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The Chemistry of Dimethylamino Isocyanate. A Novel Nitrogen Ylid[1]

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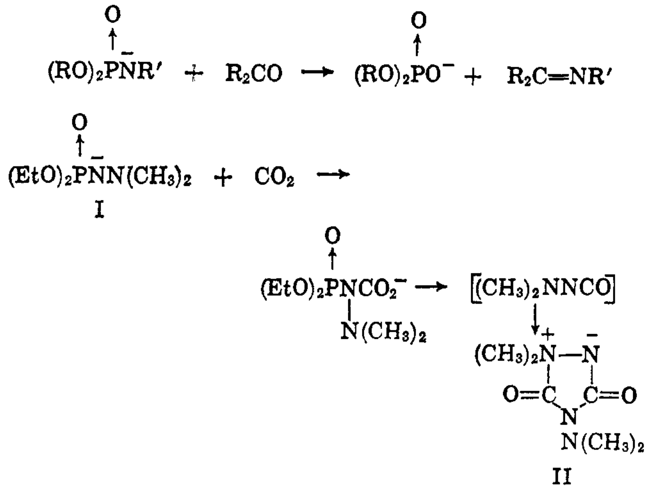
Through the phosphoramide synthesis, dimethylamino isocyanate has been prepared in the form of an unusual dimer. This dimer has been characterized as a cyclic hydrazinium ylid and undergoes a variety of rather interesting reactions including methyl group migration, equilibration with other isocyanates to form new dimers, and dealkylation reactions. The pyrolysis of N-dimethylaminourethan to give a variety of triazoles, a related reaction, is also described in some detail.

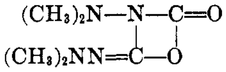
The reaction of phosphoramidate anions with carbonyl molecules represents a very convenient synthesis for a variety of unsaturated nitrogen compounds.[2] As a variant of this reaction we have examined the carboxylation of the phosphoramidate anion I derived from N,N-dimethylhydrazine in an attempt to prepare dimethylamino isocyanate. The parent isocyanate has not been obtained under any circumstances; however, a very reactive dimer was obtained whose structure has been identified as the nitrogen ylid II (see Scheme I). The establishment of this structure and the chemistry of II and its analogs are the subjects of this paper.

SCHEME I



Results

The carboxylation of the phosphoramidate anion I was carried out in benzene solution at 10°. This solution after several days at room temperature deposited a crystalline product which was ultimately characterized as the dimer II. The product was a crystalline, hygroscopic material obtained in 37% yield and was most conveniently purified by sublimation. It melted sharply at 178°, and both microanalytical and ebullioscopic molecular weight data were in excellent agreement with the dimer structure. *A priori* there are five classical structures that can be written for this dimer.



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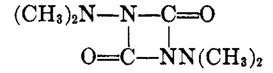

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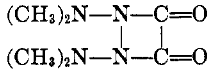

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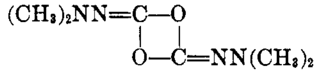

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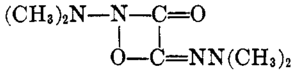

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Some of these, notably **3** and **5**, do not appear very likely from a thermodynamic point of view. Also **1** and **2** are, of course, analogous to ketene dimers, and it has been established that aromatic isocyanates do form reasonably stable dimers having the latter structure.[3,4] However, the nmr spectrum of the dimer showed equal peaks at τ 7.00 and 6.71 which must be assigned to the methyl hydrogens. Accordingly the compound is unsymmetrical thereby eliminating the structures **2**, **3**, and **4**. Hydrolysis of the dimer with neutral water at room temperature provided in high yield the urea IV (independently synthesized from dimethylhydrazine and phosgene), and this clearly establishes the NNCNN structure in the parent molecule. Accordingly we are left with structure **1** which was expected to eliminate

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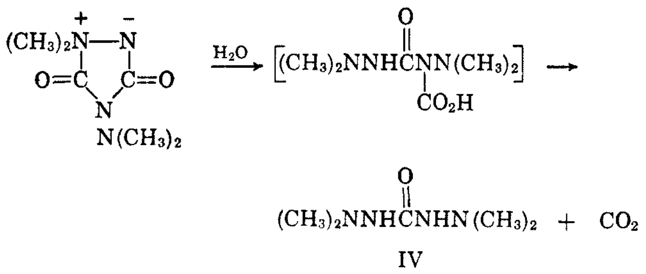
(1) Presented at the Symposium on Ylid Chemistry, University of Cincinnati, Oct 17, 1966.

(2) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **84**, 1316 (1962).

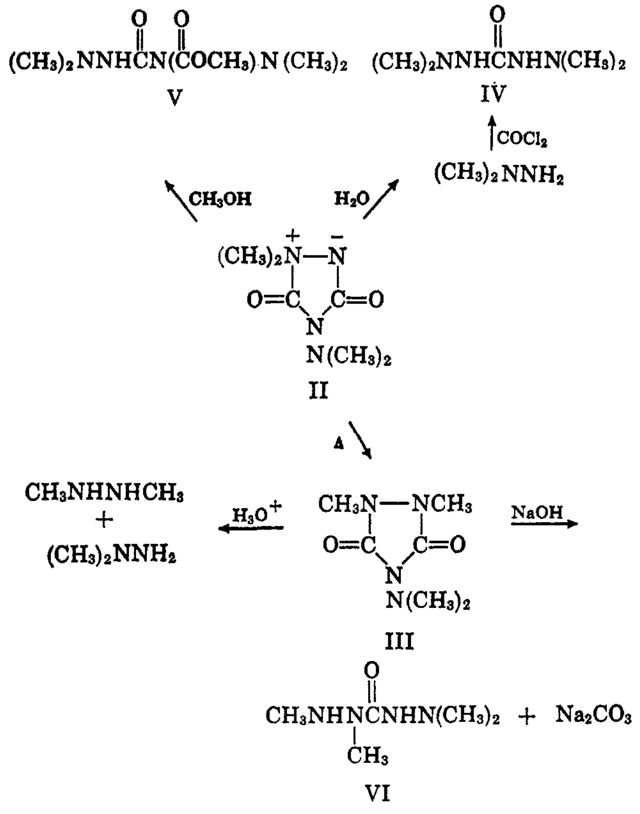
(3) R. G. Arnold, J. A. Nelson, and J. J. Verbane, *Chem. Rev.*, **57**, 58 (1957).

(4) C. J. Brown, *J. Chem. Soc.*, 2931 (1955).

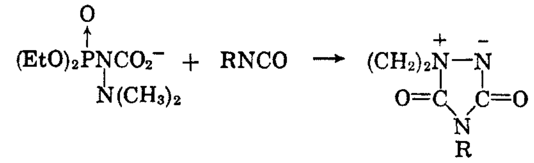


carbon dioxide to form carbodiimide on pyrolysis. However, when this pyrolysis was carried out at 200°, there was no gas evolution, and a new liquid dimer (III) having the same analysis was obtained in essentially quantitative yield (Scheme II). The nmr spectrum of this new dimer also showed equal peaks at τ 6.88 and 7.16 indicating two types of methyl groups. This product on hydrolysis with hydrochloric acid gave high yields of symmetrical and unsymmetrical dimethylhydrazine hydrochlorides which could be readily separated by virtue of their solubility properties. Hydrolysis on the alkaline side gave an 85% yield of the carbohydrazide VI which was characterized by spectroscopic and analytical data and also by acid hydrolysis to an equimolar mixture of symmetrical and unsymmetrical dimethylhydrazine hydrochlorides. The structure of the triazole III is accordingly on a firm foundation and thus the pyrolysis of II clearly involves the migration of a methyl group. It should also be noted that the ylid II could be accurately titrated with perchloric acid in acetic acid whereas the triazole III was neutral. These reactions are summarized in Scheme II and are all consistent with the postulated ylid structure of the dimer II.

SCHEME II



As indicated above, the yield of the ylid dimer II was not very good and its separation in pure form from the reaction mixture was tedious. In order to carry out additional structural work and chemical investigation of this ylid system a better synthesis was desirable. Accordingly we investigated the synthesis of mixed ylid dimers by trapping the reactive dimethylamino isocyanate with another isocyanate, and this was quite successful. The ylid VIIa was a solid melting at 99° and was obtained in 62% yield. Its counterpart from *t*-octyl isocyanate (71% yield) melted at 97° and was stable enough to survive rapid recrystallization from hot water. Both of these ylids showed carbonyl absorption in the infrared at 1790 and 1670 cm^{-1} quite comparable to that of the original dimer II of dimethylamino isocyanate. Like II they also could be titrated as monobasic amines against perchloric acid. Consequently VIIa because of the convenience of its preparation was chosen for additional chemical investigation.

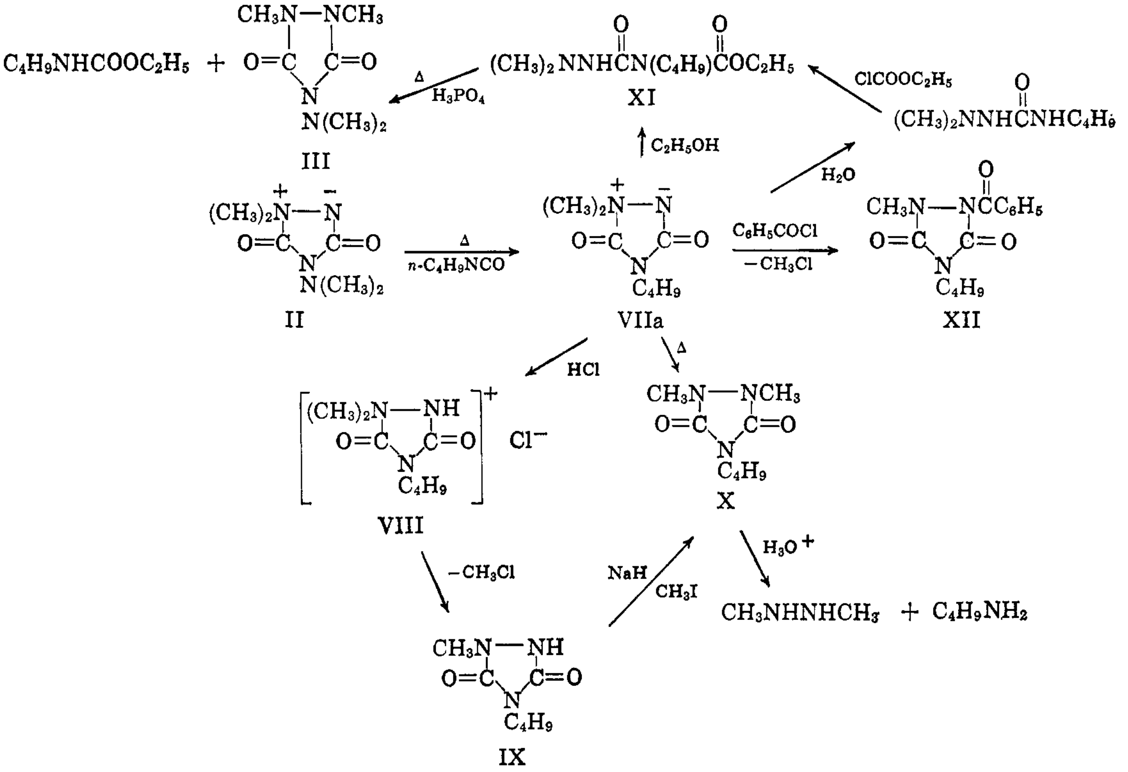


VIIa, R = *n*-Bu
VIIb, R = *t*-Oct

This product, whose nmr spectrum contained but a single band assignable to methyl hydrogens, underwent hydrolysis, alcoholysis, and pyrolysis reactions which were quite comparable to the dimethylamino isocyanate dimer II (Scheme III). The structure of the ethanolysis product XI was determined chemically by independent synthesis and by its decomposition to N-*n*-butylurethan. The latter pyrolysis reaction also gave the triazole III as a coproduct and suggests that dimethylamino isocyanate was formed in this reaction as an intermediate. The ylid VIIa like II also gave the triazole X *via* a methyl migration when heated. The structure of X was verified by an investigation of its hydrolysis products. It is also of interest to note the mixed dimer VIIa could be prepared directly from the dimer II by warming the latter with excess *n*-butyl isocyanate.

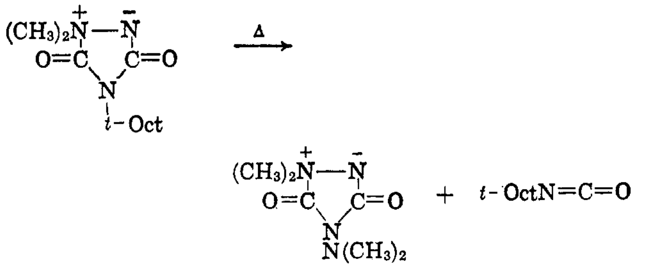
Additional evidence that dimethylamino isocyanate dimer and its analogs are cyclic hydrazinium ylids was furnished by examination of the reaction between VIIa and dry hydrogen chloride in benzene. The product VIII was a crystalline, hygroscopic solid which decomposed slowly at room temperature and rapidly at its melting point of 90° to give methyl chloride and the triazole IX. The structure of IX was confirmed by its physical properties and by its methylation to give X. A comparison of the infrared spectra of the ylid VIIa and its hydrochloride salt VIII is also instructive. Unlike the ylid, the carbonyl absorption of the salt appears at the normal position of 1780 with no band at 1670 cm^{-1}. The shift in the carbonyl frequency to higher values in going from the salt or cyclic amide X to the ylid is a general phenomenon and presumably reflects the delocalization present in the ylid carbonyl system. The reaction of another electrophile, benzoyl chloride, with the ylid VIIa was also examined. This reaction again involved spontaneous loss of methyl chloride, and the product obtained in 74% yield was the

SCHEME III



triazole XII. These reactions are all summarized in Scheme III.

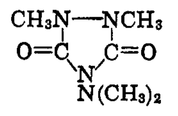
The chemistry of the *t*-octyl ylid VIIb was not investigated in any detail since this material was found to be thermally unstable. Indeed at a temperature of 90° (just above its melting point) it decomposed to the symmetrical dimer II and *t*-octyl isocyanate in nearly quantitative yield. This phenomenon which is not characteristic of the *n*-butyl analog VIIa is presumably a consequence of steric strain in VIIb.



Although the derivatives of dimethylamino isocyanate are accessible through the phosphoramidate synthesis, this route is not very convenient. Accordingly the direct phosgenation of N,N-dimethylhydrazine was investigated in some detail but with a conspicuous lack of success. In view of the great reactivity of the ylid II toward electrophilic reagents this result was not unexpected. We were, however, able to establish a route to some of the rearrangement products of dimethylamino isocyanate by pyrolysis of N-dimethylaminourethan XIII. At 200° in the presence of phosphoric acid catalyst a 49% yield of the triazole III was obtained. Presumably this originates from the cyclic hydrazinium ylid which in turn is derived from dimethylamino isocyanate. In support of this it was found possible to trap dimethylamino isocyanate by conducting the urethan pyrolysis in the presence of an added isocyanate or isothiocyanate. Under these conditions the triazoles XIV–XVI derived from methyl migration (see Scheme IV) were isolated in good yield in every case attempted except that where phenyl isocyanate was employed as the trap. Here the yield of XIV was only 16% and it was accompanied by a considerable amount of N-phenylurethan, the origin of which is uncertain. The pyrolysis of N-dimethylaminourethan in the presence of a suitable trap does, however, represent a versatile synthesis of a variety of methyl-substituted triazoles.

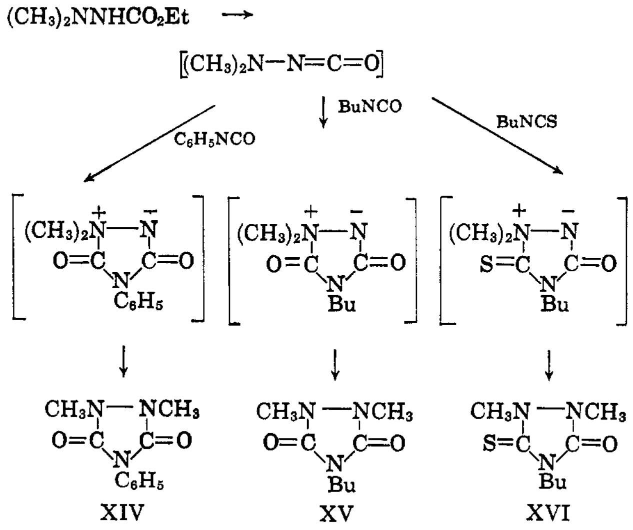
$$(CH_2)_2NNHCO_2Et \xrightarrow{H_3PO_4} [(CH_3)_2NNCO] \longrightarrow$$

XIII



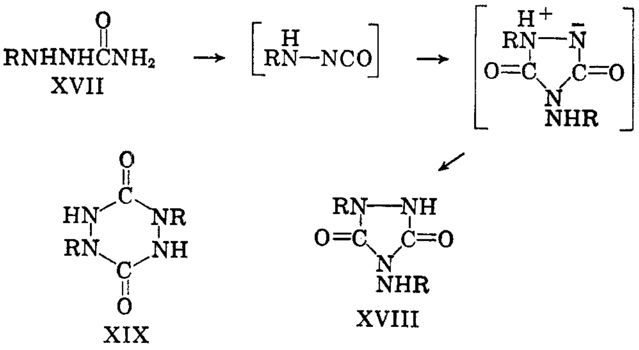
III

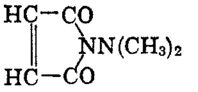
SCHEME IV



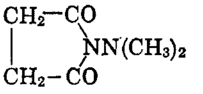
It is interesting to note that a reaction closely related to the dimethylaminourethan pyrolysis has been reported. Thus Busch conducted the pyrolysis of 1-alkylsemicarbazides XVII and obtained products which he believed were the triazoles XVIII.[5] This was questioned, however, on the basis that the triazoles were not basic and the *p*-urazine structure (XIX) was an alternative possibility (Scheme V). However, it is quite evident at this point that aminotriazoles such as III and XVIII are not basic, and that the triazole product Busch obtained was probably formed as indicated. To confirm the lack of basicity of an N-amino group flanked by two carbonyls, we prepared the imides XX and XXI

SCHEME V





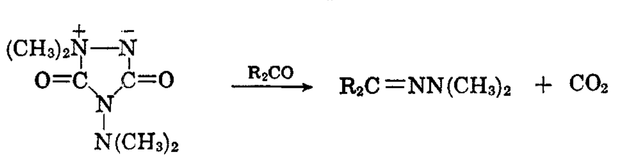
XX



XXI

and found that neither compound could be titrated with perchloric acid in acetic acid medium.

The reaction of dimethylamino isocyanate with ketones and aldehydes was also investigated very briefly. At 200° the dimer II gave with cyclohexanone in 17% yield the hydrazone derived from unsymmetrical dimethylhydrazine and, in addition, carbon dioxide. Better yields of similar hydrazones were obtained (40–50%) when the dimethylamino isocyanate dimer was generated *in situ* by pyrolysis of the urethan XIII in the presence of the carbonyl compound.



Discussion

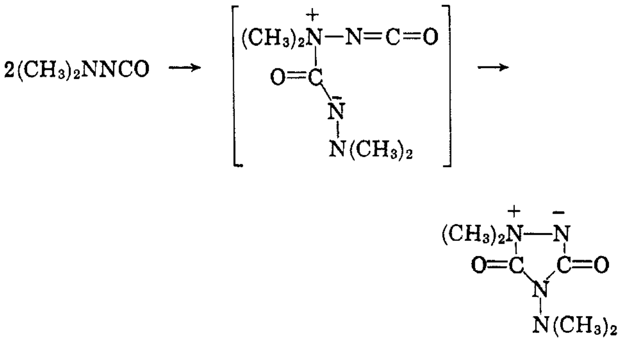
It should be pointed out that the assignment of the ylid structure to the dimer II is not completely unambiguous in the absence of detailed X-ray crystallographic examination of this molecule. It is a historical fact that structural assignments of dimers of reactive molecules such as isocyanates and ketenes must be cautiously made on the basis of chemical evidence. In this case, however, the only alternate structure which can be considered is 1, and the chemistry of the dimers II and VIIa is not consistent with this structure. Also these dimers are polar, high melting solids, and this fact strongly argues against structure 1. Furthermore, nitrogen ylids of related structure such as *p*-nitrobenzyldimethylammonium-N-acetylimine (XXII) and trimethylammonium-N-benzoylimine (XXIII) have been

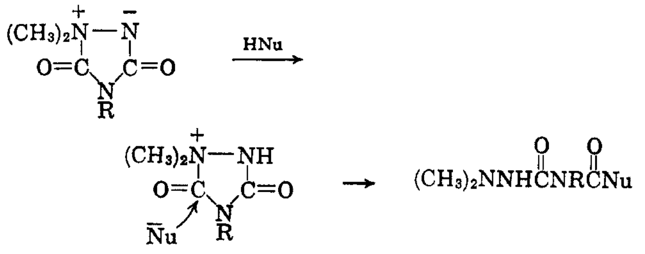
$CH_3CO\overset{-}{N}-\overset{+}{N}(CH_3)_2CH_2C_6H_4NO_2\text{-}p$ XXII

$C_6H_5CO\overset{-}{N}-\overset{+}{N}(CH_3)_3$ XXIII

prepared and characterized, respectively, by Wawzonek and Hinman.[6,7] Indeed a variety of nitrogen ylids have been described, and their chemistry has recently been reviewed in some detail.[8]

The fact that dimethylamino isocyanate can be isolated only as its dimer is not surprising in view of its structure. Dimer formation may be viewed most simply as a consequence of attack of the nucleophilic dimethylamino nitrogen on the carbonyl group of a second isocyanate molecule. It is also of interest that none of the reaction products of dimethylamino isocyanate dimers with active hydrogen molecules is derived from the monomer. Thus reaction of an active hydrogen species (HNu) may be pictured as protonation of the imine nitrogen followed by attack of the nucleophile (Nu) on the carbonyl carbon atom adjacent to the cationic nitrogen with subsequent cleavage of the C–N bond. The timing of these steps is of course uncertain.





The methyl group migration which is characteristic of the nitrogen ylids described here is also not without precedent. It is of course reminiscent of the Stevens rearrangement and a similar reaction has in fact been observed by Wawzonek with the ylid XXII.[7,8]

Finally the equilibration of dimethylamino isocyanate dimer II with other isocyanates to form similar ylid mixed dimers is of some special interest. We do not believe that this reaction involves prior dissociation of the dimer to dimethylamino isocyanate in view of our inability to detect any chemical evidence for presence of the monomeric species. Rather we consider that the exchange reaction may proceed as indicated through a seven-membered ring which in turn would extrude di-

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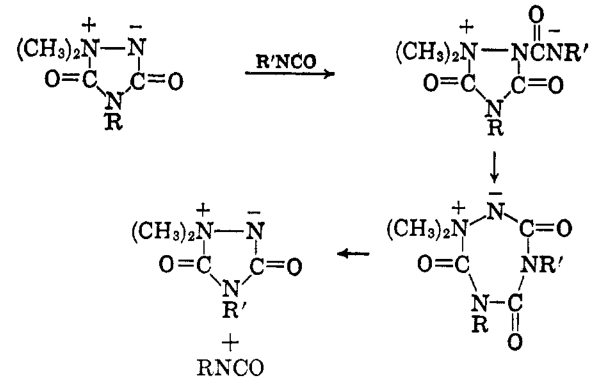
[5] M. Busch. *J. Chem. Soc.*, **80**, 488 (1901); *Ber.*, **34**, 2311 (1901).

[6] S. Wawzonek and E. Yeakey, *J. Am. Chem. Soc.*, **82**, 5718 (1960).

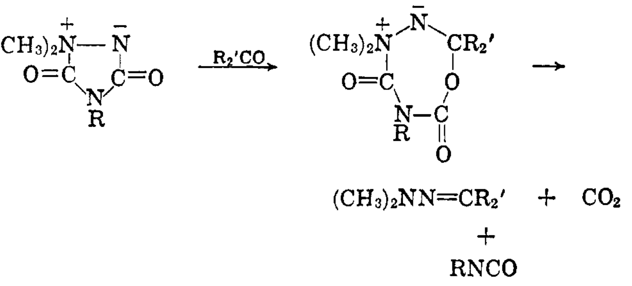
[7] R. L. Hinman and M. C. Flores, *J. Org. Chem.*, **24**, 660 (1959).

[8] A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, p 251.

SCHEME VI



methylamino isocyanate (Scheme VI). A similar picture may be developed for the reaction of aldehydes and ketones with dimethylamino isocyanate. In this case, however, the large ring has the capability to lose carbon dioxide and does in fact do so.



Experimental Section[9]

Dimethyl N-Dimethylaminophosphoramidate (I).—To a stirred solution of 138 g (1.0 mole) of diethyl phosphite, 154 g of carbon tetrachloride, and 250 ml of xylene at 20–40° was added 118 g (2.0 moles) of *unsym*-dimethylhydrazine. After the addition the mixture was stirred at room temperature for 30 min and filtered. The filtrate was stripped and the residue was distilled. There was obtained 120.5 g (61%) of product, bp 85° (0.25 mm).

Anal. Calcd for $C_6H_{17}N_2O_3P$: C, 36.73; H, 8.67; N, 14.28. Found: C, 36.62; H, 8.54; N, 14.37.

Dimethylamino Isocyanate Dimer (II).—To a slurry of 9.6 g (0.2 mole) of 50% sodium hydride in 200 ml of dry benzene was added 39.2 g (0.2 mole) of diethyl N-dimethylaminophosphoramidate. After the addition, which was conducted at 30°, the mixture was allowed to stand overnight during which time the stoichiometric quantity of hydrogen was evolved. The mixture was filtered under an atmosphere of nitrogen and cooled to 10°. At 10° carbon dioxide was passed slowly through the solution. When gas absorption had ceased, the mixture was allowed to come to room temperature and stand for 6 days without stirring. During this period a semicrystalline precipitate formed. The supernatant solvent was decanted and the soluble portion of the residue was recrystallized from 1 l. of hot benzene. The crystalline product was purified by sublimation at 130–140° (0.25 mm). There was obtained 5.5 g (32%) of colorless material which melted sharply at 178°. The product was hygroscopic and had to be stored in the absence of moisture. The hydrazinium ylid absorbed strongly at 1670 and 1790 cm^{-1} in the infrared. Its nmr spectrum showed equal strong bands at τ 7.0 and 6.7 (as measured against tetramethylsilane). The dimer was dissolved in glacial acetic acid and titrated with 0.1 *N* perchloric acid. An equivalent weight of 175 was obtained.

Anal. Calcd for $C_6H_{12}N_4O_2$: C, 41.86; H, 6.98; N, 32.50; mol wt, 172. Found: C, 41.76; H, 6.73; N, 32.40; mol wt, 174 (ebullioscopic).

A sample of the dimer was dissolved in water. The solvent was removed under reduced pressure leaving a white, crystalline solid (IV) which was recrystallized from isooctane, mp 149–150°.

Anal. Calcd for $C_5H_{14}N_4O$: C, 41.09; H, 9.59; N, 38.32; mol wt, 146. Found: C, 41.12; H, 9.72; N, 38.26; mol wt, 145.

The dimer was dissolved in anhydrous methanol. After removal of the solvent under reduced pressure, a white, crystalline solid (V) remained and was recrystallized from a small amount of pentane, mp 59–60°.

Anal. Calcd for $C_7H_{16}N_4O_3$: C, 41.17; H, 7.84; N, 27.45; mol wt, 204. Found: C, 41.28; H, 7.87; N, 27.31; mol wt, 203 (ebullioscopic).

Independent Synthesis of N,N'-Bisdimethylaminourea (IV).—*unsym*-Dimethylhydrazine, (30.0 g, 0.5 mole) was added to 50.5 g (0.5 mole) of triethylamine and diluted with 100 ml of benzene. Phosgene (24.8 g, 0.25 mole), diluted with 100 ml of benzene, was added dropwise to the amine mixture at 10–15° over a 90-min period. After the addition the mixture was stirred at 15° for 2 hr and for 30 min at 65°.

The warm mixture was filtered and the precipitate was washed with 100 ml of warm benzene. The filtrate and washings were combined and stripped under reduced pressure. A crystalline residue weighing 24.2 g remained. The residue was extracted with 200 ml of boiling isooctane. From the cooled isooctane extract the product (4.7 g, 12.9%) precipitated, mp 149–150°. The infrared spectrum of this material was identical with that of the solid obtained from the hydrolysis of the dimer. A mixture melting point was undepressed.

The Pyrolysis of II to III.—The ylid dimer II (5.0 g, 0.029 mole) was held at 200° for 15 min. During the heating period there was no gas evolution. The liquid was distilled, 190° (20 mm), to yield 4.8 g (96%) of straw yellow distillate, $n^{25}D$ 1.4845. The product III absorbed strongly at 1730 with an overtone at 1780 cm^{-1} which later was found to be characteristic for this class of compounds. The nmr spectrum showed two equally strong peaks at τ 6.88 and 7.16. The product was not basic when titrated with 0.1 *N* perchloric acid in glacial acetic acid.

Anal. Calcd for $C_6H_{12}N_4O_2$: C, 41.86; H, 6.98; N, 32.50; mol wt, 172. Found: C, 42.00; H, 7.18; N, 32.67; mol wt, 171 (ebullioscopic).

Hydrolysis of III.—The triazole III (8.6 g, 0.05 mole) was refluxed with 100 ml of concentrated hydrochloric acid for 6 days. The solution was stripped under reduced pressure (20 mm) to give a semicrystalline residue. The residue was taken up in 50 ml of acetone and filtered. The precipitate was recrystallized from acetonitrile to give 4.0 g (95% yield) of a white, crystalline solid whose infrared spectrum was identical with that of an authentic sample of *sym*-dimethylhydrazine dihydrochloride, mp 167° (mixture melting point undepressed).

The acetone filtrate was stripped under reduced pressure to yield a viscous residue which slowly crystallized on standing. The product (4.0 g, 95% yield), which was recrystallized from *n*-butyl alcohol, had an infrared spectrum identical with that of an authentic sample of *unsym*-dimethylhydrazine hydrochloride, mp 81–82° (mixture melting point undepressed).

The Saponification of III to VI.—The dimer III (17.2 g, 0.1 mole), was treated with 50% NaOH (16.0 g, 0.2 mole), and the mixture was diluted with 70 ml of H_2O. After refluxing for 4 hr, the solution was stripped under reduced pressure and filtered, and the filtrate was distilled. A viscous liquid (VI, 12.6 g, 85% yield) was collected: bp 100° (0.2 mm), $n^{25}D$ 1.4729. The nmr spectrum of the product confirmed its structure. A band at τ 7.533 assigned to the six hydrogens of the $(CH_3)_2N$ moiety was twice as strong as the band at 7.083 assigned to the methyl hydrogens of the CH_3NH moiety. The hydrogens on the methyl groups adjacent to the carbonyl group absorbed at τ 7.667 and appeared to be split by the hydrogen on the adjacent nitrogen atom. A small peak at τ 5.133 was assigned to the amine hydrogen while that of 2.533 was assigned to the amide hydrogen. The infrared spectrum of the distillate contained bands at 1670 and 1540 cm^{-1} confirming the presence of a secondary amide.

Anal. Calcd for $C_5H_{14}N_4O$: C, 41.09; H, 9.59; N, 38.35; mol wt, 146. Found: C, 41.05; H, 9.62; N, 38.27; mol wt, 147 (ebullioscopic).

The product was hydrolyzed exactly as described in the previous procedure. Both symmetrical and unsymmetrical dimethylhydrazine were obtained in equivalent yields as their hydrochloride salts. The white, crystalline precipitate obtained from the filtration was established by a comparison of infrared spectra to be sodium carbonate.

Synthesis of Mixed Dimer VIIa from *n*-Butyl Isocyanate.—Diethyl N-dimethylaminophosphoramidate (98 g, 0.5 mole)

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[9] All melting points are uncorrected.

was added slowly to a slurry of 50% sodium hydride (24 g, 0.5 mole), in 2 l. of benzene. After the addition, which was conducted at 25–30°, the mixture was allowed to stand overnight during which time the stoichiometric quantity of hydrogen was evolved. The mixture was filtered in an atmosphere of nitrogen and cooled to 5–10°. At this temperature carbon dioxide was passed slowly though the solution. When gas absorption had ceased, 49.5 g (0.5 mole) of *n*-butyl isocyanate was added all at once and the solution was allowed to come to room temperature with stirring. After standing for 4 days the solution had deposited a gummy precipitate. The upper benzene layer was decanted away and the gummy residue was washed twice with 100-ml portions of benzene. The benzene layers were combined and stripped under reduced pressure (20 mm). The residue which solidified on standing was washed well with isooctane followed by an ether wash. The white, crystalline product was recrystallized twice from carbon tetrachloride to give 56.8 g (62% yield) of white, shimmering platelets, mp 98–99°.

Anal. Calcd for $C_8H_{15}N_3O_2$: C, 51.87; H, 8.16; N, 22.73; mol wt, 185. Found: C, 51.79; H, 7.90; N, 22.67; mol wt, 184 (ebullioscopic).

Characteristically, the product contained strong bands in its infrared spectrum at 1790 and 1670 cm^{-1}. Besides containing the normal bands for the *n*-butyl group the nmr spectrum of the product showed a strong band at τ 6.733 assigned to the methyl hydrogens. The product when dissolved in glacial acetic acid and titrated potentiometrically with 0.1 *N* perchloric acid was found to have an equivalent weight of 184.

This product was also obtained by equilibration of the dimethylamino isocyanate dimer II with *n*-butyl isocyanate. A mixture of the solid dimer II (1.72 g, 0.01 mole) and *n*-butyl isocyanate (3.9 g, 0.04 mole) was refluxed at 150° for 15 min. On cooling the mixture solidified. The solid was recrystallized twice from carbon tetrachloride to give 3.0 g (81% yield) of white crystals, mp 98–99°. The infrared spectrum of the product was identical with that of VIIa prepared by the procedure described above.

Hydrolysis of VIIa.—The ylid VIIa (2.0 g, 0.011 mole) was dissolved in 20 ml of water and the solution refluxed overnight. After stripping the solution under reduced pressure a liquid residue was obtained which crystallized on standing. The product (1.4 g, 83% yield), was recrystallized from isooctane, mp 48–49°. The infrared spectrum of the product was identical with that of N-dimethylamino-N′-*n*-butylurea which had been prepared from *unsym*-dimethylhydrazine and *n*-butyl isocyanate. A mixture melting point was undepressed.

Anal. Calcd for $C_7H_{17}N_3O$: C, 52.48; H, 11.32; N, 26.23. Found: C, 52.61; H, 11.15; N, 26.01.

Alcoholysis of VIIa.—The ylid VIIa (10.0 g, 0.054 mole) was dissolved in 30 ml of ethanol and the solution was refluxed for 2 hr. After stripping the solution under reduced pressure a liquid residue remained which was distilled to give 7.0 g (60% yield) of the colorless liquid distillate XI: bp 80–81° (0.2 mm), n^{25}_{D} 1.4505.

Anal. Calcd for $C_{10}H_{21}N_3O_3$: C, 51.95; H, 9.09; N, 18.18. Found: C, 51.93; H, 9.29; N, 18.17.

Independent Synthesis of XI.—To N-dimethylamino-N′-*n*-butylurea (11.5 g, 0.072 mole) was added slowly with cooling ethyl chloroformate (7.8 g, 0.072 mole). The viscous mixture was allowed to stand for 0.5 hr and then dissolved in 100 ml of *t*-butyl alcohol. Potassium *t*-butoxide (8.06 g, 0.072 mole) was added slowly while the temperature was kept below 20° by means of an ice bath. After the mixture had been stirred for 1 hr at room temperature it was filtered. The filtrate was stripped under reduced pressure to give a liquid residue which when distilled gave 12.2 g (75% yield) of colorless distillate: bp 85–88° (0.25 mm), n^{25}_{D} 1.4510. The infrared spectrum of the distillate was identical with that of the product obtained by the alcoholysis of VIIa as described above.

Pyrolysis of the Alcoholysis Product XI.—The product obtained from the ethanolysis of VIIa (3.7 g, 0.016 mole), was heated at 150° for 2 hr. There was no weight loss during the heating. The pyrolyzed solution was distilled to give two fractions. The first fraction (2.0 g, 74% yield) had an infrared spectrum and physical constants identical with those of an authentic sample of N-*n*-butylurethan: bp 52° (0.25 mm), n^{25}_{D} 1.4280.

The second fraction (1.2 g, 86% yield), had an infrared spectrum and physical constants identical with those of the triazole III previously described.

The Pyrolysis of VIIa to X.—The cyclic hydrazinium ylid VIIa (2.0 g, 0.011 mole), was heated at 170° for 2 hr. There was no weight loss and the infrared spectrum of the crude product showed only a trace of isocyanate (weak absorption at 2230 cm^{-1}). The liquid which resulted from the pyrolysis was distilled to give 1.7 g (85% yield) of a slightly yellow liquid product: bp 96° (0.2 mm), n^{25}_{D} 1.4700. The infrared spectrum of this product X showed strong carbonyl absorption at 1680 with a weak overtone at 1750 cm^{-1}. The nmr spectrum showed a single peak at τ 6.9 attributed to the N-methyl hydrogen atoms.

Anal. Calcd for $C_8H_{15}N_3O_2$: C, 51.87; H, 8.16; N, 22.73; mol wt, 185. Found: C, 51.63; H, 8.11; N, 22.54; mol wt, 186 (ebullioscopic).

A 5.5-g (0.03 mole) sample of the triazole X was diluted with 100 ml of concentrated HCl and the mixture was refluxed for 48 hr. The solution was stripped under reduced pressure to give a semicrystalline residue. The residue was filtered and the precipitate was washed well with acetone. The infrared spectrum of the precipitate (4.8 g, 86% yield) was identical with that of an authentic sample of *sym*-dimethylhydrazine dihydrochloride, mp 167°. The acetone filtrate was stripped under reduced pressure to give a viscous residue which crystallized on standing (2.6 g, 80% yield), mp 195°. The infrared spectrum of salt was identical with that of an authentic sample of *n*-butylamine hydrochloride.

Reaction of the Ylid VIIa with Hydrogen Chloride.—A solution of 46.8 g (0.25 mole) of the ylid VIIa in 400 ml of dry benzene was saturated with dry hydrogen chloride at 10°. When HCl absorption had ceased, the white, crystalline precipitate which had formed was removed by filtration and washed with 100 ml of cold benzene. The product (49.3 g, 90% yield) was extremely hygroscopic and slowly decomposed when allowed to stand at room temperature. It was stored successfully for 1 month at 0° without noticeable decomposition.

A sample (15 g, 0.068 mole) of this adduct was warmed slowly to 90° at which point 1.35 l. of methyl chloride (88% yield) was rapidly evolved. The gas was identified from its infrared spectrum which was superimposable on the spectrum of an authentic sample of gaseous methyl chloride. The residue from the pyrolysis was distilled to give 9.0 g (78% yield) of viscous, colorless liquid, bp 126° (0.1 mm). The distillate crystallized on standing, mp 52°. The product IX absorbed in the carbonyl region at 1700 with a weak overtone at 1760 cm^{-1} and showed N-H absorption. The nmr spectrum clearly defined the structure. The amide hydrogen absorbed at τ 0.817 and the methyl hydrogens at 6.833. Absorption owing to the *n*-butyl group was typical.

Anal. Calcd for $C_7H_{13}N_3O_2$: C, 49.12; H, 7.60; N, 24.56. Found: C, 49.33; H, 7.63; N, 24.71.

Methylation of IX to X.—The triazole IX (4.2 g, 0.024 mole) was added to a slurry of 50% sodium hydride (1.2 g, 0.024 mole) in 50 ml of dry diethylene glycol dimethyl ether. The slurry was refluxed for 3 hr. The solution was cooled to room temperature and methyl iodide (7.05 g, 0.05 mole) was added slowly. After the addition the mixture was stirred for 1 hr and filtered, and the filtrate was stripped. After removal of the solvent the product X (3.5 g, 80% yield) was collected as a light yellow liquid distillate: bp 96° (0.1 mm), n^{25}_{D} 1.4695. The infrared spectrum of the distillate was identical with that of X prepared as described above.

Treatment of VIIa with Benzoyl Chloride.—The cyclic hydrazinium ylid VIIa (4.62 g, 0.025 mole) was dissolved in 100 ml of dry benzene. Benzoyl chloride (3.5 g, 0.025 mole) was added slowly at room temperature and the mixture was allowed to stand for 48 hr. Solvent was removed under reduced pressure and the residue was distilled to give a colorless, viscous liquid: 5.0 g (74% yield), bp 156° (0.2 mm). The product XII had an infrared spectrum typical of this class of triazoles, with strong carbonyl absorption at 1720 with a weak overtone at 1780 cm^{-1}.

Anal. Calcd for $C_{14}H_{17}N_3O_3$: C, 61.09; H, 6.18; N, 15.27; mol wt, 275. Found: C, 61.05; H, 6.10; N, 15.12; mol wt, 277 (ebullioscopic).

Preparation of the Ylid VIIb from *t*-Octyl Isocyanate.—Diethyl N-dimethylaminophosphoramidate (19.6 g, 0.1 mole) was added slowly to a slurry of 50% sodium hydride (4.8 g, 0.1 mole) in 200 ml of benzene. After the addition, which was conducted at 30°, the mixture was allowed to stand overnight during which time the stoichiometric quantity of hydrogen was evolved. The mixture was filtered under an atmosphere of nitrogen and cooled to 10°. At 10° carbon dioxide was passed slowly through the solution. When gas absorption had ceased, *t*-octyl isocyanate (15.5 g, 0.1 mole) was added all at once. The solution was allowed to stand at room temperature for 5 days during which time a semicrystalline solid settled out. The solution was filtered and the precipitate was washed well with cold water. The crystalline residue which remained was recrystallized rapidly from hot water to give 17 g (71% yield) of white, shimmering crystals, mp 96–97°. The infrared spectrum of the product contained strong bands at 1790 and 1670 cm^{-1}. A strong band at τ 6.783 in the nmr spectrum was assigned to the methyl hydrogens. The product was titrated with 0.1 *N* perchloric acid to give an equivalent weight of 242.

Anal. Calcd for $C_{12}H_{23}N_3O_2$: C, 59.71; H, 9.62; N, 17.45; mol wt, 241. Found: C, 59.57; H, 9.62; N, 17.48; mol wt, 246 (ebullioscopic).

A dry sample of the ylid VIIb (4.8 g, 0.02 mole), was heated at 90° for 1 hr. On cooling a semicrystalline product was obtained. The mixture was filtered to give 1.5 g (90% yield) of white, crystalline solid, mp 175° (from benzene). The infrared spectrum of the solid was identical with the spectrum of the dimethylaminoisocyanate dimer II. A mixture melting point was not depressed.

The filtrate was distilled to give 2.8 g (92% yield) of distillate, bp 68° (30 mm). The product was identical in its physical properties and infrared spectrum with those of an authentic sample of *t*-octyl isocyanate.

Preparation of the Triazole III from N-Dimethylaminourethan.—To N-dimethylaminourethan (101 g, 0.76 mole) was added 5 drops of 85% phosphoric acid. The mixture was heated with stirring at 200–210° and the alcohol was removed slowly as formed. After an 8-hr period, the equivalent of alcohol (34.9 g) was completely collected and the solution was cooled. The reddish brown liquid was distilled to give 31.8 g (49% yield) of straw-yellow liquid: bp 93–94° (0.1 mm), $n^{25}D$ 1.4840. The infrared and nmr spectra of the product were identical with those of the triazole III, obtained from the pyrolysis of the dimethylamino isocyanate dimer II.

Preparation of X from N-Dimethylaminourethan and *n*-Butyl Isocyanate.—N-Dimethylaminourethan (33.0 g, 0.25 mole), *n*-butyl isocyanate (46.5 g, 0.5 mole), and 5 drops of 85% phosphoric acid were combined. The mixture was heated with stirring at 200–210° for 8 hr. The mixture was distilled to give two fractions; the first (25.4 g, 70% yield), bp 93° (30 mm), $n^{25}D$ 1.4280, proved from its physical properties and infrared spectrum to be identical with an authentic sample of *n*-butylurethan. The second fraction (19.3 g, 42% yield) was identical in all respects with the triazole X obtained from the pyrolysis of VIIa: bp 131° (30 mm), $n^{25}D$ 1.4700.

Preparation of XIV from Phenyl Isocyanate.—N-Dimethylaminourethan (33.0 g, 0.25 mole), phenyl isocyanate (59.5 g, 0.5 mole), and 5 drops of 85% phosphoric acid were combined. The mixture was heated with stirring at 200° for 18 hr. The dark, viscous solution which resulted was distilled to give a liquid distillate, bp 103–115° (0.25 mm), which crystallized on standing. The solid was recrystallized from isooctane giving 24.2 g (60% yield) of white crystals, mp 52–53°. A mixture melting point with authentic sample of N-phenylurethan was not depressed.

A second fraction was collected at 156–160° (0.2 mm) and also crystallized on cooling. The solid XIV was recrystallized from CCl_4 to give 8.0 g (16% yield) of a white, crystalline solid, mp 123–124°. The infrared spectrum of the product was typical of related triazoles with strong carbonyl absorption at 1680 and a weak overtone at 1740 cm^{-1}.

Anal. Calcd for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.36; N, 20.48; mol wt, 205. Found: C, 58.67; H, 5.27; N, 20.36; mol wt, 204 (ebullioscopic).

A sample of the crystalline triazole was refluxed for 14 hr with concentrated hydrochloric acid. The solution was stripped, the semicrystalline residue was filtered, and the precipitate was washed well with acetone. The product was recrystallized from acetonitrile, mp 167–169°. A mixture melting point with an authentic sample of *sym*-dimethylhydrazine hydrochloride was undepressed. From the size of the precipitate it was apparent that the rate of hyrolysis was extremely slow. This was verified by an investigation of the acetone filtrate which was found, *via* infrared, to contain a substantial quantity of starting triazole.

Preparation of XVI from Butyl Isothiocyanate.—N-Dimethylaminourethan (33.0 g, 0.25 mole), *n*-butyl isocyanate (28.8 g, 0.25 mole), and 5 drops of 85% phosphoric acid were mixed. The mixture was heated at 200–210° for 48 hr during which time alcohol (11.5 g, 100% yield) was collected as it formed. The dark residue was distilled to give 27.2 g (54% yield) of pale yellow distillate, bp 105–107° (0.05 mm). The compound showed strong carbonyl absorption at 1740 cm^{-1}.

Anal. Calcd for $C_8H_{15}N_3OS$: C, 47.76; H, 7.46; N, 20.89; S, 15.92; mol wt, 201. Found: C, 47.82; H, 7.61; N, 20.76; S, 15.44; mol wt, 195 (ebullioscopic).

N-Dimethylaminomaleimide.—*unsym*-Dimethylhydrazine (18.0 g, 0.3 mole), was added slowly at room temperature to a benzene solution of maleic anhydride (29.4 g, 0.3 mole). The solution was stripped at reduced pressure to give a viscous, liquid residue. Acetic anhydride (100 ml) was added to the residue and the mixture was heated with stirring at 100° for 1 hr. The mixture was distilled to give a liquid distillate, bp 95° (20 mm), which solidified on standing. The product was recrystallized from isooctane and 13 g (31% yield) of bright yellow crystals, mp 81–82°, were obtained.[10]

Anal. Calcd for $C_6H_8N_2O_2$: C, 51.43; H, 5.71; N, 20.00. Found: C, 51.35; H, 5.56; N, 19.71.

The product whose infrared spectrum was as expected for a maleimide was neutral toward 0.1 *N* perchloric acid.

Pyrolysis of Dimethylaminourethan in the Presence of Benzaldehyde.—A mixture of dimethylaminourethan (33.0 g, 0.25 mole), benzaldehyde (26.5 g, 0.25 mole), and 5 drops of 85% phosphoric acid was heated at 190–200° for 16 hr. During this time alcohol (11.0 g, 95%), was collected and 5.5 l. of carbon dioxide was evolved. The residue was distilled to give 14.8 g of liquid distillate (40% yield), bp 58° (0.25 mm). The infrared spectrum of the distillate was identical in every respect with the spectrum of the hydrazone prepared from *unsym*-dimethylhydrazine and benzaldehyde.

When the pyrolysis of the urethan was conducted in the presence of cyclohexanone in a similar manner, 16.8 g (48% yield) of liquid, bp 68° (30 mm), was obtained which was identical with the hydrazone prepared from *unsym*-dimethylhydrazine and cyclohexanone.

In both of these reactions a small amount of residue remained. The infrared spectra of the residue indicated the presence of the triazole III.

Pyrolysis of Dimethylamino Isocyanate Dimer in the Presence of Cyclohexanone.—A mixture of the dimer (1.72 g, 0.01 mole) and cyclohexanone (1.96 g, 0.02 mole) was heated at 210 for 30 min. The residue was distilled to give 0.5 g (17% yield) of distillate, bp 180°, whose infrared spectrum was identical with that of the hydrazone prepared from *unsym*-dimethylhydrazine and cyclohexanone. A second fraction (1.0 g, 59% yield) was collected at reduced pressure, bp 190° (20 mm). The infrared spectrum of this second material was identical with that of the triazole III.

Registry No.—I, 10269-98-4; II, 10269-99-5; III, 10270-00-5; IV, 10270-01-6; V, 10270-02-7; VI, 10294-79-8; VIIa, 10270-03-8; VIIb, 10270-04-9; IX, 10270-05-0; X, 10270-06-1; XI, 10270-07-2; XII, 10270-08-3; XIV, 10270-09-4; XVI, 10270-10-7; XX, 10270-11-8; N-dimethyl-N′-*n*-butylurea, 10270-12-9; dimethylamino isocyanate, 10270-13-0.

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[10] H. A. Hageman and W. L. Hubbard, U. S. Patent 3,257,414 (June 21, 1966).