was adjusted to 8 with sodium bicarbonate, and it was extracted with chloroform (3 × 25 mL). The combined organic phase was dried and evaporated to give 98 mg, 98% yield, of a mixture of epimers in a ratio of 75/25 of (+)-pilocarpine (**1a**)/(+)-isopilocarpine (**1b**).

Separation of (+)-Pilocarpine (1a) and (+)-Isopilocarpine (1b). Separation of (+)-pilocarpine (**1a**) and (+)-isopilocarpine (**1b**) was carried out on a 50-mg scale by using a Whatman Partisil Magnum 9 preparative HPLC column, 10 × 50 cm; flow rate = 5.6 mL/min; λ = 215 nm; mobile phase; 0.6% NH_4OH, 30% isopropyl alcohol, 70% hexanes; volume of injections, 0.5 mL. The separated fractions were dried and evaporated resulting in diastereomerically pure materials with an efficiency of 98%.

3,4-Didehydropilocarpine (23). A solution of allylic alcohol **15** (330 mg, 1.2 mmol) in 4 mL of trifluoroacetic acid/water, 1/1, was stirred at room temperature for 2 h and then evaporated leaving a residue which was dissolved in 3 mL of saturated sodium bicarbonate and extracted with chloroform (3 × 3 mL). The combined organic phase was dried and evaporated to give 239 mg, 98% yield, of lactone **23**: ^{1}H NMR δ 1.12 (t, 3 H), 2.35 (q, 2 H), 3.55 (s, 3 H), 3.73 (s, 2 H), 4.55 (s, 2 H), 6.83 (s, 1 H), 7.45 (s, 1 H). Anal. Calcd for $C_{11}H_{14}N_2O_2$: C, 64.1; H, 6.8; N, 13.6. Found: C, 63.8; H, 7.0; N, 13.5.

(±)-Pilocarpine. A mixture of unsaturated lactone **23** (205 mg, 1 mmol) and 150 mg of 10% Pd/C in 100 mL of methanol was shaken at 50 psi of hydrogen for 24 h. The mixture was filtered, the catalyst was washed with 20 mL of warm methanol, and the filtrate and washing were combined and evaporated to give 202 mg, 98% yield, of (±)-pilocarpine as a colorless oil: ^{1}H NMR δ 1.08 (t, 3 H), 1.53 (m, 1 H), 1.83 (m, 1 H), 2.18 (dd, 1 H), 2.60 (m, 2 H), 2.80 (m, 1 H), 3.55 (s, 3 H), 4.05 (dd, 1 H), 4.15 (dd, 1 H), 6.75 (s, 1 H), 7.40 (s, 1 H).

Acknowledgment. We are indebted to Mark Distefano for preparing some of the starting materials and to John O'Connell for obtaining the NOESY spectrum.

The Photolysis of Carbamoyl Azides in the Presence of Carbodiimides

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Received September 23, 1985

The photolysis of some *N,N*-dialkylcarbamoyl azides in the presence of carbodiimides gives two types of products: cyclic ammonio amates **1** (from *N,N*-dialkylamino isocyanates, formed by a photo-Curtius rearrangement of the azides) and five-membered mesoinoic 5-(dialkylamino)-1,2,4-triazoles **7**, the structure of which was confirmed by independent synthesis. The formation of **7** constitutes a novel reaction path of carbamoyl azides.

Dialkylcarbamoyl azides undergo photo-Curtius rearrangement to give transient *N,N*-dialkylamino isocyanates, which can be isolated in a matrix[1] or react in various ways[2] such as by adding nucleophiles[3] or heterocumulenes such as isocyanates,[4-6] isothiocyanates,[6,7] carbodiimides,[5] or acetylenes.[8] In an earlier short communication[5] we mentioned the formation of two isomeric products from the photolysis of carbamoyl azides in the presence of carbodiimides. The major isomer was assigned the structure **1**, analogous to that of other amino isocyanate–heterocumulene adducts. We shall show here that this is correct. The minor isomer was earlier[5] assigned structure **2**, which is not correct. Proof for its having the structure **7** is given below.

Results and Discussion

Solutions of dialkylcarbamoyl azides in diethyl- or diisopropylcarbodiimide, with or without dichloromethane diluent, were photolyzed to give mixtures of two isomers. Their ratio was not very reproducible from run to run and appears not to depend much on concentration (over a range of 1.3 mol % in dichloromethane to pure carbodiimide), temperature, or wavelength (300 or 254 nm). By NMR, the ratio was found to be between 1.5 and 1.9. Isolation always involved losses of the minor isomer, giving apparent ratios of 2.8 to 3.3 of the pure isomers. Separation of the mixture requires great care, because mixtures and the pure minor isomers are very hygroscopic. The NMR spectra of both isomers show all four alkyl groups to be unchanged and still attached to nitrogen. The mass spectra indicate that both isomers are monomeric 1:1 adducts. The infrared spectra of **1** show high frequency bands in the carbonyl region, such as 1790 cm^{-1} for **1a** (R = Me, R′ = *i*-Pr), whose minor isomer has the highest C=X band at 1662 cm^{-1}. Dialkylamino isocyanate generated thermally in the presence of carbodiimides did not produce any minor isomers—these were formed exclusively by photolysis of systems containing both dialkylcarbamoyl azide and carbodiimide. The two isomers could not be interconverted by photolysis or any other means tried. Conclusive structure proof is given below for **1**—for which details have not yet been published—and for the lesser isomers (**7**).

The Structure of Isomers 1. Isomers **1** are five-membered cyclic ammonio amates, analogous to those already described,[4-8] with an imino group in position 5. Like the former, they revert to the starting materials upon heating and by photolysis. Isomer **1a** (R = Me, R′ = *i*-Pr) was completely destroyed in 2 min at 212 °C. Thermolysis and photolysis of **1a** in dilute solution gave the dimer of

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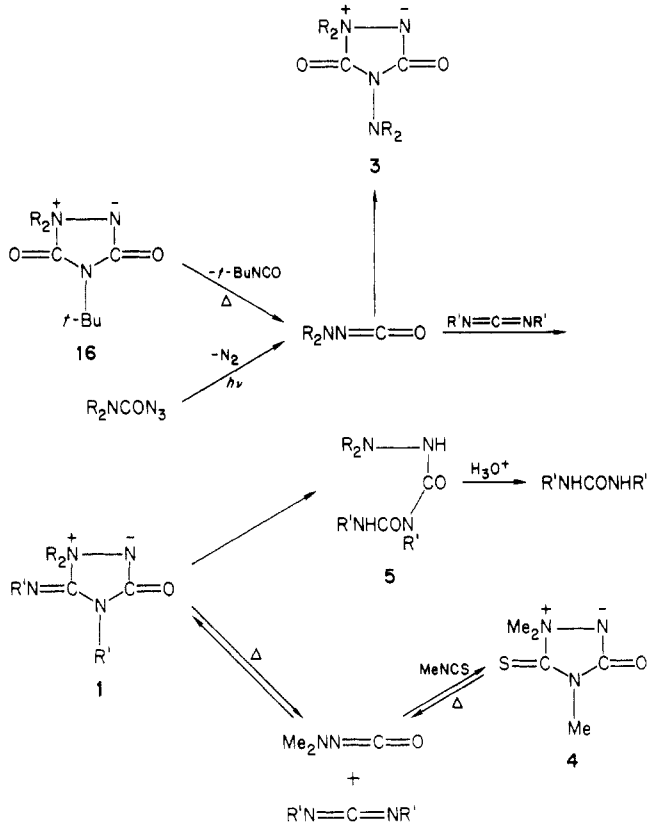
Scheme I. Formation and Reactions of the Major Isomers from Carbamoyl Azides and Carbodiimides



dimethylamino isocyanate **3** and diisopropylcarbodiimide. The dimethylamino isocyanate formed in the thermolysis could be trapped by methyl isothiocyanate[6] to give **4** (Scheme I). Acid hydrolysis of **1a** gave 4-[(isopropylamino)carbonyl]-4-isopropyl-1,1-dimethylsemicarbazide (**5**) and 1,3-diisopropylurea, confirming the sequence of atoms. Base hydrolysis also gave 1,3-diisopropylurea. Alkylation or acylation of our ammonio amates occurs on N-2 and the carbonyl oxygen (position 3) conjugated with it,[7] followed by removal of one of the alkyl groups on N-1, through nucleophilic attack by halide ion.[7,8] Accordingly, a small sample of **1a** reacted vigorously with benzoyl chloride, to give a product mixture with a NMR spectrum in which the ratio of integrals, *N*-methyl to isopropyl methyl, had changed to 1:4 from 2:4. Furthermore, the mass spectrum of **1a** shows a prominent loss of *i*-PrNCO, absent in that of its isomer. The mass spectral cracking pattern of the major isomers is in complete agreement with the assigned structure.

The Structure of the Minor Isomers. The reactivity of the minor isomers differs drastically from those of the major ones. Heating **7a** (R = Me, R′ = *i*-Pr) neat to 212 °C for 10 min did not change it. No reversion to starting materials occurs upon photolysis, the compounds are recovered. They are rather stable toward aqueous acid and base and resist catalytic hydrogenation. Hydrolysis of **7a** (R = Me, R′ = *r*-Pr) and **7b** (R = Me, R′ = Et) with 12% aqueous sodium hydroxide for 13 h at 90 °C gave dimethylamine and 1,4-dialkylurazoles **6**, indicating an exocyclic dialkylamino group, originating with the carbamoyl azide (Scheme II). This fits the mesoionic structure **7**, but structure **8** also seemed possible. Mesoionic **7** is particularly appealing, since there is a simple photochemical reaction path leading to it. Benzyne addition to a member of this particular mesoionic system, anhydro-3-hydroxy-1,4-diphenyl-1,2,4-triazolium hydroxide, is known.[9] With the minor isomer from dimethylcarbamoyl azide and diisopropylcarbodiimide, benzyne gave a 31% yield of 2-isopropyl-3-(dimethylamino)indazole (**9**) readily explained by benzyne addition to **7a**, followed by elimination of isopropyl isocyanate. For positive structure proof, we synthesized both **7** and **8**.

Synthesis of 8 (Scheme III). 1,1-Dimethyl-3-isopropylurea (**10**), made from isopropylamine and dimethylcarbamoyl chloride in 96% yield, was treated with phosgene to give 1,1-dimethyl-2-chloro-3-isopropylformamidine (**11**). This, with isopropylhydrazine, gave a 65% yield of **12**. The structure of **12** was ascertained by treating it with benzaldehyde, to give a 95% yield of 1,4-diisopropyl-3-(dimethylamino)-5-phenyl-5*H*-1,2,4-triazoline, which showed no NH in its IR spectrum and the ^{1}H NMR splitting expected. Thus, the isopropylhydrazine had reacted at the terminal N. Treating **12** with phosgene and base gave 1,4-diisopropyl-3-(dimethylamino)-1,2,4-triazol-5-one (**8**), which turned out to be completely different from the minor isomer **7a**.

Synthesis of 7. Isopropylideneisopropylhydrazine reacted with 1,1-dimethyl-2-chloro-3-isopropylformamidine hydrochloride (**11**) and base to give a 92% yield of **13**, which could be hydrolyzed by acid to **14**, which gave back **13** when treated with acetone and acid. Treating **14** with phosgene should convert it to the amino isocyanate **15**, expected to cyclize to **7**.[10] This was indeed observed, and the mesoionic triazole **7a** (R = Me, R′ = *i*-Pr) was identical in all respects with the minor isomer from dimethylcarbamoyl azide and diisopropylcarbodiimide.

The mass spectra of 1, 7, and **8** correlate well with the assigned structures. All three classes show prominent parent peaks, at 70 eV nominal ionization voltage. The ammonio amate's **1** most important fragmentation is the loss of R_2NNCO, second most important is the loss of R′NCO, i.e., the 3-C=O together with 4-NR′. Loss of the alkene corresponding to R′ depends on the nature of R′ and is much more prominent with R′ = *i*-Pr than with R′ = Et. The mesoionic **7** conforms to Ollis' findings,[14] in our case the loss of R′NNCO and the formation of the ion R_2NCNR', followed by loss of the olefin corresponding to R. Metastable ion peaks confirm this fragmentation course. In the case of **7a**, successive loss of two propene molecules is seen (212–170* – 128*), to give the base peak of *m/e* 128. With R′ = Et, the successive loss of two ethylenes becomes less prominent. Loss of methyl from **7a** and **7b** is the first step of the third ranking fragmentation. The triazolone **8** has as the most important fragmentations the successive loss of two propene molecules, as has **7a**. Loss of R′NNCO·, to give *i*-PrNCNMe$_2^+$ and the loss of propene to give $HNCNMe_2$ is clearly seen, but is less important than in **7a**.

Mechanisms of Formation of 7a. Earlier work[1,3,12] indicates that dialkylcarbamoyl azides do not give carbamoylnitrenes upon photolysis (while arylcarbamoyl azides may[2]). A search for nitrene trapping products in photolyses of dialkylcarbamoyl azides[12] did not show any nitrene products, using cyclohexane, cyclohexene, acetonitrile, and methanol as traps. For this reason, and by analogy with

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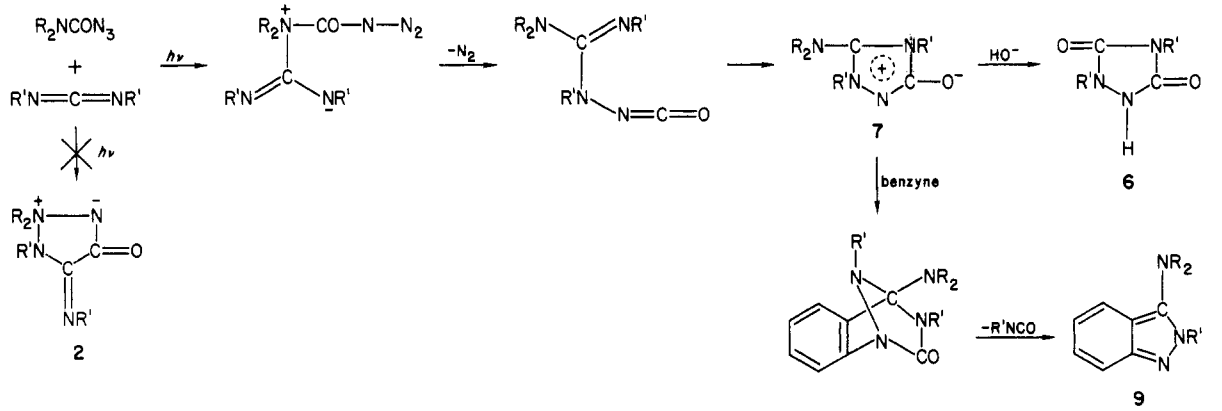
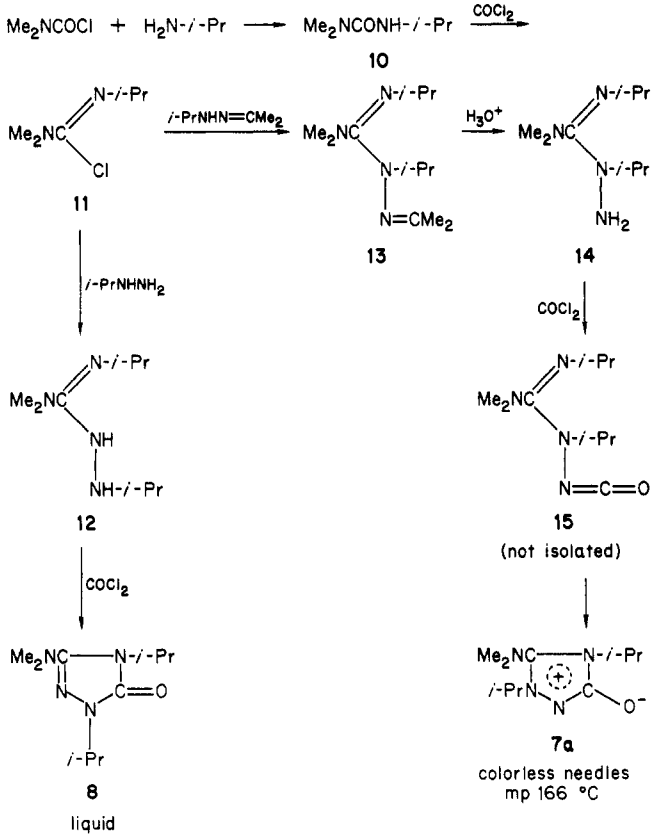
Scheme II. Formation and Reactions of the Minor Isomers from Carbamoyl Azides and Carbodiimides



Scheme III. Synthesis of the Isomers 7a and 8



other carbonyl azides,[15] we believe the rearrangement to dialkylamino isocyanates to be concerted. Dialkylamino isocyanates add to carbodiimides to give 1 exclusively (93% yield for **1a**, using thermally generated Et_2NNCO), and the photo-Curtius rearrangement of dialkylcarbamoyl azides usually gives high yields of amino isocyanate. Thus, any proposed mechanism for the formation of **7** must explain (a) the observed need for the photoreaction, (b) the lack of sensitivity to azide concentration, (c) the lack of interconvertibility of the two products, and (d) the necessity of using the azide rather than the amino isocyanate. (Amino isocyanate and carbodiimide are present in irradiated solutions of **1**, but the minor isomer is not produced, see above). Some kind of common intermediate is required to explain the lack of concentration dependence of the product isomer ratio. Since thermal reactions do not produce the minor isomers (but only thermolysis products of the major ones), an azide–carbodiimide exiplex is an attractive assumption. In this hypothesis, only the exiplex is formed, with partitions between nitrogen plus amino isocyanate and carbodiimide in one path and formation of **13** in the other. We have no spectral evidence for the exiplex, but consider it a reasonable intermediate.

The use of methyl or ethyl isocyanates with ethyl- or isopropylcarbodiimides gives both isomers. Di-*tert*-butylcarbodiimide and *N*-*tert*-butyl-*N'*-(ethoxycarbonyl)-carbodiimide did not give either isomer, presumably because of steric hindrance and the amide resonance of the ester group, respectively.

Experimental Section

General. Proton NMR spectra were taken with a JEOL PS-100 or a Varian XL-200 spectrometer. ^1H and ^{13}C NMR shifts are reported in units of ppm, downfield from Me_4Si, in $CDCl_3$ unless stated otherwise. Assignments of ^{13}C signals were confirmed by APT or off-resonance decoupled spectra. ^{15}N chemical shifts are in ppm from external nitromethane; negative numbers are upfield from $MeNO_2$. Both the reference nitromethane and the sample (usually in $CDCl_3$) contained 0.07 M chromium(III) 2,4-pentanedioate. Control experiments showed that its presence did not affect signal positions. Pulses (10^5–10^6) of 8 μs and 0.8-s acquisition time were employed. Several seconds between pulses were required if $Cr(acac)_3$ was not used. Perkin-Elmer Models 621 and 283 and Cary 14 spectrometers were used for IR and UV spectra. Melting points are uncorrected. Mass spectra were taken on a Hitachi RMU-6 instrument, using 70 eV nominal ionization voltage. Metastable peaks are denoted m*.

Photolyses of Carbamoyl Azides in the Presence of Carbodiimides. Irradiations were performed in Rayonet photochemical reactors, using fluorescent UV lamps with a maximum emission at 300 nm. Silica photolysis tubes were suspended in the center of the reactor and contained axial cooling fingers, through which glycol–water mixtures at −10 °C were pumped. The tubes were filled to 26 cm, the length of the 16 UV lamps surrounding them. Typically, mixtures of the azide and a fivefold molar quantity of carbodiimide were diluted with enough dichloromethane to fill to 26 cm. Photolyses were terminated when nitrogen evolution became slow, usually due to coloration developing during the photolyses. This was usually at about 50–70% of the theoretical nitrogen evolution. The **photolysis of dimethylcarbamoyl azide in the presence of diethylcarbodiimide** provides an example. Dimethylcarbamoyl azide (2.18 g, 19 mmol) and diethylcarbodiimide (10g, 106 mmol) and 70 mL of dichloromethane were irradiated for 34 h to 75% of the theoretical N_2 volume and 24 h longer for another 11% of nitrogen yield. Solvent and unreacted starting materials were evaporated in vacuo, to leave 4.42 g of residue, kept at 1 mm of pressure over night. Separation on 240 g of silica gel (Baker, 60–200 mesh, 5-3405) with a 20:25:20:35 mixture of methanol, ethyl acetate, petroleum ether, and chloroform gave first some impurities, then **1b** (R = Me, R' = *i*-Pr) in fractions of 250–500 mL, then **1b** and

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carbodiimide (500–660 mL) and then **7b** (1500–2300 mL), to obtain 890 mg (28%) of **1b** and 550 mg (17%) of **7b**. This 45% total yield (based on nitrogen evolved) reflects separation losses. Typical yields product mixtures are about 75%, as determined by NMR spectroscopy with chlorobenzene as an internal standard. **7b** is very hygroscopic and becomes an oil when exposed to the atmosphere for only 5 min; **1b** is also hygroscopic. Final recrystallization from 400 parts of anhydrous ether or benzene–ether had to be done in a glovebox.

1,1-Dimethyl-4-ethyl-5-(ethylimino)-3-oxo-1,2,4-triazolidinium hydroxide inner salt (1b): 28% yield; mp 100–101 °C; ^{1}H NMR 1.28 (s, 6 H), 3.22 (s, 6 H), 3.73 (q, 4 H); IR (prominent absorptions) 1760, 1742, 1680 cm^{-1}. Anal. Calcd for $C_8H_{16}N_4O$: C, 52.15; H, 8.75; N, 30.41. Found: C, 52.27; H, 9.16; N, 30.51.

Anhydro-3-hydroxy-1,4-diethyl-5-(dimethylamino)-1,2,4-triazolium hydroxide (7b): 17% yield; mp 84–86 °C; ^{1}H NMR 1.35 (t, 3 H), 1.43 (t, 3 H), 2.94 (s, 6 H), 3.73 (2 q, 4 H); IR 1660, 1205 cm^{-1}. Anal. Calcd for $C_8H_{16}N_4O$: C, 52.15; H, 8.75; N, 30.41. Found: C, 52.39; H, 8.49; N, 30.20.

Analogously prepared were the following.

1,1-Dimethyl-4-isopropyl-5-(isopropylimino)-3-oxo-1,2,4-triazolidinium hydroxide inner salt (1a): 39% yield; mp 141–143 °C; IR (KBr) 1790, 1743, 1650 cm^{-1}; UV (CH_2Cl_2) 254 nm (363); ^{1}H NMR 1.20 (d, 6 H), 1.52 (d, 6 H), 3.25 (s, 6 H), 4.12 (m, 1 H), 4.38 (m, 1 H); ^{13}C NMR (*i*-Pr) 20.58, 24.75, 46.89, 46.77, (NMe) 55.62, (ring sp^2) 144.24, 160.99; ^{15}N NMR −431.4 (presumably N$^-$), −266.6 (perhaps *i*-PrN=), −250.1, −167.2. Anal. Calcd for $C_{10}H_{20}N_4O$: C, 56.58; H, 9.50; N, 26.39. Found: C, 56.57; H, 9.15; N, 26.39.

Anhydro-3-hydroxy-1,4-diisopropyl-5-(dimethylamino)-1,2,4-triazolium hydroxide (7a): 14% yield; mp 166–167 °C; IR 1655, 1210 cm^{-1}; UV 252 nm (4800); ^{1}H NMR 1.44 (d, 6 H), 1.55 (d, 6 H), 2.87 (s, 6 H), 4.24 (m, 1 H), 4.31 (m, 1 H); ^{13}C NMR (*i*-Pr) 20.23, 20.39, 46.30, 50.18, (NMe) 41.76, (ring sp^2) 144.9, 158.8; ^{15}N NMR (Me_2N) −376.7, (ring N) −219.6, −180.9, −164.3. Anal. Calcd for $C_{10}H_{20}N_4O$: C, 56.58; H, 9.50; N, 26.39. Found: C, 56.40; H, 9.80; N, 26.85.

1,1-Diethyl-4-isopropyl-5-(isopropylimino)-3-oxo-1,2,4-triazolidinium hydroxide inner salt (1d): 33% yield; mp 99 °C; IR ($CHCl_3$) 1740, 1670 cm^{-1}; ^{1}H NMR 1.19 (t, 6 H), 1.21 (d, 6 H), 1.49 (d, 6 H), 3.29 and 3.45 (2 q, 4 H), 4.13 and 4.41 (2 m, 2 H).

Anhydro-3-hydroxy-1,4-diisopropyl-5-(diethylamino)-1,2,4-triazolium hydroxide (7d): 12% yield; mp 168–171 °C; IR ($CHCl_3$) 1650 cm^{-1}; ^{1}H NMR 1.11 (t, 6 H), 1.42 (d, 6 H), 1.58 (d, 6 H), 3.12 (q, 4 H), 4.10 and 4.41 (2 m, 2 H).

1,1,4-Triethyl-5-(ethylimino)-3-oxo-1,2,4-triazolium hydroxide inner salt (1c) was prepared by using 254-nm light and tituration of the residue with ether to give a 37% yield of **1c**: mp 88–89 °C; IR 1730 (s), 1680 (vs) cm^{-1}; ^{1}H NMR, overlapping triplets between 1 and 1.3 ppm and overlapping quartets apparently centered at 3.8, 3.47, and 3.34 ppm, integral ratio of the triplet and the quartet region s, 3:2. Anal. Calcd for $C_{10}H_{20}N_4O$: C, 56.58; H, 9.50; N, 26.39. Found: C, 56.53; H, 9.57; N, 26.16. **7c** was not detected in this experiment but probably was formed.

Preparation of 1a by a Thermal Route. 1,1-Dimethyl-4-*tert*-butyl-3,5-dioxo-1,2,4-triazolidinium hydroxide inner salt (16)[6] (556 mg, 3 mmol) and 15 mL of diisopropylcarbodiimide were heated to 96 °C for 1 h. Recrystallization from small amounts of warm chloroform gave 595 mg (2.8 mmol, a 93% yield) of **1a**, and none of its isomer **7a**, as shown by examining the ^{1}H NMR spectrum of the reaction mixture before recrystallization.

Chemistry of the Ammonio Amates 1. Thermolysis of 1a in the Presence of Methyl Isothiocyanate. **1a** (2.12 g, 10 mmol) was heated with a fivefold excess of methyl isothiocyanate in 50 mL of benzene for 2.5 h at reflux, to give 1.46 g (91% yield) of **4**, mp 150–151 °C, together with some **1a**. To demonstrate the existence of an equilibrium of the aminimides and their components (Scheme I), 20 mg of **4** was heated with in few drops of diisopropylcarbodiimide in refluxing benzene for 90 min. The IR spectrum of the residue showed it to be a mixture of **1a** and **4**. **Authentic 4** was prepared[7] by heating 1,1-dimethyl-4-*tert*-butyl-3,5-dioxo-1,2,4-triazolidiniumum hydroxide inner salt **16** (5.55 g, 30 mmol) and methyl isothiocyanate (6.57 g, 90 mmol) in 25 mL of refluxing benzene for 3 h to give 4.1 g of **4**, mp 146–148 °C, a 86% yield. Crystallization from chloroform–hexane gave material of mp 149 °C. Anal. Calcd for $C_5H_9N_3SO$: C, 37.72; H, 5.70; N, 26.38; S, 20.13. Found: C, 37.97; H, 5.77; N, 26.05; S, 20.28. ^{1}H NMR 3.42 (6), 3.38 (3); IR 1710, 1550, 1460, 1450 cm^{-1}. Metastable peaks in the mass spectrum indicated the loss of MeNCO and MeNCS from the parent molecule.

Hydrolysis of 1a. (a) Acid Hydrolysis. **1a** (0.5 g) in 2 mL of water and 0.5 mL of concentrated HCl were kept at room temperature for 6 days, while the progress of the hydrolysis was followed by ^{1}H NMR spectroscopy. An intermediate, presumably **5**, built up to a maximum concentration after 5 h and then decayed. After 6 days, the solution was neutralized and extracted with chloroform. *N,N'*-Diisopropyl urea (0.17 g, 50%), mp 191–192 °C (lit.[11] mp 192 °C) was isolated by crystallization from isopropyl alcohol–petroleum ether and identified by its mass, IR, and NMR spectra. GLC of the residue of the mother liquor, on a 1-m cyanosilicone column at 110 °C gave *N*-isopropyl-2,2-dimethylhydrazinecarboxamide, mp 65–67 °C, identical with authentic material made from isopropyl isocyanate and 1,1-dimethylhydrazine, mp 67–69 °C (hexane).

(b) Base Hydrolysis. **1a** (2.1 g, 10 mmol) and 20 mL of 10% aqueous sodium hydroxide were heated to reflux for 16 h. The neutralized solution was extracted four times with chloroform to give 1.11 g (77%) of *N,N'*-diisopropylurea, mp 192 °C (lit.[11] mp 192 °C).

Chemistry of the Minor Isomers 7. Thermolysis. Isomer **7a** (R = Me, R' = *i*-Pr) (10 mg) was heated in an NMR tube to 212 °C for 10 min. The ^{1}H NMR spectrum showed the presence of unchanged material only. Attempted **catalytic hydrogenation** (Parr hydrogenator, methanol, 40 psi, with Pd or Pt on alumina) did not change the material either. (A) **Acid hydrolysis** with HCl gas in dry chloroform **7a** gave a solid hydrochloride, mp 173–175 (dec), which was quite hygroscopic. **7a** (250 mg) in 0.5 mL of 17% hydrochloric acid did not change during 7 days at room temperature or 2 h of reflux and was recovered. **Alkaline hydrolysis** of **7a** (212 mg, 10 mmol) with 600 mg of NaOH in 5 mL of water for 13.5 h at 82 °C, followed by neutralization and extraction with chloroform, gave a quantitative yield of 1,4-diisopropylurazole (**6**, R = *i*-Pr), mp 89–90 °C, recrystallized from propanol–hexane, mp 90.5–91.5 °C. Anal. Calcd for $C_8H_{15}N_3O_2$: C, 51.88; H, 8.16; N, 22.68. Found: C, 52.16; H, 7.89; N, 22.89.

(B) Isomer **7b** (R = Me, R' = Et) (200 mg) was heated with 5 mL of 12% sodium hydroxide for 2.25 h. After neutralization and chloroform extraction, 100 mg (58%) of crude 1,4-diethylurazole (**6**, R = Et) was obatined. Chromatography on a silica column with chloroform as the eluent gave pure product, mp 43–44 °C (from ether–hexane). It was identical with authentic material obtained (a) by the pyrolysis of 1,1,4-triethyl-3,5-dioxo-1,2,4-triazolidinium hydroxide inner salt[3] and (b) by synthesis from urazole and diazomethane:[12] To a solution of 128 mmol of diazomethane in 300 mL of ether was added 3.2 g (31.6 mmol) of urazole. After 12 h at −20 °C, 0.68 g of unreacted urazole was filtered. Vacuum distillation gave a fraction [bp 95–97 °C (1.8 mmHg), 4.53 g] which showed no NH absorption in its IR spectrum. Purification by GLC on a QF-1-0065 flurosilicone column at 135 °C gave pure material. The ^{1}H NMR spectrum showed OCH_2 at 4.32 ppm (2 H, q) and NCH_2 at 3.6 ppm (3.9 H, m); the IR spectrum (CCl_4) showed strong absorptions at 1720 and 1605 cm^{-1}, as expected for **1,4-diethyl-3-ethoxy-1,2,4-triazol-5-one (17)**. Anal. Calcd for $C_8H_{15}N_3O_2$: C, 51.88; H, 8.16; N, 22.68. Found: C, 51.83; H, 8.05; N, 22.67. **17** (0.128 g, 0.69 mmol) was heated with 10 drops of concentrated hydrochloric acid to 110 °C for 30 min. Neutralization and extraction with ether gave 1,4-diethylurazole (**6**, R = Et) (76 mg, 70% yield), identical with that prepared by pyrolysis of **3** (R = R' = Et)[5] and of proper analysis. Anal. Calcd for $C_6H_{11}N_3O_2$: C, 45.85; H, 7.00; N, 26.75. Found: C, 45.79; H, 7.18; N, 26.85. ^{1}H NMR 3.55 (m, 3.8 H), 1.24 (t, 6.0), (NH) 9.4 (br, 0.6 H); IR (CCl_4) 3165 and 3080 (br), 1760 (s), 1680 (s) cm^{-1}.

Benzyne Addition to 7a. 2-Isopropyl-3-(dimethylamino)indazole (9). To a solution of 636 mg (3 mmol) of **7a** in 15 mL of 1,2-dichloroethane at 60 °C was added in portions a suspension benzenediazonium 2-carboxylate (1.2 g, 8.1 mmol) in 15 mL of dichloromethane. After the gas evolution had subsided, the solvent was removed and the dark residue dissolved in ether and filtered. Dry HCl deposited a dark oil. It was washed with ether, 30% cold aqueous sodium hydroxide was added, and the

mixture was extracted with benzene. Chromatography on neutral alumina with benzene gave a pale yellow liquid (0.19 g 31%), almost pure. The hydrochloride was recrystallized from 2-propanol, to give colorless needles of **2-isopropyl-3-(dimethylamino)indazole hydrochloride (9·HCl)**; mp 169.5–171 °C. Anal. Calcd for $C_{12}H_{18}N_3Cl$: C, 60.12; H, 7.57; N, 17.53. Found: C, 59.95; H, 7.60; N, 17.53. **9**: ^1H NMR 1.85 (d, J = 7 Hz, 6 H), 3.24 (s, 6 H), 4.98 (m, 1 H), 7.24 (t, 1 H J = 8 Hz), 7.60 (t, 1 H J = 8 Hz), 7.88 (d, 1 H, J = 8 Hz), 7.96 (d 1 H J = 7 Hz); mass spectrum, m/z (relative intensity) 203 (parent peak m, 92), 188 (M – Me, 19), 161 (M – 42, 100), 160 (M – i-Pr and/or H_2C=NMe, 44), and others.

Synthesis of 1,4-Diisopropyl-3-(dimethylamino)-1,2,4-triazol-5-one (8) (Scheme III). 1,1-Dimethyl-3-isopropylurea (10) was prepared by adding dropwise 60 g (1 mol) of isopropylamine in 100 mL of dry CH_2Cl_2 to a cooled solution of 43 g (0.4mol) of dimethylcarbamoyl chloride in 50 mL of CH_2Cl_2. After 1 h at room temperature the solvent was evaporated and the residue boiled with 500 mL of benzene. Isopropylammonium chloride was removed by filtration of the hot solution, the filtrate evaporated, and the residue recrystallized from a 1:1 mixture of benzene and hexane, to yield colorless needles, mp 110–111 °C, 50 g (96%). Anal. Calcd for $C_6H_{14}N_2O$: C, 55.35; H, 10.84; N, 21.52. Found: C, 55.16; H, 11.13; N, 21.80. ^1H NMR 1.16 (d, J = 6 Hz, 6 H), 2.89 (s, 6 H), 3.99 (m, 1 H), 4.26 (1 H, br); IR (KBr) 1610 (C=O) cm^{-1}; mass spectrum (70 eV), m/z (relative intensity) 130 (M^+, 34), 115 (M^+ – Me, 12) 72 (M^+ – i-Pr, 97), 44 ($^+NMe_2$, 100).

***N,N*-Dimethyl-*N'*-isopropylchloroformamidinium Hydrochloride (11).** Phosgene (6.0 g, 60 mmol) in 20 mL of dry THF was added at 0 °C to a solution of 6.5 g (50 mmol) of **10** in 20 mL of THF, at a rate at which CO_2 evolution was moderate. After 1.5 h at room temperature, the clear solution was evaporated and cooled in ice. Filtration and several washings with dry ether gave a colorless solid: mp 73–76 **C**; 99% yield (9.2 g); ^1H NMR (CF_3COOH) 1.43 (6 H, d, J = 6 Hz), 3.36 (6 H, s), 4.28 (1 H, m), 7.7 (1 H, br); IR (neat) 3200–2700 (br), 1630 (vs). This hydrochloride is very hygroscopic and unstable. For use in the subsequent reactions, excess phosgene and solvent were removed in vacuo, and the residue was employed while fresh.

***N,N*-Dimethyl-*N''*-isopropyl-*N'*-(isopropylamino)-guanidine (12).** The chloroform–amidinium chloride **11** from 13 g (0.1 mol) of the urea **10** dissolved in 50 mL of dichloromethane was added dropwise at 0 °C to a mixture of triethylamine (20 g, 0.2 mol) and isopropylhydrazine[13] (8 g, 0.11 mol) in 150 mL of dichloromethane. After 1.5 h at reflux, the triethylammonium hydrochloride was filtered off and the solution evaporated. Treating the residue with a concentrated, cold sodium hydroxide solution, extracting with ether, and distilling at 5 mmHg gave a fraction with bp 75–76 °C (12 g, 65%). It is very sensitive to air, turning deep orange on exposure, and must be kept in ampules under nitrogen: ^1H NMR 1.00 (6 H, d, J = 7 Hz), 1.10 (6 H, d, J = 7 Hz), 2.70 (6 H, s), near 3.1 (2 H, m and br, [NH], 3.50 (1 H, m) and 5.5 (1 H, br); IR (neat) 3275 (br), 1605 (s) cm^{-1}; mass spectrum (70 eV); m/z (relative intensity) 186 (M^+, 54), 128 (M^+ – i-Pr, 10), 71 (100). Anal. Calcd. for $C_9N_{22}N_4$: C, 58.02; H, 11.90, N 30.07. Found: C, 57.66, H, 12.07, N, 30.39.

3-(Dimethylamino)-1,4-diisopropyl-1,2,4-triazol-5-one (8). Phosgene was passed through 1.86 g (10 mmol) of **12** and 2 g (20 mmol) of triethylamine in 20 mL of benzene at 0 °C for 5 min. After evaporation, the residue was treated with aqueous potassium hydroxide and extracted with benzene. Removal of benzene and triethylamine in vacuo gave a liquid, which was chromatographed on basic alumina with hexane to give 0.63 g (30% yield) of a colorless liquid: ^1H NMR 1.30 (6 H, d, J = 7 Hz), 1.50 (6 H, d, J = 7 Hz), 2.70 (6 H, s), 4.12 (1 H, m), 4.41 (1 H, m); IR (neat) 2970, 2875, 2800, 1685, 1575, 1410, 1340, 1260, 1240, 1210, 1130, 1095, 1040, 955, 885, 830 cm^{-1}; mass spectrum, m/z (relative intensity) 212 (M^+, 42), 170 (M^+ – H_3CC=CH_2, 67, m* = 136.3), 155 (170 – Me, 30, m* = 141.3), 128 (170 – H_3CCH=CH_2, 100, m* = 96.4), 99 (128 – 29, 21, m* = 76.6). A sample was purified for analysis by GLC on a 2-m QF1 column at 140 °C. Anal. Calcd for $C_{10}H_{20}N_4O$: C, 56.58; H, 9.50; N, 26.39. Found: C, 56.70; H, 9.30; N, 26.46.

Attempted Base Hydrolysis of 8. The 5-(dimethylamino)-triazolone **8** (212 mg, 1 mmol) was heated with 5 mL of 12% aqueous sodium hydroxide to 80–83 °C for 10 h. Of the starting material, 195 mg (92%) was recovered unchanged.

Synthesis of the Minor Isomer 7a (Scheme III). Anhydro-2,4-diisopropyl-5-(dimethylamino)-3-hydroxy-1,2,4-triazolium Hydroxide (7a). *N,N*-Dimethyl-*N',N''*-diisopropyl-*N'*-(isopropylideneamino)guanidine (13). Isopropylideneisopropylhydrazine[13] (23 g, 0.3 mol) and triethylamine (40 g, 0.4 mol) in 150 mL of dry dichloromethane was added dropwise to the chloroformamidinium chloride **11** from 26 g (0.2 mol) of **10**. The mixture was kept at reflux for 1.5 h, concentrated to half its volume, cooled in an ice bath, and diluted with 200 mL of ether. Triethylammonium chloride was separated, filtered, and washed with ether. The colorless residue from the ether solutions was treated with 40% aqueous KOH, with cooling, to give a yellow liquid, bp 80–82 °C (3.8 mmHg). Chromatography, in hexane, on a short column of basic alumina and distillation gave a liquid: bp 75–76 °C (3.5 mmHg); 38 g (92% based on **10**); ^1H NMR 0.97 (6 H, d, J = 7 Hz), 1.20 (6 H, d, J = 7 Hz), 1.64 (3 H, s), 1.95 (3 H, s), 2.81 (6 H, s), 3.37 (1 H, m), 3.51 (1 H, m); IR (neat) 2960, 2925, 2865, 1610 (s) cm^{-1}, and others; mass spectrum (70 eV); m/z (relative intensity) 226 (M^+, 3), 211 (M^+ – Me, 13), 113 (M^+ – i-PrNN=CMe_2 and/or Me_2NC=NiPr, 42), 71 (113 – H_3CCH=CH_2, 100, m* = 44.6). Anal. Calcd for $C_{12}H_{26}N_4$: C, 63.67; H, 11.58; N, 24.75. Found: C, 63.39; H, 11.32; N, 24.49.

***N*-Amino-*N',N'*-dimethyl-*N,N''*-diisopropylguanidine (14).** The hydrazone **13** (38 g, 0.17 mol) was treated with 190 mL of 18% hydrochloric acid with ice cooling and then heated to 80 °C for 8 h. The ice-cooled solution was made alkaline, and the colored oil on the top was dissolved in ether. Drying and distillation [bp 75–78 °C (7 mmHg)] gave almost colorless **14** (30 g, 96%): ^1H NMR (CCl_4) 1.00 (6 H, d, J = 7 Hz), 1.02 (6 H, d, J = 7 Hz), 2.68 (6 H, s), 3.14 (1 H, m), 3.60 (1 H, m), 3.63 (2 H, br); IR (neat, CCl_4) 3330, 2930–2870, 1610 (s) cm^{-1}; mass spectrum (70 eV), m/z (relative intensity) 186 (M^+, 6), 170 (M^+ – NH_2, 7, m* = 155.4), 113 (M^+ – i-$PrNNH_2$, 23, m* = 68.7) 71 (113 – $MeCH$=CH_2, 100, m* = 44.6). Anal. Calcd for $C_9H_{22}N_4$: C, 58.02; H, 11.90; N, 30.07. Found: C, 57.70; H, 11.66; N, 29.70.

Anhydro-2,4-diisopropyl-5-(dimethylamino)-3-hydroxy-1,2,4-triazolium Hydroxide (7a). Phosgene was passed through a solution of the aminoguanidine **14** (12 g, 65 mmol) in 50 mL of benzene at 60 °C for 20 min. The residue left by evaporating the benzene was treated with 40% aqueous sodium hydroxide and the organic matter dissolved in dichloromethane at 0 °C. Drying with magnesium sulfate and evaporation in vacuo gave a viscous residue, which solidified when treated with petroleum ether. Recrystallization from benzene–hexane gave colorless needles of **7a**, mp. 166–166.5 °C, 12.2 g (89%). The material was identical in all respects with the minor isomer obtained from the photolysis of dimethylcarbamoyl azide in the presence of diisopropyl carbodiimide.

Acknowledgment. We are grateful for support of some of this work by the NIH (Grant CA12816) and by Hoffmann-La Roche Inc., Nutely, NJ.

Registry No. **1a**, 32515-30-3; **1b**, 32418-50-1; **1c**, 32418-51-2; **1d**, 101518-27-8; **4**, 55052-36-3; **6** (R = Pr-*i*), 101518-30-3; **6** (R = Et), 39636-12-9; **7a**, 101518-26-7; **7a**·HCl, 101518-38-1; **7b**, 101518-25-6; **7d**, 101518-28-9; **8**, 101518-32-5; **9** (R = Me, R' = Pr-*i*), 101518-31-4; **9**·HCl (R = Me, R' = Pr-*I*), 101518-37-0; **10**, 34862-63-0; **11**, 101518-33-6; **12**, 101518-34-7; **13**, 101518-35-8; **14**, 101518-36-9; **16** (R = Et), 54930-99-3; **16** (R = Et, 4-ethyl), 32515-29-0; **17**, 39636-07-2; Me_2NCON_3, 13750-17-9; EtN=C=NEt, 693-29-8; Et_2NCON_3, 922-12-3; *i*-PrN=C=NPr-*i*, 693-13-0; *i*-PrNHCONHPr-*i*, 4128-37-4; $Me_2NNHCONHPr$-*i*, 101518-29-0; N_2=CH_2, 334-88-3; 2-$O_2^-CC_6H_4N_2^+$, 1608-42-0; *i*-$PrNH_2$, 75-31-0; Me_2NCOCl, 79-44-7; *i*-$PrNHNH_2$, 2257-52-5; *i*-PrNHN=CMe_2, 7423-01-0; urazole, 3232-84-6.