frared spectrum was identical with that of a sample of the starting nitrosourea.

Reaction of N-Nitroso-N-(2,2-diphenylcyclopropyl)urea with Varying Amounts of Lithium Ethoxide. In order to demonstrate that a full molar quantity of lithium ethoxide was needed to decompose the nitrosourea, the amounts of base were varied in a series of decomposition reactions. To 0.281 g. (0.0010 mole) of N-nitroso-N-(2,2-diphenylcyclopropyl)urea stirring in 15 ml. of anhydrous ether at 0° was added lithium ethoxide in partial molar quantities (see Table I). In each case, stirring was continued until gas evolution had ceased and the solution then filtered. When the solvent was removed on a rotary evaporator, the gummy yellow material was triturated with pentane to give the unreacted solid nitrosourea and a solution of any diphenylallene formed. After evaporation of the pentane, the amount of diphenylallene was determined by weighing.

Salt of *p*-Toluenesulfonic Acid. The sodium, lithium, and ammonium salts of *p*-toluenesulfonic acid were prepared by neutralizing an ethyl alcohol solution of the acid, respectively, with solutions of sodium hydroxide, lithium ethoxide, and ammonia in ethyl alcohol. The solid salts were isolated by removal of the solvent with a rotary evaporator.

Table I

Amount of LiOEt, %	Gas evolution, %	Diphenyl-allene isolated, %	Recovered nitro-sourea, %	Diazotate isolated, %
25	22	19	78	0
50	47	42	53	0
75	61	52	36	3
100	76	75	0	17

Acknowledgment. The authors gratefully acknowledge the financial assistance received from the U. S. Army Research Office (Durham), and also thank the National Science Foundation for their generous support of this work.

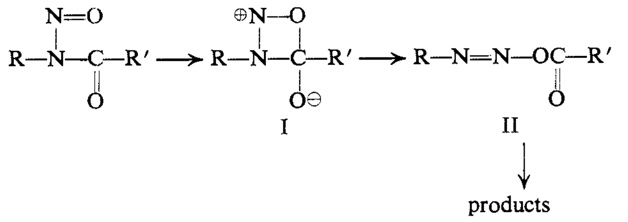
A Study of the Mechanism of the Thermal Conversion of N-Nitroso-N-(2,2-diphenylcyclopropyl)urea to 2,2-Diphenyldiazocyclopropane[1]

D. L. Muck and W. M. Jones[2]

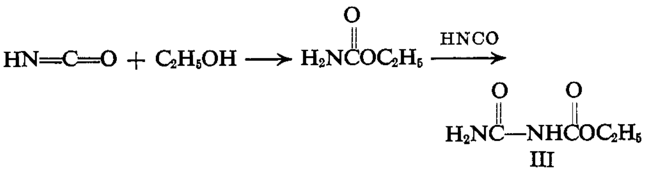
Contribution from the Department of Chemistry, University of Florida, Gaineville, Florida. *Received July 6, 1965*

Abstract: The mechanism of the thermal decomposition of N-nitroso-N-(2,2-diphenylcyclopropyl)urea in nonpolar solvents has been investigated. A mechanism postulating removal of a terminal NH_2 proton by the nitroso oxygen atom through a cyclic transition state, followed by collapse to give isocyanic acid and the diazohydroxide, is presented. Results reported earlier for the thermal decomposition of N-nitroso-N-methylurea substantiate this reaction scheme, and make it appear to be general for the thermal decomposition of alkylnitrosoureas.

The mechanism of the thermal decomposition of N-nitrosoamides has been examined carefully and there seems to be little doubt that the reaction proceeds by initial rearrangement (probably through intermediate I) to give the diazoester II which then loses nitrogen to give the observed products.[3]



On the other hand, the thermal decomposition of N-nitroso-N-alkyl(or aryl)ureas has received relatively little attention. In fact, to the best of our knowledge, only two systems have been studied. The first, N-nitroso-N-methylurea, was investigated in 1919 by Werner[4] who studied the decomposition in refluxing ethyl alcohol. The major product observed by Werner was ethyl allophanate (III), which he postulated was formed from the reaction of isocyanic acid and ethanol.



$$HN{=}C{=}O + C_2H_5OH \longrightarrow H_2NCOC_2H_5 \xrightarrow{HNCO} H_2NC{-}NHCOC_2H_5$$

III

Werner did not attempt to explain the origin of the isocyanic acid. He also examined the product from the neat decomposition of the nitrosourea and identified it as trimethyl isocyanurate (IV). Werner proposed the ester to be formed from the trimerization of methyl isocyanate, but again made no mention of its origin.

Later, in 1956, Huisgen and Reimlinger investigated the thermal decomposition of N-nitroso-N-methylurea in benzene.[3a] Under these conditions, the trimethyl isocyanurate (IV) was isolated in 30% yield. The origin of this ester again was presumed to be from the

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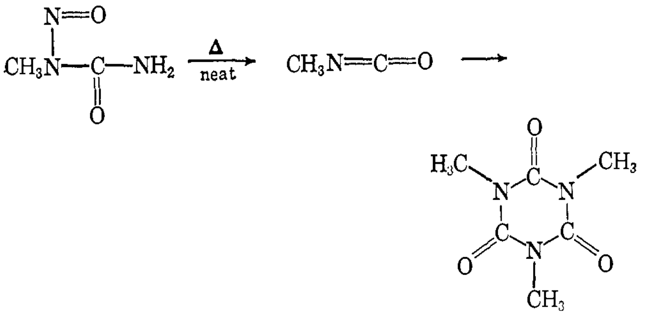
(1) A portion of this work was taken from a dissertation submitted by D. L. Muck in partial fulfillment of the requirements for the Degree Doctor of Philosophy at the University of Florida.

(2) Alfred P. Sloan Fellow.

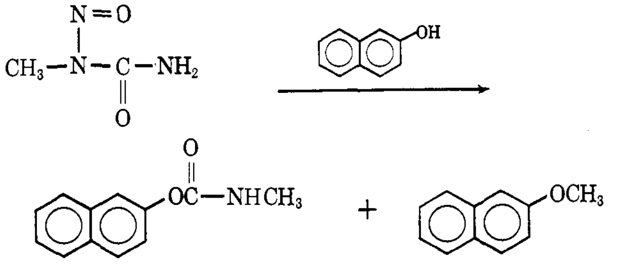
(3) (a) A. R. Huisgen and H. Reimlinger, *Ann.*, **599**, 183 (1956); (b) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2893 (1957); (c) E. H. White and C. A. Aufdermarsh, Jr., *ibid.*, **83**, 1174, 1179 (1961).

(4) E. A. Werner, *J. Chem. Soc.*, **115**, 1093 (1919).

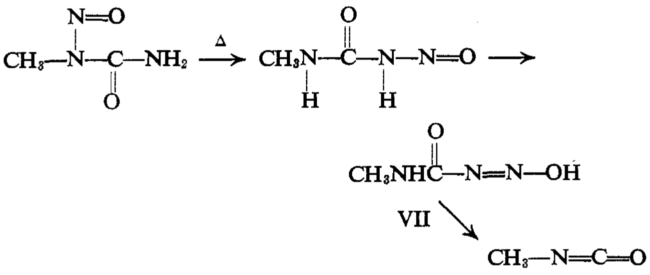


IV

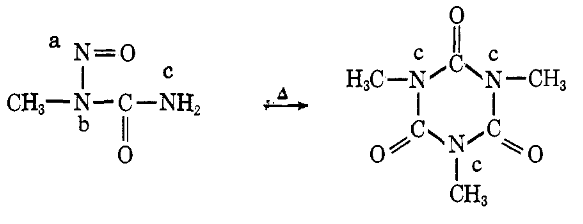
trimerization of methyl isocyanate. Evidence in support of the intermediacy of $CH_3—N=C=O$ was obtained by effecting the decomposition in the presence of β-naphthol. From this set of conditions was obtained 13.7% of the expected urethan V plus 23.5% of β-naphthyl methyl ether VI. As a reasonable explanation for these results, Huisgen and Reimlinger proposed initial migration of the nitroso group to give the diazohydroxide VII followed by dehydration and loss of nitrogen to give some methyl isocyanate.

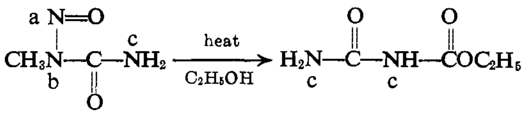


V VI

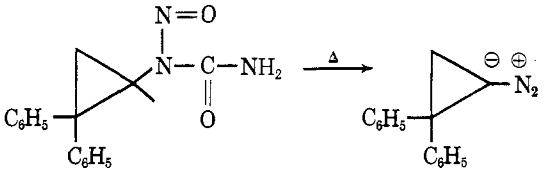


However, some four years later, Clusius and Endtinger[5] reported a thorough investigation of this same reaction employing tagged nitrogen and made the rather surprising observation that the NH_2 nitrogen (c) of the nitrosourea appeared in the trimethyl isocyanurate rather than the nitrogen to which the nitroso was attached (as would be expected by the Huisgen and Reimlinger mechanism). Clusius and Endtinger also studied the decomposition in ethyl alcohol, and isolated the ethyl allophanate (III) as reported earlier by Werner. Again using tagged nitrogen, the NH_2 nitrogen of the nitrosourea was observed to be present in both positions of the allophanate ester. Clusius and Endtinger were not able to justify either of these results and concluded their paper with the statement that "a convincing formulation for the reaction mechanism is not yet possible."





Shortly after these reports, a study of the thermal decomposition of N-nitroso-N-(2,2-diphenylcyclopropyl)urea (VIII) was carried out in our laboratories,[6] and it was reported that only the products that would result from initial formation of 2,2-diphenyldiazocyclopropane (IX) were found, with no 2,2-diphenylcyclopropyl isocyanate being detected.

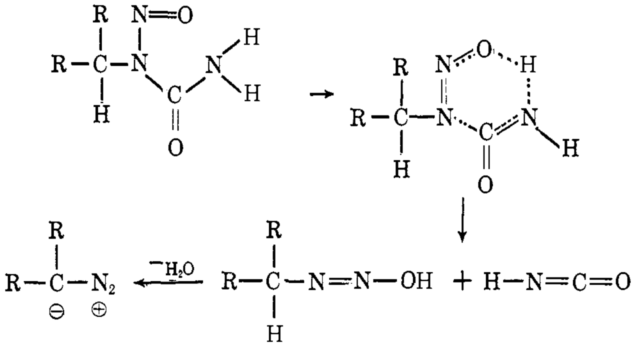


VIII IX

The purpose of this paper is to propose a mechanism for these reactions that is consistent with all of the above observations and to present some additional observations that support this mechanism.

The proposed mechanism is outlined in Scheme I. The proton transfer and expulsion of isocyanic acid may be either stepwise or concerted. It is arbitrarily pictured as a concerted reaction.

Scheme I



Application of this mechanism to the system of Huisgen and Reimlinger gives as the initial products diazomethane and isocyanic acid instead of methyl isocyanate. However, we have found that diazomethane reacts quite rapidly with isocyanic acid to give methyl isocyanate.

$$CH_2N_2 + H—N=C=O \longrightarrow CH_3—N=C=O$$

Trimerization of methyl isocyanate from this source would lead to isocyanuric acid trimethyl ester with the correct positioning of the N^{15} found by Clusius and Endtinger.

However, when an attempt was made to effect this trimerization under Huisgen and Reimlinger's reaction conditions, negligible amounts of the trimer were ob-

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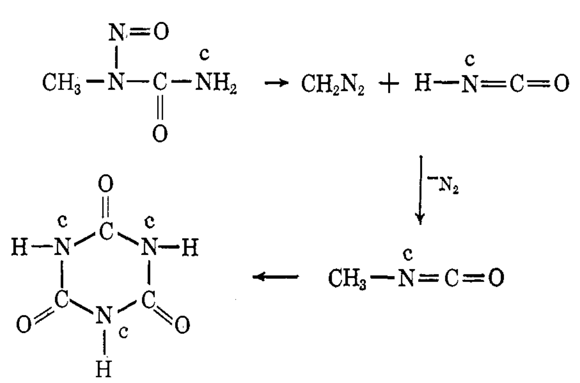
(5) K. Clusius and F. Endtinger, *Helv. Chim. Acta*, **43**, 2063 (1960).

(6) W. M. Jones, M. H. Grasley, and D. G. Baarda, *J. Am. Chem. Soc.*, **86**, 912 (1964).



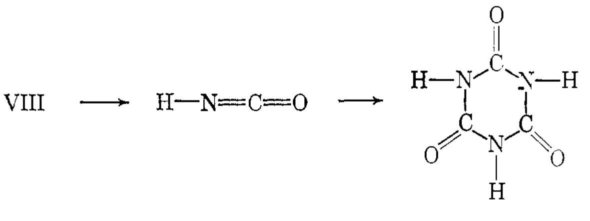
tained. Methyl isocyanate is known to polymerize to the trimer IV during attempts to distil it,[7] so apparently the reaction is greatly reduced when the monomer is diluted with a solvent such as benzene. This information sheds doubt on the possibility of methyl isocyanate being the precursor to the cyanurate ester under Huisgen and Reimlinger's conditions, but does not eliminate it from consideration under the conditions used by Werner.

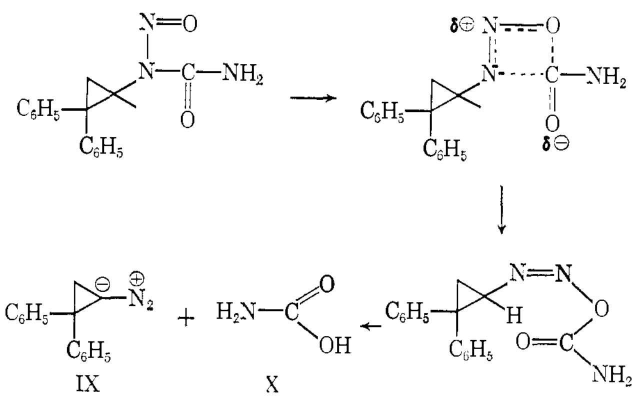
A more feasible explanation of the observations of Huisgen and Reimlinger as well as Clusius and Endtinger would involve initial trimerization of isocyanic acid[8] to cyanuric acid followed by reaction with diazomethane to give the trimethyl ester. This possibility was confirmed by treating cyanuric acid with diazomethane. Reaction was not as rapid as with isocyanic acid, but the reaction did proceed at a reasonable rate at 0° to give the predicted product.

The proposed mechanism also explains the observation of Huisgen and Reimlinger that 23.5% of methyl β-naphthyl ether (VI) is also formed in their reaction.

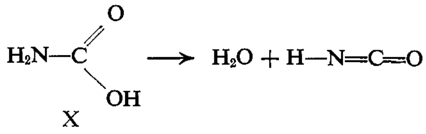
Application of this same scheme to the N-nitroso-N-(2,2-diphenylcyclopropyl)urea system (VIII) readily explains the observed products resulting from decomposition of 2,2-diphenyldiazocyclopropane (IX).

Further evidence for the proposed scheme arises from a more careful examination of the products arising from the decomposition of the nitrosocyclopropylurea VIII. Thus, in addition to the decomposition products of 2,2-diphenyldiazocyclopropane, there was invariably noted a white insoluble solid. Much of this was found in the condenser above the reaction flask. Examination of this solid showed that it was cyanuric acid (isolated in 82% yield). The formation of this nonvolatile material in the condenser left no doubt but that it arose from the well-known trimerization of isocyanic acid.[8]



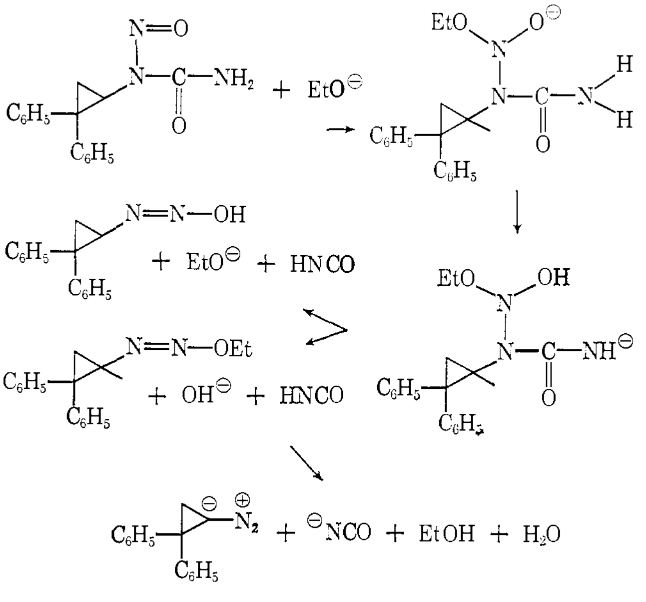


One possible alternate reaction route that could not *a priori* be excluded involves a rearrangement analogous to that believed to occur in the thermal decomposition of N-nitrosoamides. However, in order for this mechanism to explain the various observations, carbamic acid (X) must dehydrate under the reaction conditions to give isocyanic acid. This possibility was tested by treating lithium and sodium carbamate with p-toluenesulfonic acid in refluxing benzene. The only products were ammonium p-toluenesulfonate and the alkali metal p-toluenesulfonates. Thus, carbamic acid apparently decomposes in the normal fashion[9] in refluxing benzene to give carbon dioxide and ammonia.



Another bit of pertinent data was obtained when the corresponding dimethylamide derivative, N-nitroso-N-(2,3-diphenylcyclopropyl)-N′,N′-dimethylurea,[10] was found not to evolve nitrogen when heated under normal reaction conditions. When this compound was heated more strongly, it was slowly transformed into unknown products without gas evolution. Examination of this crude decomposition product revealed none of the normal diazocyclopropane decomposition product, diphenylallene.

Scheme II



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[7] K. H. Slotta and R. Tschesche, *Ber.*, **B60**, 295 (1927).

[8] I. Heilbron, "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, New York, N. Y., 1953.

[9] C. Faurholt, *J. chim. phys.*, **22**, 1 (1925).

[10] W. M. Jones, D. L. Muck, and T. K. Tandy, Jr., *J. Am. Chem. Soc.*, **88**, 68 (1966).

Finally, the similarity between the mechanism proposed in Scheme I and the mechanism which is believed to obtain in the alkoxide-induced conversion of N-nitroso-N-cyclopropylureas to diazocyclopropanes should be pointed out.[10] It is believed that the reaction proceeds by initial attack of alkoxide on the nitroso nitrogen followed by proton transfer, loss of isocyanic acid, and loss of base. This is outlined in Scheme II.

Experimental Section

The melting points were taken in a Thomas–Hoover Unimelt apparatus and are uncorrected. The infrared spectra were recorded with a Perkin-Elmer Infracord spectrophotometer and the elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

Materials. The solvents (anhydrous ethyl ether, petroleum ether, benzene, *n*-heptane, and THF) used in this work were all Fisher certified reagents and were used without further purification. The cyanuric acid used was purchased from the K & K Laboratories, Inc.

Reaction of Diazomethane with Isocyanic Acid. Through an ether solution of diazomethane (0.0175 mole in 60 ml., prepared from N-nitroso-N-methyl-*p*-toluenesulfonamide[11]) was bubbled a slow stream of isocyanic acid (generated by the thermal depolymerization of cyanuric acid at 380–400°) in dry argon. The yellow color disappeared in 2 or 3 min., and the resulting colorless solution had a very strong odor, presumably of methyl isocyanate. Since the reaction of methyl isocyanate with aniline has been reported to give a solid derivative,[12] this solution then was poured into a benzene solution of about a threefold molar excess of aniline (4.88 g., 0.0525 mole). After standing overnight, removal of the solvent with a rotary evaporator left a small amount of unreacted aniline and a white solid. This mixture was taken up in ether, washed with 1 *N* aqueous hydrochloric acid, 5% aqueous sodium bicarbonate, and water, and dried over anhydrous magnesium sulfate. Evaporation of this dry ether solution gave a white solid, m.p. 142–150°. Recrystallization from a hot ethanol–water solvent mixture gave white plates, m.p. 151° (lit.[12] m.p. 151°), in a yield of 0.700 g. (0.00470 mole), which corresponds to 27% if quantitative formation of the isocyanate is assumed.

Reaction of Diazomethane with Cyanuric Acid. Cyanuric acid (0.500 g., 0.00387 mole) was stirred in anhydrous ether at 0° and an ether solution of diazomethane added (0.163 g., 0.00387 mole). The yellow color of diazomethane was gone after 30 min. of stirring, so more diazomethane was added until the color persisted. The resulting solution was filtered and the solvent was removed from the filtrate with a rotary evaporator. A white solid remained, m.p. 171–173°, which was recrystallized from hot ethanol–water to give 0.400 g. (0.00234 mole, 61%) of white crystals, m.p. 173–174° (lit.[7] m.p. 174–175°).

Attempted Trimerization of Methyl Isocyanate. Methyl isocyanate was prepared by the reaction of diazomethane and isocyanic acid. A benzene solution of diazomethane was prepared by the base-induced decomposition of N-nitroso-N-methylurea.[11] Through this solution was bubbled a stream of isocyanic acid (generated by the thermal depolymerization of cyanuric acid at 380–400°) in dry argon until the yellow color just disappeared. The resulting benzene solution of methyl isocyanate was then heated to reflux. The strong odor of isocyanate was still present after 2 hr., so refluxing was continued overnight. When the benzene was then removed with a rotary evaporator, a negligible amount of residue remained in the reaction flask.

Determination of Cyanuric Acid from the Thermal Decomposition of N-Nitroso-N-(2,2-diphenylcyclopropyl)urea in *n*-Heptane. N-Nitroso-N-(2,2-diphenylcyclopropyl)urea (0.281 g., 0.0010 mole) was stirred in 15 ml. of *n*-heptane and heated to 90°. When gas evolution had ceased and the yellow color of the nitrosourea had disappeared, the solution was cooled and filtered with suction. The white solid obtained was added to that which was scooped from the neck of the flask to give 0.035 g. (0.00027 mole, 81.6%) of product stable to 280°. Infrared spectra of this material (KBr and Nujol mull) were identical with the corresponding spectra of a known sample of cyanuric acid (the spectra vary depending on the sampling agent used).

Reaction of Sodium Carbamate with *p*-Toluenesulfonic Acid in Refluxing Benzene. Sodium carbamate (0.083 g., 0.0010 mole) was ground in a small amount of THF for a few minutes and this paste was diluted with 15 ml. of benzene. The resulting solution was heated to reflux and 0.190 g. (0.0010 mole) of *p*-toluenesulfonic acid (monohydrate) dissolved in 2 ml. of THF was added with stirring. After 1 hr., the solution was filtered to give 0.235 g. of white solid. An infrared spectrum of this product showed it to be a mixture of sodium *p*-toluenesulfonate and ammonium *p*-toluenesulfonate (compared with a spectrum of an authentic mixture of these materials). None of the absorptions characteristic of cyanuric acid were observable.

Reaction of Lithium Carbamate with *p*-Toluenesulfonic Acid in Refluxing Benzene. Lithium carbamate (0.067 g., 0.0010 mole) was treated with 0.190 g. (0.0010 mole) of *p*-toluenesulfonic acid under the same conditions shown before for the protonation of sodium carbamate. Similar to the case of sodium carbamate, only ammonium *p*-toluenesulfonate and lithium *p*-toluenesulfonate were observed as products.

Attempted Thermal Decomposition of N-Nitroso-N-(2,2-diphenylcyclopropyl)-N′,N′-dimethylurea[10] in *n*-Heptane. N-Nitroso-N-(2,2-diphenylcyclopropyl)-N′,N′-dimethylurea (0.309 g., 0.0010 mole) was stirred in 15 ml. of *n*-heptane which subsequently was heated to reflux. During 3 hr., the solution turned from yellow to deep orange in color, but there was no net gas evolution observed. After removing the solvent with a rotary evaporator, an infrared spectrum was taken on the gummy material remaining. There was no peak at 5.2 μ typical of diphenylallene. However, there did appear to be considerable loss of starting material, with an unknown olefin as one of the products.

Preparation of Lithium Carbamate. To about 15 ml. of liquid ammonia and two small crystals of anhydrous ferric nitrate stirring in a 50-ml., round-bottom flask was added 0.70 g. (0.10 mole) of lithium wire in small pieces. Stirring was continued for 1 hr., yielding a dark grey suspension through which anhydrous carbon dioxide was bubbled. As the volume of the solution decreased, anhydrous ether was slowly added over 30 min. to hold a constant volume. The resulting light brown suspension was filtered and the solid was pumped under vacuum to remove any remaining ammonia. This light tan powder (3.90 g., 0.0795 mole, 79.5%) was stable to 280°. This procedure was developed from the method of Blair[13] in which he prepared the ammonium carbamate separately from gaseous carbon dioxide and ammonia before reaction with the metal amide. Significant infrared absorptions (KBr) were observed at 2.86, 2.95, 3.10, 6.20, 6.30, 6.41, 7.05, 8.48, 8.90, and 12.10 μ. A satisfactory analysis could not be obtained due to varying amounts of solvated ammonia.

Sodium Carbamate. Sodium carbamate was prepared by the method of Bernard[14] from ammonium carbamate by allowing it to react over a period of hours with sodium chloride initially dissolved in liquid ammonia. A small amount of sodium chloride contaminated the white solid obtained. Characteristic infrared absorption maxima (KBr) were observed at 2.90, 3.10, 6.00, 6.20, 6.30, 7.15, 8.85, and 12.18 μ. *Anal.* Calcd. for CH_2NNaO_2: C, 12.90; H, 2.15; N, 15.05. Found: C, 13.14; H, 2.33; N, 15.42 (adjusted from values actually found to compensate for the sodium chloride present: found 6.52% Cl, corresponding to 10.75% NaCl).

Acknowledgment. The authors gratefully acknowledge the financial assistance received from the National Science Foundation for the generous support of this work.

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(11) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 166.

(12) J. W. Boehmer, *Rec. trav. chim.*, **55**, 379 (1936).

(13) J. S. Blair, *J. Am. Chem. Soc.*, **48**, 96 (1926).

(14) M. A. Bernard, *Ann. chim.* (Paris), 6, 81 (1961).