely in composition to dichlorourea was obtained by direct chlorination of an aqueous solution of the product obtained above. A soft white solid product was obtained that showed 53.5% available chlorine. Calcd. for dichlorourea ($CH_2ON_2Cl_2$): Cl, 55.1. This product also reacted with an excess of concentrated aqueous ammonia to form biurea.

Biurea (*$H_2NCONHNHCONH_2$*). The chlorinated urea product (20–35% available chlorine) obtained above was dissolved in approximately 25 volumes of water. The resulting solution was slowly poured into an excess of concentrated aqueous ammonia. A vigorous evolution of gas occurred and the solution became yellow in color. On cooling a white precipitate formed. The resulting solid was separated by filtration and was crystallized from hot water, m.p. 255° dec.; yield 16%.

Method of Curtius and Heidenreich. Six grams (0.1 mole) of urea was heated with 2.5 g. (0.05 mole) of hydrazine hydrate in a closed tube at 130° for 1 hr. The residue was recrystallized from hot water. The yield of biurea was about 20% based upon the amount of urea employed.

Anal. Calcd. for biurea, $C_2H_6N_4O_2$; C, 20.38; H, 5.08; N, 47.4. Calcd. for *p*-urazine, $C_2H_4N_4O_2$: C, 20.7; H, 3.45; N, 48.3. Found for the ammoniated chlorourea product: C, 20.51, 20.47; H, 5.00, 5.01; N, 46.80, 46.53. Found for biurea prepared by the method of Curtius and Heidenreich[4]: C, 20.51; H, 5.06; N, 46.51. Found for *p*-urazine prepared by the method of Curtius and Heidenreich[4]: C, 20.85; H, 3.12; N, 47.54.

Diethylbiurea (*$C_2H_5NHCONHNHCONHC_2H_5$*). Five grams of the dichlorourea (53.5% available chlorine) prepared above was dissolved in 100 ml. of ice water. This solution was gradually poured into 10 g. of a 70% solution of ethylamine. A vigorous reaction ensued and much heat was generated. The white solid that formed melted at 247–250° and gave a depression of the melting point when mixed with biurea. Yield about 2 g. or 60% of the theory.

Anal. Calcd. for $C_6H_{14}N_4O_2$: C, 41.4; H, 8.05; N, 32.1. Found: C, 41.65, 41.80; H, 8.56, 8.26; N, 31.90, 31.99.

Stollé[9] has prepared diethylbiurea by the reaction of ethylamine on hydrazodicarbonazide ($N_3CONHNHCON_3$) and reported a melting point. of 255°. Mauguin[10] reported its melting point at 250°.

SYRACUSE UNIVERSITY RESEARCH INSTITUTE
SYRACUSE 10, N. Y.

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[6] G. F. Grillot and R. C. Chang, U.S. Patent 2,855,435 (Oct. 7, 1958). Assigned to W. R. Grace & Co.

[7] J. S. Chalsty and S. S. Israelstam, *Chem. & Ind. (London)*, November 1954, page 1452.

[8] Lime (calcium oxide) can replace the zinc oxide in this preparation.

[9] R. Stollé, *Ber.*, **43**, 2470 (1910).

[10] C. Mauguin, *Ann. de chemie et de phys.* (8), **22**, 318 (1911).

The Dialkylation of Cyanoacetic Ester with Chloromethylmethylethoxysilanes

OMAR W. STEWARD[1] AND LEO H. SOMMER

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Sommer *et al.*[2] reported an attempt to introduce a second trimethylsilylmethyl group into malonic ester using chloromethyltrimethylsilane and diethyl sodiotrimethsilylmethylmalonate. The only product obtained was trimethylsilylmethyl ethyl ether, the product of a Williamson type reaction.

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[1] Dow Corning Corp., Midland, Mich.

[2] L. H. Sommer, G. M. Goldberg, G. H. Barnes, and L. S. Stone, Jr., *J. Am. Chem. Soc.*, **76**, 1609 (1954).