are essentially spherical in shape, as opposed to the more nearly planar cyclohexanols, little or no difference would be expected. The differences between the borneols and the norborneols are due to the presence of more polarizable matter (methyl groups) in the former.

In the case of the 4-phenylcyclohexanols, the small effects described above appear to be swamped by the effect of the relatively much more polar phenyl group, which has a moment in the direction opposite to that of the equatorial hydroxyl group. This leads to a lower dipole moment for the *trans* isomer and a higher one for the *cis*.

A large difference is also observed for the two 3,5-dimethylcyclohexanols. In the *cis,trans* isomer, the two equatorial methyl groups are even closer to the axial hydroxyl group than an alkyl group in the 4-position, and thus more induced polarization, which lowers the net moment, is possible. Therefore the moment of the axial isomer is considerably lower than those for the 4-substituted axial cyclohexanols.

In summary, the dipole moment of an alicyclic alcohol is dependent upon the conformation of the hydroxyl group, upon the type of alkyl group on the ring, and upon the position on the ring of the alkyl group(s). The moment differences can be appreciable, amounting to as much as 0.3 D. for the compounds studied to date. While these differences are variously attributable, they are large enough to have considerable usefulness, and indicate that calculations based on additivity of group moments are subject to more limitations than previously realized. It is hoped that the further studies now in progress will provide additional information on the polarizability of other alkyl groups and their effect on functional groups at other positions on the cyclohexane ring.

This work also shows that alkyl groups in the four position have a small but significant polar effect, by virtue of the induced moments, on the axial hydroxyl group (and probably other functional groups) at the 1-position of the cyclohexane ring, and thus would be expected to alter the reactivity of such functional groups. This conclusion has also been reached by Kwart and Takeshita[16] on the basis of entirely different lines of evidence.

Acknowledgments. The authors are especially indebted to Professor R. H. Cole for his advice and assistance in this work. Thanks are also due to Dr. R. M. Meighan for his help in determining the dipole moments, to Professors J. A. A. Ketelaar and W. T. King and Dr. R. L. Kay for helpful advice, and to Dr. W. H. Jones of Merck and Co., Inc., for carrying out the high-pressure reduction of *p*-phenylphenol.

(16) H. Kwart and T. Takeshita, *J. Am. Chem. Soc.*, **86**, 1161 (1964).

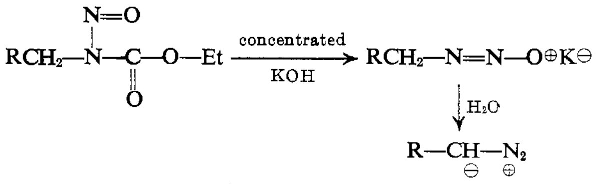
The Mechanism of the Lithium Ethoxide Induced Conversion of N-Nitroso-N-(2,2-diphenylcyclopropyl)urea to 2,2-Diphenyldiazocyclopropane[1]

W. M. Jones,[2] D. L. Muck, and T. K. Tandy, Jr.

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

Abstract: Historically, the base-induced conversion of N-nitrosoamides, -carbamates, and -ureas to diazoalkanes has been postulated as proceeding *via* base attack on the carbonyl carbon to give a dioazotate intermediate. In the course of our investigations on the lithium ethoxide induced conversion of N-nitroso-N-(2,2-diphenylcyclopropyl)-urea to 2,2-diphenyldiazocyclopropane, we have obtained two pieces of information that *exclude* this path for our reaction. Ethyl carbamate was not formed in this reaction and lithium 2,2-diphenylcyclopropyldiazotate, the normally presumed intermediate, was synthesized and found to be totally unaffected by reaction conditions that lead to efficient conversion of the nitrosourea to the diazocyclopropane. An alternate mechanism involving attack of the base on the nitroso nitrogen is postulated. The pyrrolidine-induced decomposition of the nitrosourea also appears to proceed by this mechanism.

As early as 1902, direct evidence was presented for the course of von Pechmann's[3] hydroxide-induced conversion of nitrosocarbamates to diazoalkanes. At that time Hantzsch and Lehmann[4] actually isolated the potassium salts of methyl and benzyl diazohydroxide (I) and showed that treatment with water gave the corresponding diazoalkanes.



$$\mathrm{RCH_2{-}\overset{\displaystyle N{=}O}{\overset{|}{N}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}O{-}Et} \xrightarrow[\text{KOH}]{\text{concentrated}} \mathrm{RCH_2{-}N{=}N{-}O^{\oplus}K^{\ominus}} \xrightarrow{H_2O} \mathrm{R{-}\underset{\ominus}{CH}{-}\underset{\oplus}{N_2}}$$

$R = H, C_6H_5$

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[1] Based upon dissertations submitted by D. L. Muck and T. K. Tandy, Jr., to the Faculty of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

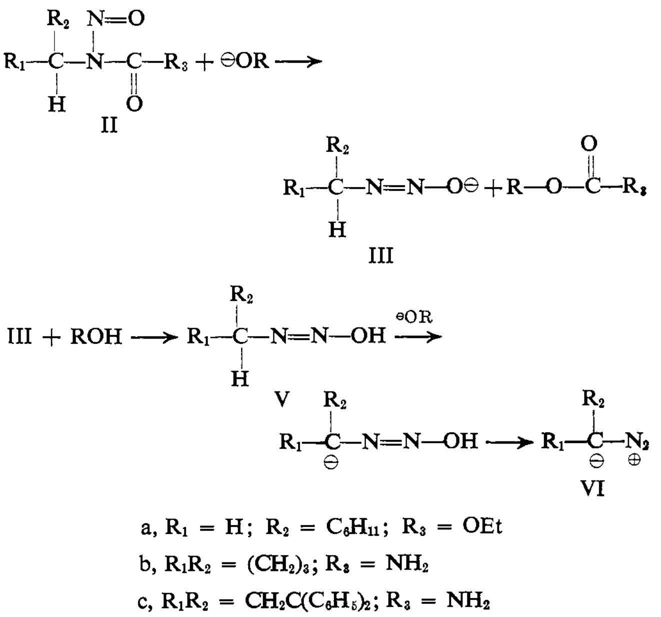
[2] Alfred P. Sloan Fellow.

[3] H. von Pechmann, *Ber.*, 27, 1888 (1894).

[4] A. Hantzch and M. Lehmann, *ibid.*, 35, 897 (1902).

This scheme was expanded (Scheme I) in 1955 by Gutsche and Johnson[5] as a result of a thorough study of the methoxide-induced conversion of a series of N-nitroso-N-benzylcarbamates to the corresponding phenyldiazomethanes (which were trapped with cyclohexanone).

Scheme I



a, $R_1 = H$; $R_2 = C_6H_{11}$; $R_3 = OEt$

b, $R_1R_2 = (CH_2)_3$; $R_3 = NH_2$

c, $R_1R_2 = CH_2C(C_6H_5)_2$; $R_3 = NH_2$

d, $R_1R_2 = CH_2C(C_6H_5)_2$; $R_3 = NMe_2$

Although Gutsche and Johnson did not present direct evidence for attack of the methoxide on the carbonyl carbon to give methyl ethyl carbonate, the isolation by Bollinger, Hayes, and Siegel[6] of 67% methyl ethyl carbonate from the base-induced (1 equiv. of K_2CO_3 in MeOH) conversion of N-nitroso-N-cyclohexylurethan (II) to diazocyclohexane presents excellent precedent for the first step in the Gutsche and Johnson scheme.

A similar scheme for the formation of diazoalkanes has been suggested for the reaction of N-nitrosoamides with base. Although there has not been reported as thorough a study on the latter steps of the reaction there is ample evidence that the reaction of nitrosoamides with alkoxide in alcohol proceeds *via* appreciable alkoxide attack on the carbonyl carbon.[7]

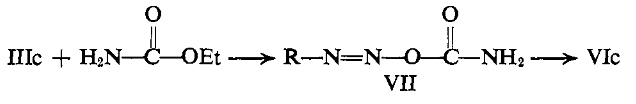
By analogy, it has been natural to assume that N-nitrosoureas also react with base by way of attack of the base on the carbonyl carbon.[8,9] This reaction path has been most explicitly presented and discussed by Applequist and McGreer[8] for the alkoxide-induced conversion of N-nitroso-N-cyclobutylurea (IIb) to diazocyclobutane. In their scheme, they do not specifically suggest attack of the alkoxide on the carbonyl carbon, but from the products that they write (the cyclobutyldiazotate anion IIIb and alkyl carbamate IVb) there can be no doubt that their mechanism does involve this first step.

The purpose of this paper is to present data that excludes the Applequist and McGreer mechanism for the alkoxide-induced conversion of N-nitroso-N-(2,2-diphenylcyclopropyl)urea to 2,2-diphenyldiazocyclopropane. An alternate mechanism is offered.

Results and Discussion

In order for the Applequist and McGreer mechanism to obtain in the conversion of the cyclopropyl nitrosourea IIc to the unstable diazocyclopropane IVc, three criteria must be met. In the first place, ethyl carbamate (IVc, R = Et) must be formed in at least as high a yield as the decomposition products of the diazocyclopropane. In the second place, lithium 2,2-diphenylcyclopropyldiazotate (IIIc) must react with alcohol to give the diazocyclopropane and, finally, at least a catalytic amount of alcohol must be present to induce the decomposition of the diazotate. In the reaction under consideration, insofar as we could determine, none of these criteria were met. The first criterion was negated by assaying a typical reaction product for ethyl carbamate. Less than 1% was found. Ethyl carbamate was independently shown to be stable to the reaction conditions. The second criterion was negated by independently synthesizing lithium 2,2-diphenylcyclopropyldiazotate, subjecting it to a mixture of lithium ethoxide and ethanol under the conditions of the reaction, and finding it to be totally unaffected. Finally, the last criterion was negated insofar as we could tell by effecting the reaction with nonalcoholated lithium ethoxide under anhydrous conditions. The reaction was complete at 0° in 20 min.

Thus, for the base-induced formation of 2,2-diphenyldiazocyclopropane, these results quite effectively exclude that portion of the Applequist and McGreer mechanism which involves reaction of the diazotate with alcohol to give the diazocyclopropane. However, these results alone do not *a priori* exclude attack of ethoxide on the carbonyl to give the diazotate and ethyl carbamate, since it is possible that the decomposition actually involves reaction of the diazotate with ethyl carbamate to give the diazourethan VII which could decompose spontaneously to the diazocyclopropane.[10–13] This possibility was excluded by exposing the diazotate to ethyl carbamate under typical reaction conditions. No reaction occurred.



$$\text{IIIc} + H_2N\text{—}\overset{O}{\overset{\|}{C}}\text{—}OEt \longrightarrow R\text{—}N{=}N\text{—}O\text{—}\overset{O}{\overset{\|}{C}}\text{—}NH_2 \longrightarrow \text{VIc}$$

VII

R = 2,2-diphenylcyclopropyl

One other reaction scheme of a similar nature that was considered is reaction of a small amount of alkoxide

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(5) C. D. Gutsche and H. E. Johnson, *J. Am. Chem. Soc.*, **77**, 109 (1955).

(6) F. W. Bollinger, F. N. Hayes, and S. Siegel, *ibid.*, **72**, 5592 (1950).

(7) R. Huisgen and J. Reinertshofer, *Ann.*, **575**, 174 (1952); R. Huisgen, *ibid.*, **573**, 173 (1951); C. D. Gutsche and I. Y. C. Tao, *J. Org. Chem.*, **28**, 883 (1963); see also C. D. Gutsche, *Org. Reactions*, **8**, 389 (1954).

(8) D. E. Applequist and D. E. McGreer, *J. Am. Chem. Soc.*, **82**, 1965 (1960).

(9) J. Tempe, H. Heslot, and J. Morel, *Compt. rend.*, **258**, 5470 (1964).

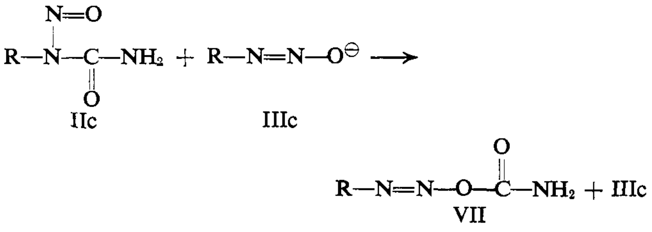
(10) For a discussion on the preparation and properties of this diazotate, see T. K. Tandy, Jr., and W. M. Jones, *J. Org. Chem.*, 30, 4257 (1965).

(11) E. Mueller, W. Hoppe, H. Hagenmaier, H. Haiss, R. Huber, W. Rundel, and H. Suhr, *Ber.*, **96**, 1712 (1963).

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

(13) For many examples of the thermal conversion of diazoesters, see E. H. White and R. J. Baumgarten, *J. Org. Chem.*, **29**, 2070 (1964); E. H. White and C. A. Aufdermarsh, *J. Am. Chem. Soc.*, **83**, 1174 (1961); E. H. White, *ibid.*, **77**, 6013 (1955); A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 2893 (1957); A. R. Huisgen and R. Reimlinger, *Ann.*, **599**, 183 (1956).

with nitrosourea to give the diazotate plus ethyl carbamate, followed by reaction of the diazotate with the starting nitrosourea to give the diazourethan (VII) plus a molecule of diazotate.



$$\underset{\text{IIc}}{\mathrm{R{-}N(N{=}O){-}C({=}O){-}NH_2}} + \underset{\text{IIIc}}{\mathrm{R{-}N{=}N{-}O^{\ominus}}} \longrightarrow \underset{\text{VII}}{\mathrm{R{-}N{=}N{-}O{-}C({=}O){-}NH_2}} + \text{IIIc}$$

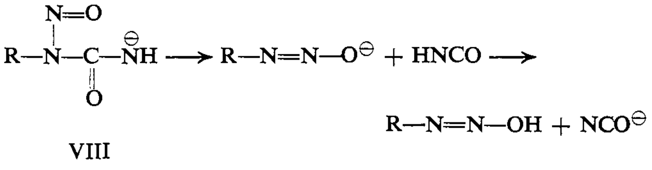
R = 2,2-diphenylcyclopropyl

This possibility was excluded by treating the nitrosourea with lithium diazotate. Again, no reaction occurred.

All of these observations lead to one almost inescapable conclusion: the conversion of the nitrosocyclopropylurea to the diazocyclopropane does not proceed by attack of the base on the carbonyl carbon. Furthermore, lithium 2,2-diphenylcyclopropyldiazotate is probably not an intermediate in the reaction.

There are at least two other points on the nitrosourea where attack of the base could occur. These are the NH_2 and the nitroso group. Attack at each of these points will be considered separately.

Attack on the NH_2 Group. Attack of the base on the NH_2 group would most likely proceed by simple proton abstraction to give anion VIII.[14] The one reasonable route that this anion could follow to the diazocyclopropane would be by loss of isocyanic acid to give the diazotate, followed by an acid–base reaction of the diazotate with isocyanic acid to give cyanate ion and the diazohydroxide, an intermediate that could react further to give the diazocyclopropane.



$$\underset{\text{VIII}}{\mathrm{R{-}N(N{=}O){-}C({=}O){-}NH^{\ominus}}} \longrightarrow \mathrm{R{-}N{=}N{-}O^{\ominus}} + \mathrm{HNCO} \longrightarrow \mathrm{R{-}N{=}N{-}OH} + \mathrm{NCO^{\ominus}}$$

R = 2,2-diphenylcyclopropyl

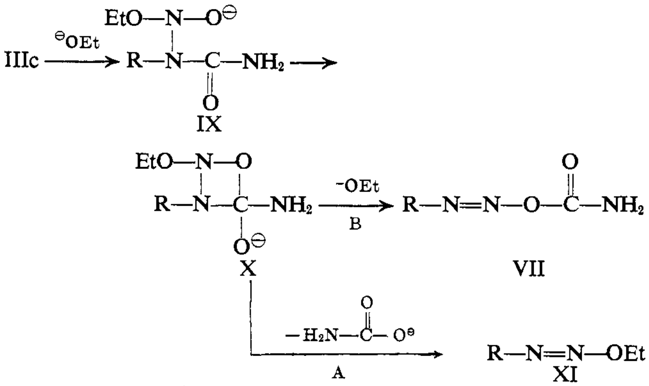
This scheme appeared attractive since lithium cyanate is a major product of our reaction.[15]

However, the scheme was excluded by our finding that under our reaction conditions the diazotate is stable to isocyanic acid.

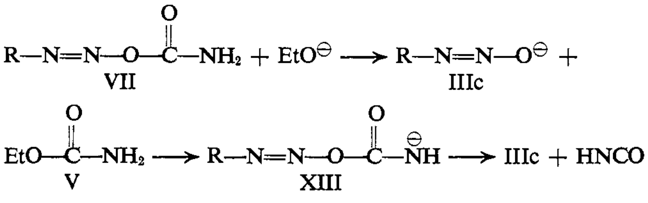
Attack on the Nitroso Group. The final reasonable point for attack of the base is on the nitroso nitrogen. This would give rise to intermediate IX which could react further by either of two paths.

In the first case, the negative oxygen could attack the carbonyl carbon to give the cyclic intermediate X which could then collapse according to Scheme II to give either the diazo ether XI and lithium carbamate (XII), or the diazourethan VII. The former of these possibilities (path A) was excluded by independently showing that lithium carbamate does not decompose to lithium cyanate (the observed reaction product) under the conditions of the reaction. Decomposition of the diazourethan VII to the diazocyclopropane could proceed by any of three routes. In the first, VII could react with base to give ethyl carbamate and the cyclopropyl diazotate. This possibility has already been excluded by the stability of the diazotate and the absence of V. In the second, it could react with base to give the anion XIII which could collapse to isocyanic acid and the cyclopropyl diazotate. Again, this path has already been excluded. Finally, the diazourethan could possibly decompose (through XIV) by loss of carbamic acid (XV) to give the diazocyclopropane directly. However, to explain the observed lithium cyanate product, this mechanism would require either decomposition of lithium carbamate to lithium cyanate or carbamic acid to isocyanic acid. Both of these possibilities were excluded, the former as described above and the latter by treating lithium and sodium carbamate with *p*-toluenesulfonic acid under the conditions of the reaction and showing that the only products observed were those expected,[17] ammonia and carbon dioxide.

Scheme II

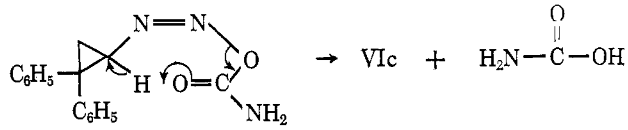


R = 2,2-diphenylcyclopropyl



$$\underset{\text{VII}}{\mathrm{R{-}N{=}N{-}O{-}C({=}O){-}NH_2}} + \mathrm{EtO^{\ominus}} \longrightarrow \underset{\text{IIIc}}{\mathrm{R{-}N{=}N{-}O^{\ominus}}} + \underset{\text{V}}{\mathrm{EtO{-}C({=}O){-}NH_2}} \longrightarrow \underset{\text{XIII}}{\mathrm{R{-}N{=}N{-}O{-}C({=}O){-}NH^{\ominus}}} \longrightarrow \text{IIIc} + \mathrm{HNCO}$$

R = 2,2-diphenylcyclopropyl



XIV

The second point in the nitrosourea group at which the negative oxygen of intermediate IX might be expected to attack is the NH_2 group. Proton abstraction by the negative oxygen of anion IX followed by (or concomitant with) collapse of the resultant anion and

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[14] E. R. Garrett, S. Goto, and J. F. Stubbins, *J. Pharm. Sci.*, **54**, 119 (1965).

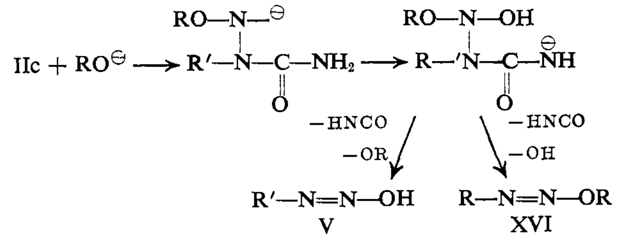
[15] As the result of a study made in 1919, Werner[16] reported that sodium cyanate was isolated from the sodium ethoxide induced decomposition of N-nitroso-N-methylurea. Werner simply determined the stoichiometry of the reaction and did not attempt to determine the origin of the cyanate. In addition to sodium ethoxide, Werner examined ammonia as a base for inducing decomposition of the nitrosourea and found ammonium cyanate to be a product of this reaction. As before, there was no mention made of a possible origin of the cyanate.

[16] E. A. Werner, *J. Chem. Soc.*, **115**, 1093 (1919).

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

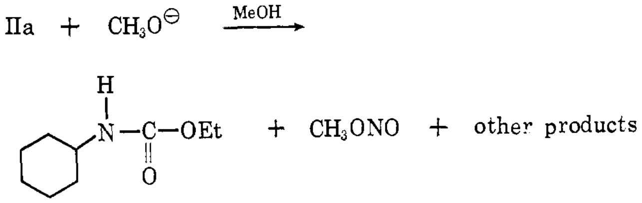
loss of ethoxide or hydroxide could give isocyanic acid plus the diazohydroxide V or the diazo ether XVI (R = Et) (Scheme III). Either the diazohydroxide or the diazo ether (R = Et) could then decompose to the observed diazocyclopropane.[18] These conversions could be assisted by isocyanic acid or, possibly, induced by base as was suggested by Gutsche[5] as well as Applequist and McGreer[8] for the last steps of their mechanisms.

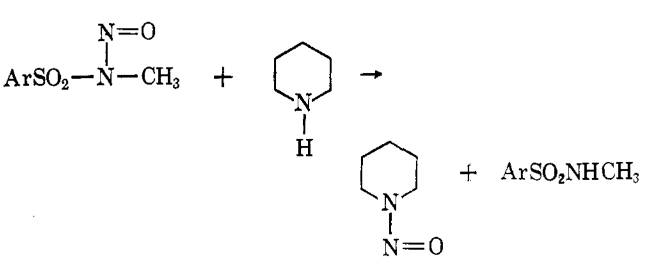
Scheme III



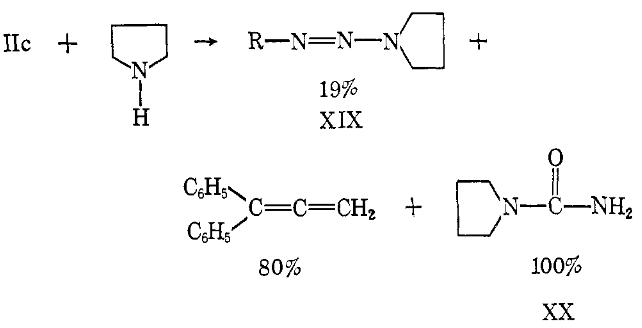
R = alkyl, hydrogen
R′ = 2,2-diphenylcyclopropyl

Although we have not been successful in obtaining direct evidence for this mechanism, it appears attractive for several reasons. In the first place, reaction of the base with the nitroso nitrogen is not without precedent. For example, Bollinger, Hayes, and Siegel[6,19] found that two of the products from the reaction of ethyl N-nitroso-N-cyclohexylcarbamate with potassium carbonate in methanol were methyl nitrite and N-cyclohexylurethan. These products obviously arose from attack of methoxide on the nitroso nitrogen. Similarly, Backer and de Boer[20] found that treatment of N-methyl-N-nitroso-*p*-toluenesulfonamide with piperidine gave only nitrosopiperidine and N-methyl-*p*-toluenesulfonamide. Again, attack of base on the nitroso nitrogen was apparently involved.





A second reason that this mechanism appears attractive is the observation that the reaction of the nitrosourea with pyrrolidine (in petroleum ether) gives, in addition to *ca.* 80% 1,1-diphenylallene (the decomposition product of 2,2-diphenyldiazocyclopropane) and a quantitative yield of N-pyrrolidylcarboxamide XX (from reaction of pyrrolidine with HNCO), up to 19% of the triazene XIX. The only two obvious sources for this material are from attack of the pyrrolidine on the nitroso nitrogen atom to give the nitrogen analog of XVI in Scheme III or by reaction of the diazocyclopropane with pyrrolidine. The latter is unlikely since it was found that none of the triazene was formed when the diazocyclopropane was generated from a different source (pyrolysis of pyrrolidinium 2,2-diphenylcyclopropyldiazotate) in the presence of pyrrolidine. However, this test is not unequivocal since the reaction, by necessity, was run at a different temperature from the reaction of pyrrolidine with the nitrosourea. Perhaps it should be pointed out that although formation of the amide XX suggests formation of isocyanic acid (which was independently shown to react with pyrrolidine to give a quantitative yield of the amide) it could also be explained by attack of the pyrrolidine on the carbonyl carbon. It is also interesting that the triazene was not formed when the nitrosourea was treated with pyrrolidine in ether. We offer no explanation for this phenomenon.



A third factor that makes this mechanism intuitively attractive is our finding that the thermal decomposition of nitrosoureas apparently also proceeds by a similar mechanism.[21]

A fourth factor to consider here is the observation that the nitrosourea also reacts with lithium hydroxide in ether to give almost 80% of the calculated nitrogen and a mixture of lithium 2,2-diphenylcyclopropyldiazotate and 1,1-diphenylallene.[22] In view of the stability of the diazotate to the reaction conditions and the formation of 74% lithium cyanate, the 80% nitrogen most certainly arose from attack of the hydroxide on the nitroso nitrogen.[23] Collapse of the resulting inter-

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(18) H. Zollinger, "Diazo and Azo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961.

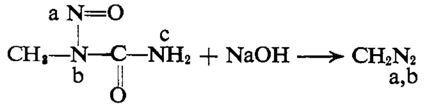
(19) F. W. Bollinger, F. N. Hayes, and S. Siegel, *J. Am. Chem. Soc.*, 75, 1729 (1953).

(20) H. J. Backer and T. J. de Boer, *Proc. Koninkl. Ned. Akad. Wetenschap*, **B54** 191 (1951); see also K. Heyns and A. Heins, *Ann.*, **604**, 133 (1957).

(21) For a detailed discussion of this reaction, see D. L. Muck and W. M. Jones, *J. Am. Chem. Soc.*, **88**, 74 (1966).

(22) Lithium 2,2-diphenylcyclopropyldiazotate is almost invariably found in varying small amounts in the reaction of the nitrosourea with both lithium ethoxide and lithium hydroxide. However, there are a variety of routes by which this could arise and therefore its formation cannot be taken as strong evidence for any mechanism.

(23) Some information concerning the hydroxide-induced decomposition of N-nitroso-N-methylurea has earlier been reported by Clusius and Endtinger.[24] As a result of a study using labeled nitrogen, these workers were able to show that the nitrogen atoms present in the diazomethane formed were those labeled a and b below, the nitroso nitrogen and the nitrogen to which it is bonded.



$$\mathrm{CH_3{-}\underset{b}{\overset{a\,N=O}{N}}{-}\overset{c}{C}({=}O){-}NH_2 + NaOH \longrightarrow \underset{a,b}{CH_2N_2}}$$

Although Clusius and Endtinger did not examine the remaining products of this reaction, it follows that the nitrogen present in the sodium cyanate produced would have to be that labeled c above. These results can readily be accommodated by the mechanism proposed here.

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

mediate would give rise to the diazohydroxide, which therefore must be considered to be a reasonable precursor to the diazocyclopropane.

Finally, it has been shown that N-nitroso-N-(2,2-diphenylcyclopropyl)-N′,N′-dimethylurea (IId) is extremely unreactive with lithium ethoxide, being recovered unchanged after 24 hr. under typical reaction conditions. Although this single observation does not require the suggested mechanism, it is certainly consistent with the scheme involving proton abstraction from the NH_2.

We are presently examining in more detail the base-induced conversion of alkylnitrosourethans and amides to diazoalkanes. Thus, although the potassium carbonate–methanol reaction scheme involving base attack on the carbonyl carbon is apparently on firm ground,[25] preliminary experiments in these laboratories indicate that their reaction with lithium ethoxide in ether does not go by this mechanism. It therefore seems distinctly possible that both the base–solvent system and the structure of the substrate spawn these differing results. A study of possible variables is now underway.

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. Vapor phase chromatographic analyses were performed with an Aerograph Hy-Fi Model 600-B or Aerograph Model A-350-B converted to an Autoprep.

Materials. The solvents (anhydrous ethyl ether, petroleum ether, and tetrahydrofuran) used in this work were all Fisher certified reagents and were used without further purification, as was the ethyl carbamate (Matheson). The pyrrolidine (Eastman practical grade) and cyclohexene (Eastman White Label) were purified by distillation before use.

Lithium Ethoxide. Lithium ethoxide was prepared by the method of Brown and co-workers[26] with the exception that a twofold molar amount of ethanol was used instead of the reported molar amount in order to increase the yield. The product was then heated on a steam bath under vacuum (2 mm.) to remove the last traces of ethanol. This procedure gave a white powder whose infrared spectrum showed none of the peaks characteristic of lithium carbonate, lithium hydroxide, or ethanol. Addition of sodium hydride to an ether suspension of this product gave no gas evolution, which indicates that there is no ethanol remaining as the alcoholate. A sample of this powder was weighed accurately, dissolved in distilled water, and titrated by first adding an excess of standard dilute hydrochloric acid and then back titrating with standard dilute sodium hydroxide. In two successive runs, values of 50.4 and 51.8 were obtained for the equivalent weight of lithium ethoxide (calcd. 51.9). The infrared spectrum was identical with that obtained by Brown and co-workers.[26]

Decomposition of N-Nitroso-N-(2,2-diphenylcyclopropyl)urea with Lithium Ethoxide in Ethyl Ether. N-Nitroso-N-(2,2-diphenylcyclopropyl)urea (0.281 g., 0.0010 mole) was stirred in 15 ml. of anhydrous ethyl ether at 0° and 0.052 g. (0.0010 mole) of lithium ethoxide was added quickly. After stirring at 0° for 20 min., 18 ml. (75%) of gas had been collected and gas evolution had ceased. The reaction mixture was filtered to give 0.055 g. of white solid. After removing the solvent from the filtrate with a rotary evaporator, the residual oil was triturated with pentane, which caused some solid to precipitate. Filtration of the pentane extracts gave 0.025 g. of white, solid material, whose infrared spectrum was identical with that of a sample of lithium 2,2-diphenylcyclopropyldiazotate. When the pentane was removed from the filtrate, 0.145 g. (76%) of oil remained whose infrared spectrum was superimposable with that of diphenylallene. A closer examination of the 0.055 g. of white solid initially obtained revealed the following: trituration with chloroform for 30 min. and filtration with suction gave 0.033 g. (73%) of a white solid whose infrared spectrum was identical with that of a sample of lithium cyanate, and removal of the chloroform with a rotary evaporator gave 0.017 g. more of the lithium 2,2-diphenylcyclopropyldiazotate (total yield, 0.042 g., 17%).

Quantitative Determination of Ethyl Carbamate Resulting from the Reaction of N-Nitroso-N-(2,2-diphenylcyclopropyl)urea with Lithium Ethoxide in Ethyl Ether. To 0.60 g. (0.00214 mole) of N-nitroso-N-(2,2-diphenylcyclopropyl)urea[27] and 30 ml. of anhydrous ether stirred at 0° was added 0.310 g. (1.5 equiv.) of lithium ethoxide. After 1.5 hr., 36.5 ml. (68%) of nitrogen had been collected and no more was being evolved. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure to a small volume. After adding 5.23 mg. of menthol (internal standard), the ether solution was analyzed by v.p.c. (5 ft. × $^{1}/_{8}$ in. column charged with Carbowax 4000 on firebrick) using a disk chart integrator. Although 1.6 mg. (corresponding to 0.86% yield) of ethyl carbamate would have been easily detected, none was observed. An infrared spectrum of the oil obtained by the evaporation of the remaining ether showed this product to be almost pure 1,1-diphenylallene.[27] An infrared spectrum (KBr) of the solid filtered from the reaction was essentially identical with that of lithium cyanate.

Stability of Lithium 2,2-Diphenylcyclopropyldiazotate to Lithium Ethoxide in Diethyl Ether. Lithium 2,2-diphenylcyclopropyldiazotate (0.244 g., 0.0010 mole) was stirred at 0° in 15 ml. of anhydrous diethyl ether containing 0.052 g. (0.0010 mole) of lithium ethoxide for 2 hr. The solvent was then removed on a rotary evaporator to give 0.288 g. (97% recovery) of white solid whose infrared spectrum was consistent with a mixture of the diazotate and lithium ethoxide. No new significant infrared absorptions were observed.

Stability of Lithium 2,2-Diphenylcyclopropyldiazotate to Lithium Ethoxide in Ethanol. Lithium 2,2-diphenylcyclopropylidazotate (0.244 g., 0.0010 mole) was stirred for 1 hr. at 0° in 10 ml. of absolute ethanol containing 0.052 g. (0.0010 mole) of lithium ethoxide. The ethanol was removed by evaporation under high vacuum. The white solid obtained as residue (0.285 g., 96% recovery) exhibited infrared absorptions that were consistent with a mixture of the diazotate and lithium ethoxide.

Stability of N-Nitroso-N-(2,2-diphenylcyclopropyl)urea to Lithium 2,2-Diphenylcyclopropyldiazotate. To 0.300 g. of N-nitroso-N-(2,2-diphenylcyclopropyl)urea dissolved in 20 ml. of anhydrous ethyl ether at 0° was added a catalytic amount (about 50 mg.) of lithium 2,2-diphenylcyclopropyldiazotate. After stirring with cooling for 6.5 hr., the reaction mixture was filtered. When the filtrate was evaporated to a small volume, a yellow solid, m.p. 92–97° dec., formed. An infrared spectrum (KBr) of this solid was superimposable with that of a known sample of starting nitrosourea.

Stability of Lithium 2,2-Diphenylcyclopropyldiazotate in the Presence of Ethyl Carbamate. To a slurry of 100 mg. (0.453 mmole) of lithium 2,2-diphenylcyclopropyldiazotate in 25 ml. of anhydrous ether cooled to 0° was added 40 mg. (0.453 mmole) of ethyl carbamate. After stirring for 7 hr., the reaction mixture was filtered to give 91 mg. (91% recovery) of the lithium diazotate. The filtrate was evaporated to a white solid whose infrared spectrum (KBr) was superimposable with that of ethyl carbamate. No 1,1-diphenylallene was detected.

Stability of Lithium 2,2-Diphenylcyclopropyldiazotate to Isocyanic Acid in Tetrahydrofuran at 0°. Lithium 2,2-diphenylcyclopropyldiazotate (0.180 g., 0.00059 mole) was stirred in 15 ml. of anhydrous tetrahydrofuran at 0° for a few minutes before adding a solution of isocyanic acid (0.023 g., 0.00059 mole) in 5 ml. of tetrahydrofuran. After stirring the homogeneous solution for 30 min. at 0°, the solvent was removed on a rotary evaporator leaving a quantity of solid whose infrared spectrum was identical with that of the starting diazotate, with none of the absorptions characteristic of lithium cyanate.

Stability of Lithium Carbamate[21] to Reaction Conditions. Lithium carbamate was checked for stability to the following sets of conditions (0.052 g. (0.0010 mole) of lithium ethoxide; 0.024 g. (0.0010 mole) of lithium hydroxide; 0.281 g. (0.0010 mole) of N-nitroso-N-(2,2-diphenylcyclopropyl)urea; 0.018 g. (0.0010 mole) of water;

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[25] Application of these conditions to the N-nitroso-N-(2,2-diphenylcyclopropyl)urea system did *not* give ethyl carbamate as a product, although almost quantitative gas evolution was observed.

[26] T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).

[27] *Cf.* W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *ibid.*, **85**, 2754 (1963), and references cited therein.

0.049 g. (0.0010 mole) of lithium cyanate; the solvent only) by stirring 0.069 g. (0.0010 mole) in anhydrous ethyl ether for 30 min., evaporating the solvent quickly under high vacuum, and then immediately taking the infrared spectrum of the residue.

In each above case, the lithium carbamate was recovered unchanged and there was no gas evolution with the nitrosourea.

Stability of Sodium Carbamate[21] to Reaction Conditions. Sodium carbamate was checked for stability to the same sets of conditions as was lithium carbamate, since a satisfactory analysis of lithium carbamate could not be obtained. In every case, the sodium carbamate was recovered in essentially quantitative yield.

Reaction of Lithium Carbamate[21] with *p*-Toluenesulfonic Acid. Lithium carbamate (0.052 g., 0.0010 mole) was stirred in 10 ml. of anhydrous tetrahydrofuran at room temperature for 1 hr. and then cooled to −50°. *p*-Toluenesulfonic acid (monohydrate) (0.190 g., 0.0010 mole) dissolved in 5 ml. of anhydrous tetrahydrofuran at −50° was quickly added, and the resulting solution was stirred at −50° for 1 hr. The reaction mixture then was warmed to room temperature and the solvent was removed on a rotary evaporator to give 0.235 g. of white solid. The infrared spectrum of this solid indicated that it was a mixture of ammonium tosylate, lithium tosylate, and some unreacted lithium carbamate (by comparison of the spectra of the known materials).

Reaction of Sodium Carbamate[21] with *p*-Toluenesulfonic Acid. Sodium carbamate was treated with *p*-toluenesulfonic acid in a manner identical with that shown before for lithium carbamate, and the same results were obtained.

Sodium Cyanate. Sodium cyanate was prepared by bubbling a stream of isocyanic acid (generated by the thermal depolymerization of cyanuric acid at 380–400°) in dry argon through a rapidly stirred suspension of sodium ethoxide in anhydrous ethyl ether at 0°. The product obtained by filtering the reaction mixture showed infrared absorptions identical with those reported by Rao.[28]

Lithium Cyanate. Lithium cyanate was prepared by bubbling a stream of isocyanic acid (generated by the thermal depolymerization of cyanuric acid at 380–400°) in argon through a rapidly stirred suspension of lithium ethoxide in anhydrous ethyl ether at 0°. The lithium cyanate obtained showed some infrared absorption characteristic of lithium hydroxide. The product was purified by stirring in absolute ethanol and then adding ether to precipitate out the lithium hydroxide. Filtration and evaporation of the solvent from the filtrate gave a white solid whose infrared spectrum was very similar to that of a sample of sodium cyanate. The infrared absorptions (KBr) appeared at 4.40, 7.60, and 8.20 μ.

Isolation of 1-(2,2-Diphenylcyclopropyl)-3,3-tetramethylenetriazene from the Decomposition of N-Nitroso-N-(2,2-diphenylcyclopropyl)urea with Pyrrolidine in Petroleum Ether. To 0.5 g. (0.0018 mole) of N-nitroso-N-(2,2-diphenylcyclopropyl)urea in 20 ml. of petroleum ether (b.p. 20–40°) stirred at 0° was added 0.4 ml. (0.0048 mole) of pyrrolidine. Nitrogen was evolved over a 2–2.5-hr. period and N-pyrrolidinylcarboxamide slowly formed. After gas evolution ceased (usually 80–93%) the reaction mixture was filtered to give a quantitative yield of the amide XX. Ultraviolet analysis of the resulting solution showed about 80% of 1,1-diphenylallene. Evaporation of the solvent gave a heavy yellow oil whose infrared spectrum showed considerable 1,1-diphenylallene. The oil was dissolved in a minimum of hot pentane and cooled to 0° overnight. The yellow crystals which had formed were filtered and washed once with pentane to yield 30–98 mg. (6–19%) of the triazene, m.p. 77–80°. Successive recrystallizations from hexane gave a pure white solid, m.p. 80–81°.

The triazene structure was assigned as a result of analysis, infrared spectrum (KBr; 3.35, 6.25, 6.70, 6.95, 7.55, 7.75, 9.85, 9.90, 12.95, 13.3, and 14.2 μ), and conversion to 2,2-diphenyldiazocyclopropane products. This latter conversion will be discussed in detail in a forthcoming publication. *Anal.* Calcd. for $C_{19}H_{21}N_3$: C, 78.30; H, 7.27; N, 14.43. Found: C, 78.38; H, 7.23; N, 14.24.

Thermal Decomposition of Pyrrolidinium 2,2-Diphenylcyclopropyldiazotate in the Presence of Pyrrolidine. A mixture of 182 mg. of pyrrolidinium 2,2-diphenylcyclopropyldiazotate and 0.4 ml. of pyrrolidine in 30 ml. of hexane was heated under reflux for 1.5 hr. The reaction mixture was then filtered to remove a small amount of white solid (probably N-pyrrolidinylcarboxamide present as starting diazotate impurity), and the filtrate was evaporated to an oil. An infrared spectrum (film) of this oil showed it to be essentially pure 1,1-diphenylallene. No absorptions consistent with 1-(2,2-diphenylcyclopropyl)-3,3-tetramethylenetriazene were observed. Neither did the product oil evolve a gas when treated with acetic acid. The latter is a fairly sensitive qualitative test for the triazene.[10]

Decomposition of N-Nitroso-N-(2,2-diphenylcyclopropyl)urea with Pyrrolidine in Ethyl Ether. To 0.600 g. (0.00214 mole) of N-nitroso-N-(2,2-diphenylcyclopropyl)urea which was stirring in 25 ml. of ether at 0° was added 0.40 ml. (0.34 g., 0.0048 mole) of pyrrolidine and 0.600 g. of anhydrous magnesium sulfate. The reaction was interrupted after 13 min. (26.0 cc. of nitrogen; 48%) and the mixture was filtered to separate the magnesium sulfate and N-pyrrolidinylcarboxamide. After evaporating the ether filtrate under reduced pressure while allowing the flask to get very cold, pyrrolidinium 2,2-diphenylcyclopropyldiazotate crystallized to a white solid. This solid was filtered, washed with a small volume of cold, anhydrous ether, and dried to yield 0.251 g. (0.000821 mole; 38%) of the diazotate, m.p. 79–83° dec. The product was dissolved in a minimum amount of ether and filtered to eliminate insoluble impurities. After again evaporating the ether to a small volume while keeping the solution very cold, white crystals, m.p. 85° dec., separated.

Significant infrared absorption bands (Nujol mull) appeared at 4.05, 6.05, 6.15, 6.25, 6.65, 8.8, 9.5, 9.9, 10.8 (very broad), 11.6 (very broad), 13.15, and 14.35 μ.

A satisfactory analysis of this diazotate could not be obtained due to its unstable nature, but compelling evidence for the proposed structure has already been presented.[10]

Reaction of Pyrrolidine with Isocyanic Acid. To a stirred solution of pyrrolidine (0.280 g., 0.0040 mole) in 10 ml. of anhydrous ether at 0° was added a solution of isocyanic acid (0.172 g., 0.0040 mole) in tetrahydrofuran. An immediate precipitate formed and there was no more change over 30 min. The solution was filtered with suction giving 0.530 g. (94.5%) of white solid, m.p. 220–221° (lit.[29] m.p. 218°). The infrared spectrum of this material compared exactly with that of the N-pyrrolidinylcarboxamide isolated from the reaction of pyrrolidine with N-nitroso-N-(2,2-diphenylcyclopropyl)urea reported herein.

Reaction of N-Nitroso-N-(2,2-diphenylcyclopropyl)urea with Lithium Hydroxide. To a solution of 0.300 g. (0.00107 mole) of N-nitroso-N-(2,2-diphenylcyclopropyl)urea in 30 ml. of anhydrous ether stirred at 0° was added 39 mg. (1.5 equiv.) of lithium hydroxide. Nitrogen slowly evolved for 5 hr. (21.2 ml., 78.5%), after which the reaction mixture was filtered. An infrared spectrum (KBr) of the white solid (129 mg.) was consistent with a mixture of lithium 2,2-diphenylcyclopropyldiazotate and lithium cyanate. The filtrate was evaporated to an oil (183 mg.) whose infrared spectrum (film) was identical with that of 1,1-diphenylallene.

N-(2,2-Diphenylcyclopropyl)-N′,N′-dimethylurea. Using 50 g. (0.21 mole) of 2,2-diphenylcyclopropanecarboxylic acid, 50.4 g. (92.5% from unreacted acid) of the urea was prepared by the method reported earlier,[27] with dimethylamine being used for the addition to the corresponding isocyanate. The melting point of the crude product, 111–113°, was raised to 112–113° by recrystallizations from chloroform–pentane (white needle crystals). Significant infrared absorptions (melt) appeared at 2.98 and 6.10 μ. *Anal.* Calcd. for $C_{18}H_{20}N_2O$: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.10; H, 7.10; N, 10.00.

N-Nitroso-N-(2,2-diphenylcyclopropyl)-N′,N′-dimethylurea. Five grams (0.0179 mole) of N-(2,2-diphenylcyclopropyl)-N′,N′-dimethylurea was used to prepare 4.1 g. (74%) of crude N-nitroso derivative, m.p. 88.5–90.5°, by the method reported earlier.[27] Successive recrystallizations from ether–pentane or chloroform–pentane mixtures yielded a pale yellow powdery solid, m.p. 87–87.5° dec. Significant infrared absorptions (Nujol mull) appeared at 5.90, 6.70, and 7.18 μ. *Anal.* Calcd. for $C_{18}H_{19}N_3O_2$: C, 69.87; H, 6.19; N, 13.58. Found: C, 69.69; H, 5.98; N, 13.39.

Attempted Decomposition of N-Nitroso-N-(2,2-diphenylcyclopropyl)-N′,N′-dimethylurea with Lithium Ethoxide. N-Nitroso-N-(2,2-diphenylcyclopropyl)-N′,N′-dimethylurea (0.309 g., 0.0010 mole) was stirred in 25 ml. of anhydrous ethyl ether at 0° and 0.052 g. (0.0010 mole) of lithium ethoxide was added quickly. After stirring at that temperature for 1 hr. and observing no gas evolution, the mixture was stirred at room temperature overnight. By then cooling the system back to 0°, it was evident that there had been no net gas evolution. Filtration and removal of the solvent from the filtrate with a rotary evaporator left a yellow gummy solid. Addition of 1 ml. of ether followed by 5 ml. of pentane dropwise precipitated a yellow solid (0.290 g., 94%), m.p. 85–87°, whose in-

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(28) C. N. R. Rao, *Coll. Indian Inst. Sci.* (Bangalore), 1961.

(29) V. W. Reppe, *et al.*, *Ann.*, **596**, 150 (1955).

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, %	Diphenylallene isolated, %	Recovered nitrosourea, %	Diazotate isolated, %
25	22	19	78	0
50	47	42	53	0
75	61	52	36	3
100	76	75	0	17

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

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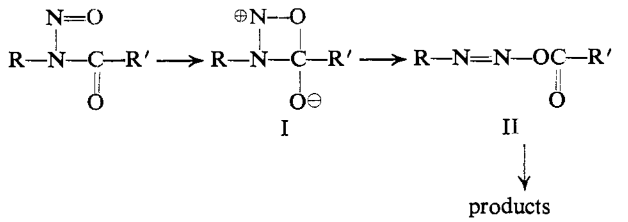
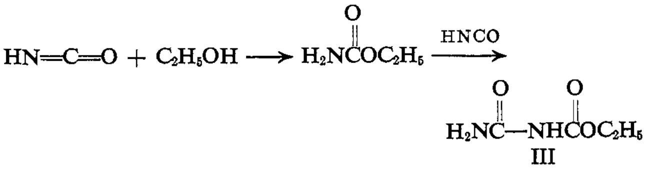
Abstract: The mechanism of the thermal decomposition of N-nitroso-N-(2,2-diphenylcyclopropyl)urea in nonpolar solvents has been investigated. A mechanism postulating removal of a terminal NH_2 proton by the nitroso oxygen atom through a cyclic transition state, followed by collapse to give isocyanic 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.



$$HN{=}C{=}O + C_2H_5OH \longrightarrow H_2N\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow{HNCO} H_2N\overset{O}{\overset{\|}{C}}{-}NH\overset{O}{\overset{\|}{C}}OC_2H_5$$

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).