(3 H, s), 2.9–4.4 (7 H, m), 7.3 (10 H, m). Anal. Calcd for $C_{22}H_{32}NI$: C, 60.41; H, 7.37; N, 3.20; I, 29.01. Found: C, 60.45; H, 7.54; N, 3.21; I, 28.59.

Irradiation of Stilbene and *tert*-Butyldimethylamine. A solution of 1 g (0.056 mol) of *trans*-stilbene and 6 g (0.59 mol) of *tert*-butyldimethylamine in 100 mL of acetonitrile was irradiated for 18.5 h. Removal of the volatile material followed by thick-layer chromatography (hexane) of the residual oil afforded a pure sample of *N*-*tert*-butyl-*N*-methyl-2,3-diphenylpropylamine: ^1H NMR δ ($CDCl_3$) 1.0 (9 H, s), 2.2 (3 H, s), 2.3–3.5 (5 H, m), 7.0 (10 H, m).

Irradiation of Stilbene and *tert*-Butylmethyl(trideuteriomethyl)amine. A solution of 0.9 g (0.1 mol) of *trans*-stilbene and 0.52 g (1.0 mol) of *tert*-butylmethyl(trideuteriomethyl)amine in 5 mL of acetonitrile was irradiated for 7.5 h. Removal of the volatile material followed by thick-layer chromatography (ethyl acetate) of the residual oil afforded a mixture of the isomers *N*-*tert*-butyl-*N*-(trideuteriomethyl)-2,3-diphenylpropylamine (**7a**) and *N*-*tert*-butyl-*N*-methyl-1,1,3-trideuterio-2,3-diphenylpropylamine (**7b**): ^1H NMR δ ($CDCl_3$) 1.00 (s, $C(CH_3)_3$), 2.19 (s, NCH_3), 2.67–3.03 (m), 7.13–7.25 (m, aromatic).

Acknowledgment. We thank Doris Hung for assistance with the mass spectral experiments. The National Science Foundation provided support for this work (Grant No. CHE78-01120) and matching funds for the purchase of the mass spectrometer and the fluorescence spectrophotometer.

Registry No. 1, 10342-97-9; **1a**, 76233-27-7; **2**, 7087-68-5; **2a** (isomer 1), 76233-28-8; **2a** (isomer 2), 76233-29-9; **2b**, 76233-30-2; **3**, 616-39-7; **3a**, 76233-31-3; **3b** (isomer 1), 76233-32-4; **3b** (isomer 2), 76233-33-5; **4a**, 76233-34-6; **4b** (isomer 1), 76233-35-7; **4b** (isomer 2), 76233-36-8; **5a**, 76233-37-9; **5b** (isomer 1), 76233-38-0; **5b** (isomer 2), 76233-39-1; **6a**, 76233-40-4; **7**, 52688-93-4; **7a**, 76233-41-5; **7b**, 76233-42-6; *trans*-stilbene, 103-30-0; trimethylamine, 75-50-3; triethylamine, 121-44-89; *tert*-butyldimethylamine, 918-02-5; butyldimethylamine, 927-62-8; isopropyldimethylamine, 996-35-0; ethyldimethylamine, 598-56-1; triisopropylamine, 3424-21-3; dabco, 280-57-9; **1a** methyl iodide, 76250-81-2.

Photochemical Reactivity of Keto Amidines. Type I Rearrangement to Aminocyclopropyl Isocyanates and Photochemical Generation of Bisisocyanates from Bichromophoric Systems

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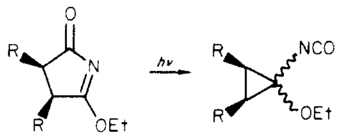
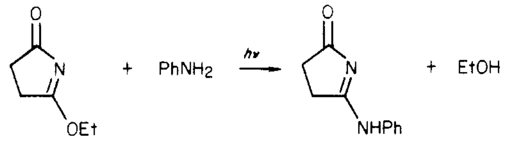
Received September 23, 1980

The photochemical rearrangement of 2-aminopyrrolin-5-ones and bis(2-aminopyrrolin-5-ones) to aminocyclopropyl isocyanates and bis(aminocyclopropyl isocyanates) is described. Specifically, 2-(dimethylamino)pyrrolin-5-one (**3**), 2-(methylphenylamino)pyrrolin-5-one (**4**), 1,4-bis[(5-oxopyrrolin-2-yl)methylamino]-2-butyne (**6**), and 1,4-bis[(5-oxopyrrolin-2-yl)phenylamino]-2-butyne (**8**) photochemically rearrange in 80 to 90% yield to (dimethylamino)cyclopropyl isocyanate, (methylphenylamino)cyclopropyl isocyanate, 1,4-bis[(isocyanatocyclopropyl)methylamino]-2-butyne, and 1,4-bis[(isocyanatocyclopropyl)phenylamino]-2-butyne, respectively, isolated as dimethylurea derivatives **9**, **10**, **13**, and **14**. The aminopyrrolinones were prepared by the addition of secondary amines to 2-ethoxypyrrolin-5-one (**1**).

We have previously described the Norrish Type I rearrangement of 2-ethoxypyrrolin-5-ones to ethoxycyclopropyl isocyanates.[1] The reaction displays a high degree of stereospecificity[2] and can be used as a synthetic method for the preparation of bicyclo[*n*.1.0] systems.[3] The ethoxycyclopropyl isocyanate is potentially a synthetically useful structural unit. It is a cyclopropanone equivalent and has been used in the synthesis of the natural product coprine.[4]



At the time Comstock and Wheeler reported the synthesis of 2-ethoxypyrrolin-5-one (**1**), they also noted that it reacted with aniline to give 2-anilinopyrrolin-5-one (**2**).[5]



1 **2**

We have observed that **1** similarly reacts with secondary amines and that the resulting aminopyrrolinones, unlike the ethoxypyrrolinones, are stable to water and other moderate nucleophiles. The ethoxypyrrolinones rapidly react with atmospheric moisture and hydrolyze to the imides from which they were synthesized.

We now report the photochemical rearrangement of 2-aminopyrrolin-5-ones to aminocyclopropyl isocyanates and the photochemical rearrangement of bis(aminopyrrolinones) to bisisocyanates. Because of the stability of the aminopyrrolinone system to nucleophiles, this latter reaction might be useful for the in situ photochemical generation of a cross-linking agent for polyurethane and

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[1] Koch, T. H.; Sluski, R. J.; Moseley, R. H. *J. Am. Chem. Soc.* **1973**, *95*, 3957.

[2] Burns, J. M.; Ashley, M. E.; Crockett, G. C.; Koch, T. H. *J. Am. Chem. Soc.* **1977**, *99*, 6924.

[3] Crockett, G. C.; Koch, T. H. *J. Org. Chem.* **1977**, *42*, 2721.

[4] Lindberg, P.; Bergman, R.; Wickberg, B. *J. Chem. Soc., Chem. Commun.* **1975**, 946.

[5] Comstock, W. J.; Wheeler, H. L. *Am. Chem. J.* **1891**, *13*, 522.

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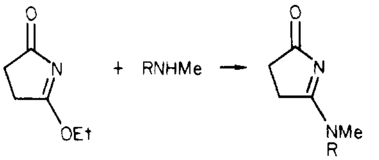
Table I. Yields for Starting Materials and Products

starting material	% yield	product	% yield
3	86	9	89
4	71	10	80
6	93	13	85
8	68	14	92

structurally related polymers.

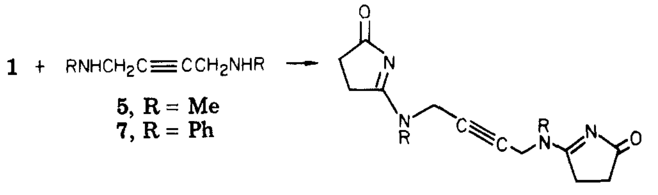
Results and Discussion

Synthesis of Reactants. All of the 2-aminopyrrolin-5-ones were prepared by the nucleophilic addition of secondary amines to 2-ethoxypyrrolin-5-one (1), prepared by the O-alkylation of succinimide.[5,6] 2-(Dimethylamino)pyrrolin-5-one (3) was prepared by the addition of gaseous dimethylamine to an anhydrous ether solution of 1 at ambient temperature. *N*-Methylaniline was much less reactive with 1; thus, addition of *N*-methylaniline to give 2-(phenylmethylamino)pyrrolin-5-one (4) required reaction in refluxing toluene for 24 h. 1,4-Bis(methylamino)-2-butyne (5) reacted with 2 equiv of 1 at ambient temperature as a neat mixture to yield the bis adduct 6. 1,4-Dianilino-2-butyne (7), like *N*-methylaniline, was less reactive, and the addition to 2 equiv of 1 was accomplished stepwise. The monoadduct was prepared in anhydrous ether at ambient temperature, and the bisadduct (8) was subsequently prepared in refluxing toluene. Isolated yields of the aminopyrrolinones ranged from 68 to 93% and are summarized in Table I.



1

3, R = Me
4, R = Ph



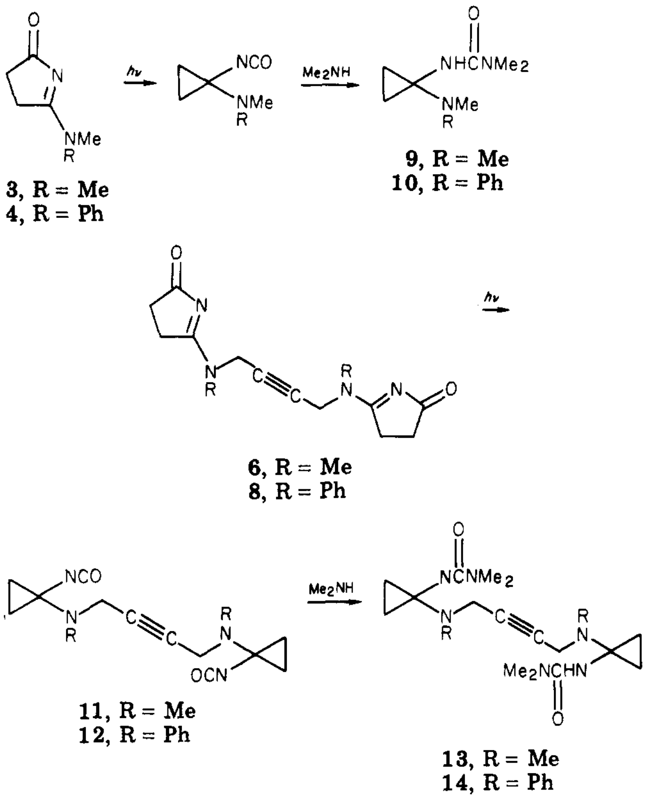
5, R = Me
7, R = Ph

6, R = Me
8, R = Ph

The structural assignments for the keto amidines are completely consistent with the spectral and analytical data reported in the experimental section. The ^{1}H NMR spectrum of 2-(dimethylamino)pyrrolin-5-one (3) shows two *N*-methyl singlets which indicates a barrier to rotation about the carbon–nitrogen single bond as observed in other amidines.[7] The barrier to rotation about the carbon–nitrogen single bonds in the bis adduct 6 gives rise to conformational isomerism also apparent in the ^{1}H NMR spectrum. The ^{1}H NMR spectra of 2-(phenylmethylamino)pyrrolin-5-one (4) and the bis adduct 8 suggest that these compounds exist as single conformers or that the barrier to rotation about the carbon–nitrogen single bond is significantly lower.

Ultraviolet Absorption. The keto amidine functionality gives rise to intense ultraviolet absorption in the region of 235 to 239 nm in tetrahydrofuran and methanol solvents. The magnitude of the molar extinction coefficients, which range from 26 000 to 58 000, and the lack of solvent shift indicate a π–π* transition. There is no resolved n–π* band. The UV spectral properties are in contrast with those of the 2-ethoxypyrrolin-5-ones which show distinct n–π* bands in the region of 275 nm and only end absorption for the π–π* transitions. Hence, substitution of an amino substituent for an ethoxy substituent results in a significant red shift of the π–π* transition with probably little shift in the n–π* transition. No through-bond or through-space coupling[8] of the two keto amidine functional groups in the ground state of the bichromophoric systems (6 and 8) is apparent from the UV spectra. There is no shift in absorption band maxima, and the molar extinction coefficients for 6 and 8 are approximately twice those for 3 and 4.

Scheme I



3, R = Me
4, R = Ph

9, R = Me
10, R = Ph

6, R = Me
8, R = Ph

11, R = Me
12, R = Ph

13, R = Me
14, R = Ph

Photochemical Reactions. Despite the differences in the chromophores of the aminopyrrolinones and the ethoxypyrrolinones, the photochemical reactivity of the two systems is similar. In all cases the aminopyrrolinones photochemically rearranged to aminocyclopropyl isocyanates (Scheme I).

2-(Dimethylamino)pyrrolin-5-one (3) and 2-(phenylmethylamino)pyrrolin-5-one (4) were irradiated through a Vycor filter with a 450-W mercury lamp in anhydrous tetrahydrofuran solvent, and the bichromophoric systems, 6 and 8, were irradiated in acetonitrile solvent at 2537 Å in a Rayonet reactor. Reactions were monitored by IR spectroscopy and thin-layer chromatography. The IR spectra indicated formation of the isocyanate functional group, characterized by an intense stretching band in the region of 4.4 to 4.5 μm. The isocyanates were not isolated but were trapped as dimethylurea derivatives by the addition of dimethylamine to the photolysates. As antici-

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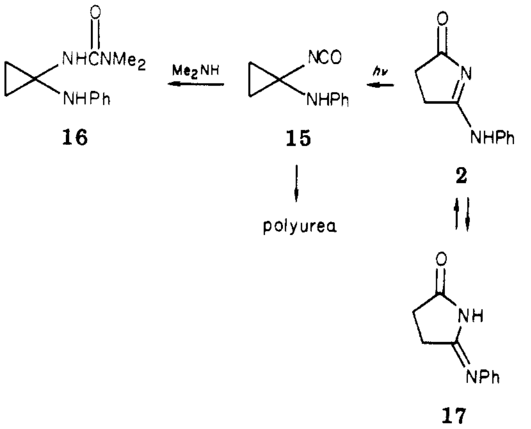
(6) Crockett, G. C.; Koch, T. H. *Org. Synth.* **1980**, *59*, 132.

(7) Fodor, G.; Phillips, B. A. In "The Chemistry of Amidines and Imidates"; Patai, S., Ed.; John Wiley: New York, 1975; p 108.

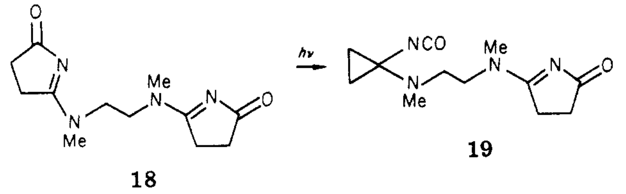
(8) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

pated, dimethylureas proved to be nicely crystalline, easily characterized derivatives. The spectral properties of the dimethylureas reported in the experimental section are completely consistent with the assigned structures **9**, **10**, **13**, and **14**. Isolated product yields range from 74 to 92% and are reported in Table I.

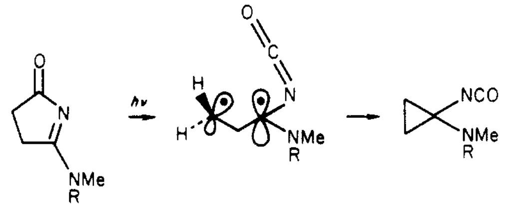
The photorearrangement of 2-aminopyrrolin-5-ones prepared by the addition of primary amines to 2-ethoxypyrrolin-5-one was briefly examined. 2-Anilinopyrrolin-5-one (**2**) was prepared as described by Comstock and Wheeler.[5] Although **2** underwent photorearrangement to anilinocyclopropyl isocyanate (**15**), the isolated yield of the dimethylurea derivative **16** was poor (<10%). Possible explanations for the low yield are the presence of the light-absorbing tautomer **17** and the polymerization of **15**. Evidence for the tautomerism is the observed shift in the UV band maximum to 265 nm.



The butyne linkage in the bichromophoric systems **6** and **8** was selected to minimize through-space interaction of the chromophores during the photorearrangement. Through-space interaction is inhibited by the rigidity of the alkyne functional group. The need to minimize through-space interaction was evident from a preliminary investigation of the photorearrangement of 1,2-bis[(5-oxopyrrolin-2-yl)methylamino]ethane (**18**). The bichromophoric system **18** appeared to rearrange in poor yield only to the monoaminocyclopropyl isocyanate **19**. On the basis of this result and the successful rearrangement of **6** and **8** to bis(aminocyclopropyl isocyanates) **11** and **12**, we presume that through-space interactions in excited **19** and possibly also in excited **18** inhibit the photochemical rearrangement. The through-space interaction in excited **19** probably involves electron transfer from the amino substituent to the excited keto amidine functional group with the possible intermediacy of an intramolecular exciplex. Intramolecular electron transfer could result in quenching of excited **19** and/or the formation of reactive radicals. The interaction is analogous to the intermolecular quenching of excited ketones by amines.[9] Through-space interaction in excited **18** might involve intramolecular excimer formation which could also lead to quenching and/or formation of reactive radicals. Studies of other bichomophoric systems suggest that these interactions would be most significant if the chromophores were connected by three methylene groups rather than two, the "$n = 3$" rule.[10] Halpern and co-workers have recently reported intramolecular excimer formation upon excitation of 1,2-bis(dimethylamino)ethane, a system with $n = 2$ analogous to **18** and **19**.[11]



A reasonable mechanism for the rearrangement of the 2-aminopyrrolin-5-ones to aminocyclopropyl isocyanates is via Norrish Type I cleavage in a n,π* state to give an intermediate σ,π type[12] 1,3-diradical. Ring closure of the 1,3-diradical forms the cyclopropane ring. Although the n–π* transition is not distinct in the UV spectra of **3**, **4**, **6**, and **8**, the form of the rearrangement and precedent[1,2] are most consistent with an ^{1}n,π* configuration for the reactive state. In nitrogen heterocycles photochemical reactivity via hidden n,π* states is not uncommon.[13]



Norrish Type I cleavage is an uncommon reaction of α,β-unsaturated ketones structurally related to **3** and **4**. Photodimerization and photocycloaddition to olefins are generally the observed reactions. There are, however, several examples in the literature of related systems which α cleave and these have been reviewed.[14] A more recent, relevant example is the photorearrangement of *N*-aryl-2-(1*H*)-pyrimidin-2-ones to 1-[3-[(alkoxycarbonyl)amino]-2-propene]-*N*-arylimines in mixed benzene–alcohol solvent.[15]

The bichromophoric systems **6** and **8** were explored to test the possibility of photochemically generating bisisocyanates in situ as cross-linking agents for polyurethanes and polyureas. The bis(aminopyrrolinones) **6** and **8** are stable to water and alcohols, intensely absorb ultraviolet light, and efficiently rearrange to bisisocyanates. Although the quantum yields have not been measured for these rearrangements, they are probably in the range of 0.1, estimated from reaction times in comparison with reaction times for the photorearrangement of 2-ethoxypyrrolin-5-one to ethoxycyclopropyl isocyanate.[1] On the basis of these favorable properties possible application to photocrosslinking is presently under investigation.

Experimental Section

Melting points were measured with Fisher-Johns and Thomas-Hoover melting point apparatuses and are uncorrected. Perkin-Elmer 337 and Varian 635 spectrophotometers were used to determine IR and UV spectra, respectively. ^{1}H NMR spectra were recorded with a Varian EM-390 spectrometer, and chemical shifts are reported in δ units from internal tetramethylsilane. Mass

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[10] Klopffer, W. In "Organic Molecular Photophysics"; Birks, J. B., Ed.; Wiley-Interscience: New York, 1973; Chapter 7.

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[15] Nishio, T.; Katahira, K.; Kato, A.; Kashima, C.; Omote, Y. *Tetrahedron Lett.* **1979**, 4211.

spectra were measured at 70 eV with Varian MAT CH-5 and CH-7 spectrometers. Microanalyses were performed by Atlantic Microlab, Atlanta, GA, and exact molecular weights were obtained at the Regional Mass Spectrometry Lab at The University of Nebraska, Lincoln, NE. 2-Ethoxypyrrolin-5-one was prepared from succinimide as previously described.[5,6] 1,4-Bis(methylamino)-2-butyne and 1,4-dianilino-2-butyne were prepared from 1,4-dichloro-2-butyne as described by Johnson.[16] Tetrahydrofuran was distilled from lithium aluminum hydride prior to use.

2-(Dimethylamino)pyrrolin-5-one (3). To a stirred solution of 5.0 g (39.4 mmol) of 2-ethoxypyrrolin-5-one in 26 mL of anhydrous ether was added gaseous dimethylamine through a syringe needle. A white crystalline solid began separating from the solution almost immediately. When precipitation was complete, the addition of dimethylamine was stopped, and the reaction mixture, open to the atmosphere, was stirred overnight to vent excess dimethylamine. The white crystals were collected by suction filtration, washed with ether, and air-dried to give 4.34 g (86%) of 2-(dimethylamino)pyrrolin-5-one, mp 121–121.5 °C. The product has the following spectral and analytical properties: IR (CH_2Cl_2) 5.86 and 6.30 μm; ^1H NMR ($CDCl_3$) δ 2.40–3.00 (m, 4 H), 3.15 (s, 3 H), 3.27 (s, 3 H); UV (THF) 235 nm (ε 25 700); mass spectrum, *m/e* (relative intensity) 126 (base), 125 (23), 111 (19), 97 (14), 82 (29), 70 (85), 69 (34), 56 (27), 55 (11), 54 (24), 44 (28), 43 (56), 42 (58).

Anal. Calcd for $C_6H_{10}N_2O$: C, 57.12; H, 7.99; N, 22.20. Found: C, 57.03; H, 8.00; N, 22.24.

2-(Phenylmethylamino)pyrrolin-5-one (4). A round-bottom flask equipped with reflux condenser, magnetic-stirring apparatus, and heating mantle was charged with 0.733 g (5.77 mmol) of 2-ethoxypyrrolin-5-one and 0.617 g (5.77 mmol) of *N*-methylaniline in 20 mL of toluene. The reaction mixture was refluxed with stirring for 24 h and cooled, and the solvent was rotary evaporated to yield 0.772 g (71%) of light brown crystals, mp 126–127.5 °C. An analytical sample of 4, prepared by recrystallization from a chloroform acetone solution (1:5 v/v), gave mp 127.5–129 °C and the following spectral absorptions: IR (THF) 5.78 and 6.42 μm; ^1H NMR ($CDCl_3$) δ 2.70 (s, 4 H), 3.63 (s, 3 H), 7.26–7.81 (m, 5 H); UV (MeOH) 239 nm (ε 28 700); mass spectrum, *m/e* (relative intensity) 188 (41), 187 (base), 132 (12), 105 (15), 104 (19), 90 (19), 82 (15), 76 (26), 57 (12), 28 (16).

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.43; N, 14.88. Found: C, 69.96; H, 6.49; N, 14.79.

1,4-Bis[(5-oxopyrrolin-2-yl)methylamino]-2-butyne (6). To a stirred solution of 2.28 g (18.0 mmol) of 2-ethoxypyrrolin-5-one in 20 mL of a 1:1 (v/v) mixture of acetone and anhydrous ether was added 1.02 g (9.1 mmol) of 1,4-bis(methylamino)-2-butyne[16] dropwise. After 2 h a white precipitate formed which was collected by vacuum filtration to give 2.3 g (93%) of 6. The material obtained was pure by ^1H NMR spectroscopy and gave mp 189–191 °C dec. An analytical sample, prepared by recrystallization from a chloroform–acetone solution (1:5 v/v), had the following physical and analytical properties: mp 191–192 °C dec; IR (CH_2Cl_2) 5.81 and 6.38 μm; ^1H NMR (D_2O) δ 2.2–3.1 (m, 4 H), 3.04 (s, 3 H), 4.14, 4.15, 4.22 (3 s, total integration 3 H); UV (MeOH) 235 nm (ε 57 600); mass spectrum, *m/e* (relative intensity) 274 (43), 163 (19) 161 (base), 160 (13), 135 (29), 134 (83), 133 (54), 121 (12), 113 (15), 112 (66), 111 (12), 82 (14), 80 (57), 79 (12), 69 (15), 68 (37), 66 (10), 58 (36), 56 (31), 55 (25), 54 (25), 43 (19), 42 (44), 41 (16).

Anal. Calcd for $C_{14}H_{18}N_4O_2$: C, 61.30; H, 6.61; N, 20.42. Found: C, 61.09; H, 6.65; N, 20.32.

1,4-Bis[(5-oxopyrrolin-2-yl)phenylamino]-2-butyne (8). An intimate mixture of 450 mg (1.91 mmol) of 1,4-dianilino-2-butyne[16] and 24.3 mg (1.91 mmol) of 2-ethoxypyrrolin-5-one was stored at ambient temperature for 2 days. The resultant solid was suspended in anhydrous ether and collected by vacuum filtration. The solid was identified spectrophotometrically as the monoadduct. The monoadduct and 1.00 g (7.87 mmol) of 2-ethoxypyrrolin-5-one in toluene solvent (40 mL) were then refluxed under a nitrogen atmosphere for 1 day. After the mixture was cooled, 382 mg of 8 as a slightly brown solid was collected by vacuum filtration. The mother liquor was concentrated and allowed to stand for 5 days. An additional 152 mg of product was collected by vacuum filtration (combined yield of 8, 68%). For preparation of an analytical sample, the material was dissolved in chloroform and decolorized with charcoal. After rotary evaporation of the chloroform, the resulting colorless solid was collected by vacuum filtration and washed with anhydrous ether. This material had the following physical properties: mp 214.5–215.5 °C; IR ($CHCl_3$) 5.82 and 6.48 μm; ^1H NMR ($CDCl_3$) δ 2.25–2.69 (m, 4 H), 4.80 (s, 2 H), 7.22–7.63 (m, 5 H); UV (MeOH) 238 nm (ε 53 000); mass spectrum, *m/e* (relative intensity) 398 (1.2) 225 (37), 224 (82), 197 (17), 196 (base), 195 (88), 174 (19), 147 (14), 146 (22), 142 (24), 131 (14), 130 (28), 119 (75), 118 (24), 115 (15), 104 (27), 92 (19), 90 (22), 76 (95), 75 (12), 54 (14), 53 (12), 51 (40), 39 (15), and 28 (22).

Anal. Calcd for $C_{24}H_{22}N_4O_2$: C, 72.34; H, 5.56; N, 14.06. Found: C, 72.55; H, 5.68; N, 13.91.

***N,N*-Dimethyl-*N'*-[(dimethylamino)cyclopropyl]urea (9).** 2-(Dimethylamino)pyrrolin-5-one (1.00 g, 7.94 mmol) was dissolved in 100 mL of dry tetrahydrofuran in a quartz immersion well apparatus. The solution was degassed with nitrogen for 15 min and then irradiated with continuous nitrogen degassing with a Hanovia 450-W mercury lamp through a Vycor filter. After 2 h of irradiation the starting material had disappeared and an isocyanate had formed as indicated by IR spectroscopy. Dimethylamine was bubbled into the photolysis solution for 15 min, after which the isocyanate disappeared as indicated by IR spectroscopy. The solvent was removed by rotary evaporation to give 1.20 g (89%) of urea 9 as a yellow solid which was pure by ^1H NMR spectroscopy. Sublimation of the product at 80–85 °C (0.03 torr) gave 1.00 g (74%) of white crystalline product, mp 135–137 °C, which gave the following spectral absorptions: IR (CH_2Cl_2) 2.91, 3.42, 3.56, 6.68 μm; ^1H NMR ($CDCl_3$) δ 0.97 (s, 4 H), 2.38 (s, 6 H), 2.96 (s, 6 H), 4.83–5.10 (br, 1 H); mass spectrum, *m/e* (relative intensity) 72 (base), 71 (26), 68 (16), 56 (20), 44 (63), 43 (11), 42 (17).

Anal. Calcd for $C_8H_{17}N_3O$: C, 56.11; H, 10.01; N, 24.54. Found: C, 56.00; H, 10.01; N, 24.50.

***N,N*-Dimethyl-*N'*-[(phenylmethylamino)cyclopropyl]urea (10).** 2-(Phenylmethylamino)pyrrolin-5-one (339 mg, 2.12 mmol) was dissolved in 100 mL of dry tetrahydrofuran in a quartz immersion well apparatus. The solution was degassed with nitrogen for 10 min prior to and during irradiation with a Hanovia 450-W mercury lamp through a Vycor filter. After 1.5 h of irradiation the starting material had disappeared as indicated by silica gel TLC, eluting with acetone. Dimethylamine was bubbled into the photolysis mixture with stirring for 15 min. The solvent was removed by rotary evaporation, and the solid residue was extracted with ether. Rotary evaporation of the ether yielded 0.371 g (80%) of 10 as a yellow solid which was pure as indicated by ^1H NMR spectroscopy. An analytical sample, obtained by sublimation at 75–80 °C (0.07 torr) had the following physical properties: mp 180–181 °C dec; IR ($CHCl_3$) 2.91, 3.40, 6.04, 6.26, 6.69 μm; ^1H NMR ($CDCl_3$) δ 1.18–1.38 (m, 4 H), 2.84 (s, 6 H), 3.17 (s, 3 H), 5.48–5.69 (br, 1 H), 6.69–7.47 (m, 5 H); mass spectrum, *m/e* (relative intensity) 233 (44), 190 (12), 189 (65), 187 (10), 160 (13), 146 (18), 145 (20), 144 (12), 133 (10), 130 (11), 121 (11), 107 (28), 106 (44), 105 (27), 104 (13), 76 (33), 72 (base), 71 (12), 58 (10), 44 (17), 43 (11).

Anal. Calcd for $C_{13}H_{19}N_3O$: C, 66.92; H, 8.21; N, 18.01. Found: C, 66.66; H, 8.20; N, 17.91.

1,4-Bis[*N*-[[(dimethylamido)amino]cyclopropyl]methylamino]-2-butyne (13). A 10-mL quartz test tube was charged with 44 mg (0.161 mmol) of 1,4-bis[(5-oxopyrrolin-2-yl)methylamino]-2-butyne (6) and 10 mL of reagent-grade acetonitrile. The test tube was equipped with a nitrogen inlet and outlet and a cold finger. The solution was degassed for 10 min prior to and during the irradiation in a Rayonet reactor equipped with 2537-Å lamps. After 2.5 h of irradiation the starting material had disappeared as determined by IR spectroscopy. Dimethylamine was then bubbled through the photolysis mixture for 10 min. Rotary evaporation of the solvent yielded 50 mg (85%) of 13 as a yellow solid which was pure as indicated by ^1H NMR spectroscopy. The material had the following physical properties: mp 166–167 °C dec; IR (CH_2Cl_2) 2.91, 3.41, 6.03, 6.66 μm; ^1H NMR ($CDCl_3$) δ 0.91 (s, 8 H), 2.41 (s, 6 H), 2.79 (s, 12 H), 3.48 (s, 4 H), 5.06 (br, 2 H); mass spectrum, *m/e* (relative intensity) 208 (15), 207 (12), 162 (17), 156 (12), 87 (15), 72 (base), 68 (11), 44 (45), 43 (15), 42 (15).

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The material could not be sufficiently purified for elemental analysis. The highest *m/e* peak in the high-resolution mass spectrum corresponded to $M^+ - N(CH_3)_2$; calcd for $C_{16}H_{26}N_5O_2$ 320.2077, found 320.2082.

1,4-Bis[*N*-[[(dimethylamido)amino]cyclopropyl]phenylamino]-2-butyne (14). A 10-mL quartz test tube was charged with 49.8 mg (0.125 mmol) of 1,4-bis[(5-oxopyrrolin-2-yl)-phenylamino]-2-butyne (8) in 10 mL of reagent-grade acetonitrile. The test tube was equipped with a cold finger and nitrogen inlet and outlet. The solution was degassed for 10 min prior to and during irridation in a Rayonet reactor equipped with 2537-Å lamps. After 1 h of irradiation the starting material had disappeared as indicated by IR spectroscopy. Dimethylamine was then bubbled through the solution for 10 min. Rotary evaporation of the solvent yielded 56.1 mg of 14 (92%) as a slightly yellow solid, mp 180–181 °C dec, which was pure by ^1H NMR spectroscopy. An analytical sample of 14 prepared by alumina TLC, eluting with ethyl acetate, had the following physical properties: mp 179–181 °C dec, IR (CH_2Cl_2) 2.91, 3.40, 6.05, 6.66 μm; ^1H NMR ($CDCl_3$) δ 1.20 (s, 8 H), 2.77 (s, 12 H), 4.42 (s, 4 H), 5.48 (br, 1 H), 6.6–7.40 (m, 10 H); mass spectrum, *m/e* (relative intensity) 488 (3.5), 372 (13), 270 (25), 269 (13), 225 (30), 220 (20), 218 (12), 198 (12), 197 (20), 183 (14), 143 (11), 132 (14), 130 (16), 72 (base). The material could not be sufficiently purified for elemental analysis. The highest *m/e* peak in the high-resolution mass spectrum corresponded to the molecular ion; calcd for $C_{28}H_{36}N_6O_2$ 488.2900, found 488.2893.

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Registry No. 1, 29473-56-1; 3, 68321-93-7; 4, 75812-67-8; 5, 75812-68-9; 6, 75812-69-0; 7, 14130-04-2; 8, 75812-70-3; 9, 45812-71-4; 10, 75812-72-5; 13, 75812-73-6; 14, 75812-74-7; dimethylamine, 124-40-3; *N*-methylaniline, 100-61-8.

Quantum Efficiencies of the Cis/Trans Photoisomerization of Protonated α,β-Unsaturated Carbonyl Compounds

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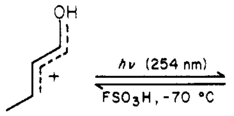
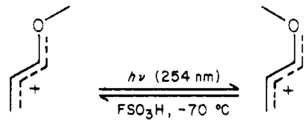
The quantum efficiencies of the photoinduced interconversion of protonated *trans*- and *cis*-pent-3-en-2-ones (1 and 2, respectively) have been measured. In FSO_3H at 25 °C with 254-nm light $\Phi_{1\to2}$ was found to be 0.64 and $\Phi_{2\to1}$ to be 0.65. These isomerizations are more efficient than the interconversions of the corresponding neutral ketones. Change of the acid medium from FSO_3H to FSO_3H/SbF_5 (1:1) or reduction in the temperature at which the irradiations were carried out substantially reduced the quantum efficiency of the conversion of 1 to 2. In both cases, this effect was attributed largely to an increase in viscosity. The quantum efficiencies of the cis/trans photisomerizations about the carbon–carbon double bonds of several other α,β-unsaturated carbonyl compounds were determined. Photoisomerism about the carbon–oxygen bond of 1-methoxyallyl cation was also found to be a relatively efficient process.

A considerable number of different types of carbocation have been found to be photoreactive.[1] These range in complexity from the protonated imines associated with the chemistry of vision[2] to the comparatively simple protonated enals.[3] Despite the variety of photoreactions which have been observed, very little quantitative work has been reported hitherto.[4]

Protonated, conjugated enals and acyclic enones have been shown to undergo cis/trans isomerization about the carbon–carbon "double" bond on irradiation in superacid media (eq 1).[3] Eventually a photostationary state is established between the two conformers, and, unlike the case with the corresponding neutral carbonyl compounds,[5-9] no other products have been detected even on prolonged irradiations. The related *O*-methyl derivatives undergo both carbon–carbon and carbon–oxygen bond isomerizations on irradiation (eq 2).[10] It would seem likely that a similar carbon–oxygen bond isomerization occurs with the protonated enals and enones; however, exchange of the proton on oxygen with the acid pool precludes the detection of such a reaction.



(1)



(2)

These protonated α,β-unsaturated carbonyl compounds represent one of the basic chromophores present in many of the carbocations that have been shown to photoisom-

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