H, J = 6 and 2 Hz), 7.02-7.10 (m, 2 H), 7.45 (dd, 1 H, J = 6 and 2 Hz).

Acknowledgment. We express our thanks to the University of California Cancer Research Coordinating Committee for partial financial assistance. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We wish also to thank Curt Breneman and Dr. Ata Shirazi for their help in obtaining NMR spectra and Dr. Hugh Webb for the MS data.

Registry No. **1**, 5398-11-8; **2**, 103934-98-1; **3c**, 103958-93-6; **3t**, 103934-75-4; **4c**, 103934-76-5; **4t**, 103934-77-6; **5**, 3453-64-3; **6**, 103934-94-7; **7c**, 103934-78-7; **7t**, 103934-79-8; **8c**, 103934-80-1; **8t**, 103934-81-2; **9**, 103934-82-3; **10**, 103934-83-4; **11**, 103934-84-5; **12**, 60231-30-3; **13**, 103934-85-6; **14**, 103934-86-7; **15**, 103934-88-9; **16**, 104011-62-3; **18**, 61200-10-0; **19**, 103934-89-0; **21**, 103934-90-3; **21** (1-phenyl), 103934-87-8; **24**, 103934-91-4; **25**, 103934-92-5; **26**, 103934-95-8; **27**, 103934-96-9; **28**, 103934-99-2; **29**, 103935-00-8; **30**, 103935-01-9; **31**, 103935-02-0; **32**, 104011-63-4; **33**, 103935-03-1; **34**, 103935-04-2; **35**, 103935-05-3; **36**, 103935-06-4; **37**, 103935-07-5; **38**, 103935-10-0; **38** (acid), 577-56-0; **39**, 103935-09-7; **40**, 103935-08-6; NMM, 930-88-1; DMAD, 762-42-5; 2-$PhCOC_6H_4CO_2H$, 85-52-9; norbornene, 498-66-8.

Photolysis of Dimethylcarbamoyl Azide in the Presence of a Cyclic Aminimide

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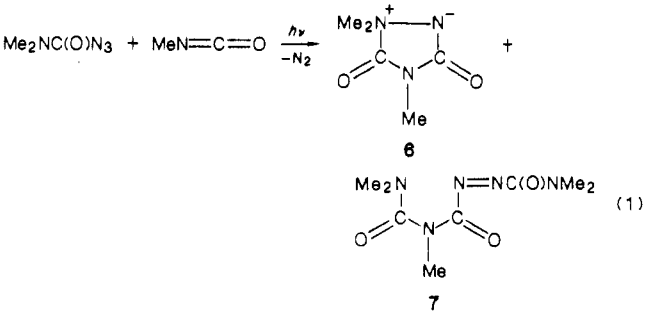
Dimethylcarbamoyl azide has been photolyzed in the presence of methyl isocyanate to produce the cyclic aminimide 1,1,4-trimethyl-1,2,4-triazolidine-3,5-dione 1,2-ylide (**6**) and the azo compound *N*-(dimethylcarbamoyl)-*N*,*N*',*N*'-trimethylazodicarboxamide (**7**). The azo compound **7** arises from a photolytic reaction between dimethylcarbamoyl azide and aminimide **6**. Mechanistic studies support a reaction path involving intermolecular-assisted loss of nitrogen from the azide as a result of interaction with aminimide **6**.

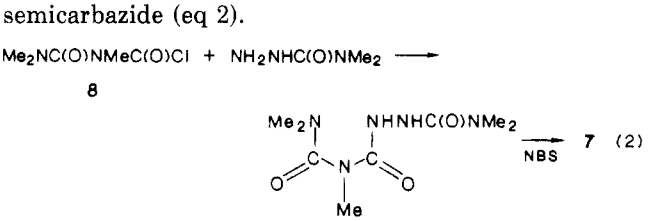
The photolysis of carbamoyl azides (**1**) provides a potential source of the intermediates shown in Scheme I.

Certain photoexcited carbamoyl azides (**2**) are known to give singlet (**3**) and triplet (**4**) nitrene intermediates as well as amino isocyanates (**5**) via a Curtius-type rearrangement. Arylalkylcarbamoyl azides give nitrene products,[1] dialkylcarbamoyl azides provide a source of amino isocyanates,[2] while diaryl derivatives apparently give both nitrene and amino isocyanate intermediates.[3] While there has been considerable work done with nitrene and amino isocyanate intermediates,[4] excited-state carbamoyl azides (**2**) have received little attention.[3] We wish to report the first example of intermolecular-assisted loss of nitrogen from a carbamoyl azide in the photoreaction of dimethylcarbamoyl azide with a cyclic aminimide, 1,1,4-trimethyl-1,2,4-triazolidine-3,5-dione 1,2-ylide (**6**).

As part of a study of the photolysis of carbamoyl azides in the presence of heterocumulenes,[5] dimethylcarbamoyl azide was photolyzed in the presence of methyl isocyanate in dichloromethane at −5 °C, producing the aminimide **6** (44%) and the azo compound **7** (40%) (eq 1).



Under these photolytic conditions, dimethylcarbamoyl azide is known to undergo loss of nitrogen with rearrangement to dimethylamino isocyanate.[2] In the presence of organic isocyanates, amino isocyanates produce cyclic aminimides such as **6** via cycloaddition reactions.[6,7] In contrast to the formation of aminimide **6**, the production of azo compound **7** was unexpected. Its structure was determined from instrumental analysis (^{1}H NMR, ^{13}C NMR, ^{15}N NMR, IR, MS), base-catalyzed hydrolysis to give trimethylurea, and an independent synthesis from 2,4,4-trimethylallophanoyl chloride (**8**) and 4,4-dimethylsemicarbazide (eq 2).

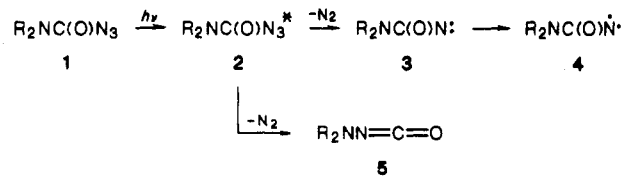


The structure of azo compound **7** suggests that it might arise from a reaction of dimethylcarbamoyl azide and aminimide **6**. Indeed, photolysis of dimethylcarbamoyl azide

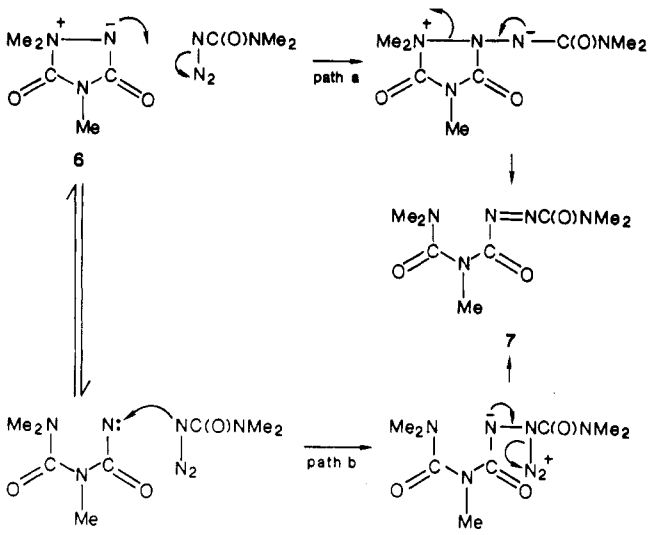
(1) Kametani, T.; Shio, M. *J. Heterocycl. Chem.* **1971**, *8*, 545.
(2) Lwowski, W.; deMauriac, R. A.; Thompson, M.; Wilde, R. E.; Chen, S.-Y. *J. Org. Chem.* **1975**, *40*, 2608.
(3) Koga, N.; Koga, G.; Anselme, J.-P. *Tetrahedron* **1972**, *28*, 4515.
(4) Lwowski, W. In *Azides and Nitrenes, Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984; Chapter 4 and references cited therein.
(5) Lwowski, W.; Kanemasa, S.; Murray, R. A.; Ramakrishnan, V. T.; Thiruvengadam, T. K.; Yoshida, K.; Subbaraj, A. *J. Org. Chem.* **1986**, *51*, 1719.
(6) Lwowski, W.; deMauriac, R. A.; Murray, R. A.; Lunow, L. *Tetrahedron Lett.* **1971**, 425.
(7) Wadsworth, W. S.; Emmons, W. D. *J. Org. Chem.* **1967**, *32*, 1279.

0022-3263/86/1951-3858$01.50/0

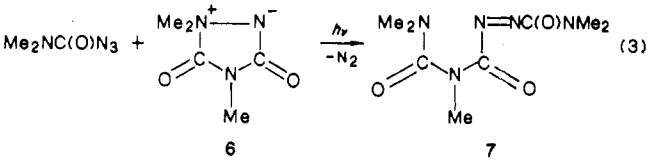
Scheme I



Scheme II

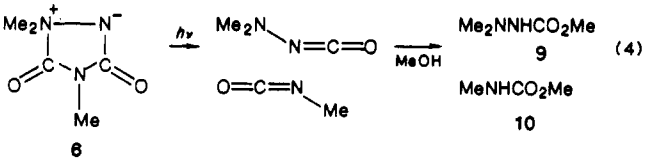


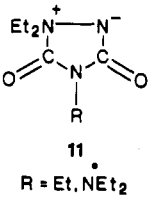
and **6** under reaction conditions does produce the azo compound **7** in 59% yield, based on decomposed aminimide **6**. It is not produced from the photolysis of either azide or aminimide **6** alone, nor from the photolysis of a mixture of methyl isocyanate and aminimide **6**. A mixture of dimethylcarbamoyl azide and aminimide **6** is stable at room temperature or under reflux in dichloromethane in the dark. Thus, azo compound **7** is a photoproduct from dimethylcarbamoyl azide and aminimide **6** (eq 3).



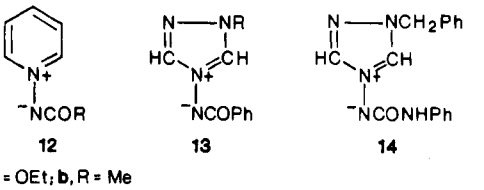
Scheme II depicts two reasonable pathways for the production of azo compound **7**.[8] Path b includes N–N bond cleavage of an aminimide[9] and reaction of the resulting nitrene with azide.[10]

Aminimide **6** was photolyzed by itself under normal reaction conditions to test for N–N bond dissociation. Infrared and NMR analysis revealed the aminimide to be decomposed (22% after a photolysis time of 72 h), with some methyl isocyanate having been produced. When the photolysis was done in dichloromethane with added methanol, both methyl *N,N*-dimethylcarbazate (**9**) and methyl methylcarbamate (**10**) were produced. These results suggest that under these conditions aminimide **6** dissociates reversibly to methyl isocyanate and dimethylamino isocyanate, both of which can be trapped by known reactions with methanol producing **9** and **10** (eq 4). A similar photolytic dissociation has been observed for the closely related aminimide **11**.[6]



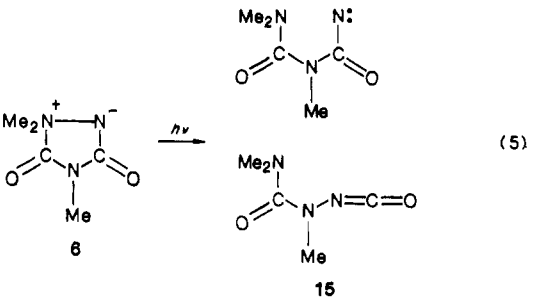


Upon photolytic N–N bond cleavage, open-chain aminimides produce nitrene intermediates and rearrangement products, depending upon the structure of the aminimide.[11] Compound **12a** provides a source of ethoxycarbonylnitrene, **12b** produces only methyl isocyanate,[12] while **13** generates both benzoylnitrene and phenyl isocyanate.[13] Carbamoylaminimide **14** produces an amino isocyanate intermediate from rearrangement.[11]

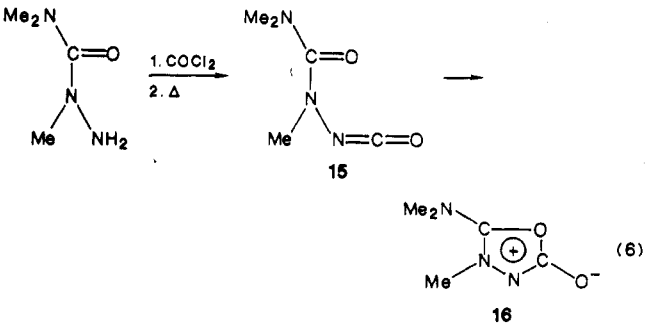


a, R = OEt; **b**, R = Me

Thus, were N–N bond cleavage occurring with aminimide **6**, both nitrene production and rearrangement producing amino isocyanate (**15**) would be likely (eq 5).



Intermediate **15** would be expected to produce isosydnone **16** by a well-known synthetic method for isosydnones.[14] We produced intermediate **15** from 2,4,4-trimethylsemicarbazide as shown and did indeed obtain 5-(dimethylamino)-4-methylisosydnone (**16**) (eq 6).



(8) Another conceivable pathway involves formation of a nitrene from dimethylcarbamoyl azide and subsequent reaction with aminimide **6**. However, it has been shown that no nitrene is produced when dimethylcarbamoyl azide is photolytically decomposed under conditions very similar to those within this work.[2]

(9) McKillip, W. J.; Sedor, E. A.; Culbertson, B. M.; Wawzonek, S. *Chem. Rev.* **1973**, *73*, 255.

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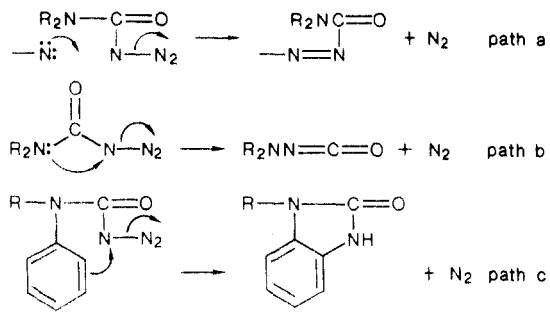
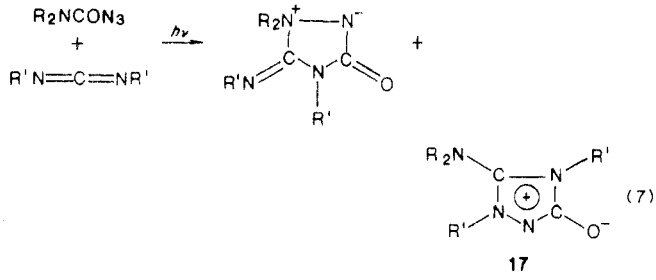
Scheme III



A careful analysis of the reaction mixture from the photolysis of aminimide **6** revealed no detectable isosydnone **16**. This observation, combined with the results of aminimide **6** photolysis in methanol, lends strong support to the conclusion that no significant amount of N–N bond cleavage is occurring in aminimide **6**.

Path a of Scheme II provides the best explanation of our data. In Scheme III one can compare this first example of intermolecular-assisted loss of nitrogen from a carbamoyl azide (path a) to the intramolecular assistance occurring in the Curtius-type rearrangement[2] (path b) and a similar intramolecular assistance in aryl-substituted carbamoyl azides (path c).[3]

The exact identity of the intermediate(s) leading to azo compound **7** is still unknown. Two reasonable possibilities are photoexcited carbamoyl azide, as mentioned by Anselme,[3] and an azide–aminimide exciplex similar to that observed by Lwowski[5] in the photolytic production of the mesoionic **17** (eq 7).



(7)

17

Experimental Section

General. Melting points are uncorrected. IR analyses were performed on a Beckman Acculab 3 instrument, UV and visible spectrum analyses on a Coleman Hitachi EPS-3T instrument, GC analyses on an Aerograph Autoprep 700 instrument, ^1H NMR analyses on a Varian Anaspect EM360 instrument with Me_4Si used as a reference, ^{13}C NMR and ^{15}N NMR analyses on a Varian XL-200 instrument, and mass spectrometric analyses on a Hitachi Perkin-Elmer RMU-6E instrument. Photolytic reactions were performed in a Rayonet photochemical reactor equipped with Rayonet photochemical reactor lamps RPR-3000A. All reactions were carried out in silica tubes, magnetically stirred, and cooled to −5 °C by a Lauda K-4/R cooling unit. Preparative TLC plates (20 × 20 cm, silica gel GF) were developed with 2:1:1 acetone/hexanes/$CHCl_3$, respectively. Quantitative analysis of 1,1,4-trimethyl-1,2,4-triazolidine-3,5-dione 1,2-ylide was made using a Beer's law plot at 1830 cm^{-1}. *N,N*-Dimethylcarbamoyl azide was similarly quantified at 2150 cm^{-1}. *N*-(Dimethylcarbamoyl)-*N,N',N'*-trimethylazodicarboxamide was quantified from UV analyses in CH_2Cl_2 at 440 nm.

Materials. Dimethylcarbamoyl azide,[15] 1,1,4-trimethyl-1,2,4-triazolidine-3,5-dione 1,2-ylide,[16] 2,4,4-trimethylallophanoyl chloride,[17] 4,4-dimethylsemicarbazide,[18] 2,4,4-trimethylsemicarbazide,[19] and methyl *N,N*-dimethylcarbazate[2] were prepared according to literature methods.

***N*-(Dimethylcarbamoyl)-*N,N',N'*-trimethylazodicarboxamide (7).** To a stirred solution of 0.91 g (8.8 mmol) of 4,4-dimethylsemicarbazide and 40 mL of CH_2Cl_2 in a 100-mL flask over a water bath (ambient) were added 0.11 g (0.88 mmol) of 4-(dimethylamino)pyridine and 1.23 mL (8.8 mmol) of triethylamine. Then, a solution of 1.45 g (8.8 mmol) of 2,4,4-trimethylallophanoyl chloride and 15 mL of CH_2Cl_2 was added dropwise over a 4-h period. After stirring for an additional 40 h, a white solid, *N*-(dimethylcarbamoyl)-*N,N',N'*-trimethyl-1,2-hydrazinecarboxamide (1.17 g 57%), was isolated by filtration: mp 187–189 °C; IR ($CHCl_3$) 1660, 1480 cm^{-1}; MS, *m/e* (relative intensity) 231 (5), 72 (100).

To a solution of 0.78 g (3.25 mmol) of *N*-(dimethylcarbamoyl)-*N,N',N'*-trimethyl-1,2-hydrazinedicarboxamide, 23 mL of CH_2Cl_2, and 0.15 mL (1.9 mmol) of pyridine in a 100-mL flask at −30 °C was added 1.16 g (6.5 mmol) of *N*-bromosuccinimide in portions over a 35-min period. After stirring for 3 h (ambient), the orange solution was washed with 2 × 15 mL of 10% Na_2CO_3, 2 × 15 mL of H_2O, 2 × 15 mL of 1 N HCl (rapidly), and 2 × 15 mL of 5% $NaHCO_3$. Solvent was removed under vacuum and the resulting oil crystallized after 24 h at 4 °C. Recrystallization from hexanes–ethyl acetate gave pale orange platelets: mp 73–74 °C; IR ($CHCl_3$) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) 3.28 (s, 1 H), 3.14 (s, 1 H), 3.01 (s, 1 H), 2.98 (s, 2 H); ^{13}C NMR ($CDCl_3$) 161.1, 159.9, 155.1, 37.4, 36.4, 36.2, 33.0; ^{15}N NMR (CH_3NO_2) 184.4, 169.0 (azo), −290.2, −294.6 (amide); UV (CH_3CN) 440 nm (48.2). *Anal.* Calcd for $C_8H_{15}N_5O_3$: C, 41.91; H, 6.60; N, 30.55. *Found*: C, 41.95; H, 6.60; N, 30.49.

5-(Dimethylamino)-4-methylisosydnone (16). To a stirred solution of 75 mL of ethyl acetate and 3.00 g (0.0195 mol) of 2,4,4-trimethylsemicarbazide in a 300-mL three-necked flask was added 1.53 mL (0.0128 mol) of trichloromethyl chloroformate in 50 mL of ethyl acetate dropwise over a 90-min period. During the addition the solution was warmed to maintain homogeneity. When the reaction mixture was cooled (ambient), a white solid appeared. The mixture was filtered and the filtrate concentrated (rotary evaporator), yielding a clear yellow oil. The oil was extracted with 4 × 10 mL of cold anhydrous ethyl ether and the ether layer concentrated under vacuum, yielding a clear yellow oil. The oil was purified by preparative TLC (silica gel, 2:2:1 acetone/hexanes/chloroform). The product with R_f 0.7 was extracted from the silica gel with ethyl ether, and the ether layer was concentrated under vacuum. Crystals formed over a 48-h period: mp 42–44 °C; IR ($CHCl_3$) 1780, 1640 cm^{-1}; NMR ($CDCl_3$) 3.2 (s, 3 H), 2.9 (s, 6 H); MS, *m/e* (relative intensity) 143 (21), 72 (100).

Photolysis of Dimethylcarbamoyl Azide in the Presence of Methyl Isocyanate. A stirred solution of 6.48 g (0.057 mol) of dimethylcarbamoyl azide, 11.6 g (0.203 mol) of freshly distilled methyl isocyanate, and 75 mL of N_2-purged CH_2Cl_2 in a 3.2 × 47 cm quartz tube was photolyzed for 70 h, resulting in 59% azide decomposition (determined by N_2 evolution). The orange solution was concentrated by evaporation and triturated with 16 × 15 mL of dry Et_2O under anhydrous conditions, yielding 2.12 g (0.015 mol, 44%) of 1,1,4-trimethyl-1,2,4-triazolidine-3,5-dione 1,2-ylide (**6**). TLC of the concentrated ether layer revealed three products. The major band, R_f 0.5, was isolated by preparative TLC, collected by extraction with 3 × 50 mL of Et_2O, dried ($MgSO_4$), and concentrated under vacuum. The resultant orange oil, *N*-(dimethylcarbamoyl)-*N,N',N'*-trimethylazodicarboxamide (**7**) crystallized after 24 h at 4 °C. The yield, determined by UV analysis, was 1.54 g (0.0067 mol, 40%).

Photolysis of Dimethylcarbamoyl Azide in the Presence of Aminimide 6. A stirred and nitrogen-purged solution of 2.43 g (21.3 mmol) of dimethylcarbamoyl azide and 1.02 g (7.09 mmol) of aminimide **6** in 60 mL of CH_2Cl_2 was prepared. Initial samples for IR and UV analyses were obtained before photolysis for 128 h. The homogeneous mixture was again sampled for analysis.

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(18) Vogelsang, C. *Recl. Trav. Chim. Pays-Das* **1943**, *62*, 5.
(19) Jensen, K. A. *Acta Chem. Scand.* **1977**, *31*, 145.

Forty-four percent (10 mmol) of the azide was decomposed (gas evolution) and 24% (1.7 mmol) of the aminimide (IR analysis) was decomposed; 1.0 mmol of azo compound **7** (UV analysis) was produced, which is 59% of the aminimide decomposed. The reaction mixture was concentrated (rotary evaporator), the aminimide **6** removed via ether trituration, and the resulting organic layer subjected to preparative TLC. The main product with R_f 0.5 was isolated and provided IR, NMR, and UV spectra identical with that of azo compound **7**.

Base Hydrolysis of *N*-(Dimethylcarbamoyl)-*N*,*N*',*N*'-trimethylazocarboxamide (7). To 0.2 g (0.9 mmol) of azo compound **7** in a 100-mL, helium-purged round-bottom flask connected by Tygon tubing to a 100-mL, three-necked flask filled and submerged in helium-purged $CHCl_3$ was added 20 mL of 10% NaOH via a syringe. The resulting yellow solution effervesced for 2 min. The solution was stirred 14 h and then extracted with 12 × 20 mL of $CHCl_3$. The chloroform layer was dried ($MgSO_4$) and concentrated under vacuum, producing a yellow oil that promptly crystallized. The yellow crystals were purified by preparative TLC (1:1:1 $CHCl_3$/hexanes/acetone). The major band at R_f 0.5 was isolated, producing a solid with spectral characteristics identical with that of 1,1,3-trimethylurea: IR ($CHCl_3$) 3500, 1650 cm^{-1}; NMR ($CDCl_3$) 2.83 (d, 6 H), 2.90 (s, 3 H).

Analysis by GC indicated the gas evolved during the reaction and collected in the 100 mL, three-necked flask was N_2. The presence of CO_2 (dissolved in the aqueous layer as Na_2CO_3) was indicated by a turquoise blue precipitate which resulted upon the addition of $CuCl_2$ (aq). The presence of carbonate ion was also indicated by the evolution of CO_2 when the aqueous layer was added dropwise to concentrated HCl. The aqueous layer was evacuated with a vacuum pump equipped with a helium-purged $CHCl_3$ trap cooled by dry ice/alcohol. After the pumping procedure, dry HCl gas was bubbled through the $CHCl_3$ in the trap, precipitating *N*,*N*-dimethylamine hydrochloride: mp 163-167 °C (lit. 171 °C); IR (Nujol) 3450, 1030, 890 cm^{-1}.

Photolysis of 1,1,4-Trimethyl-1,2,4-triazolidine-3,5-dione 1,2-Ylide (6) in the Presence of Methanol. A stirred solution of 0.526 g (3.67 mmol) of **6**, 5.00 mL of MeOH, and 55.0 mL of CH_2Cl_2 was photolyzed for 42.7 h, resulting in essentially quantitative decomposition of **6** (IR analysis). The photolysis yielded methyl methylcarbamate (**10**) [IR (CH_2Cl_2) 3450, 1730 cm^{-1}] and methyl dimethylcarbazate (**9**) [IR (CH_2Cl_2) 3450, 1738 cm^{-1}; NMR ($CDCl_3$) 3.68 (s, 3 H), 2.56 (s, 6 H)] determined by GC (QF-1, 175 °C) and the methanolysis product,[7] 1,1,4-trimethyl-4-(methoxycarbonyl)semicarbazide [NMR ($CDCl_3$) 3.78 (s, 3 H), 3.20 (s, 3 H), 2.63 (s, 6 H)], isolated by preparative GC (QF-1, 220 °C).

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Registry No. **6**, 54133-08-3; **7**, 103836-47-1; **8**, 33345-40-3; **9**, 55741-07-6; **10**, 6642-30-4; **16**, 103836-49-3; MeNCO, 624-83-9; $Me_2NC(O)N(Me)C(O)NHNHC(O)NMe_2$, 103836-48-2; $ClC(O)OCCl_3$, 503-38-8; Me_2NH·HCl, 506-59-2; dimethylcarbamoyl azide, 13750-17-9; 4,4-dimethylsemicarbazide, 40685-92-5; 2,4,4-trimethylsemicarbazide, 28163-21-5; 1,1,3-trimethylurea, 632-14-4; 1,1,4-trimethyl-4-(methoxycarbonyl)semicarbazide, 103836-50-6.

Cyclopentannulation with a 1,3-Dicarbonyl Dipole Equivalent. Synthesis of Bicyclo[3.3.0]oct-1(5)-ene-2,6-dione

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2-(2,2-Diethoxyethyl)-1,3-dithiane (**5**) in its anionic form undergoes Michael addition to 2-cyclopentenone. Acid hydrolysis of the adduct gives rise to the pair of epimeric diquinane aldols **9** and **10** as well as **11** in ratios that are sensitive to both acid concentration and reaction time. The dehydration of **9** and **10** can be controlled to deliver either the conjugated enone **12** or its β,γ isomer **13**. While **12** is the kinetic product, **13** is thermodynamically favored because of lesser steric strain. Removal of the dithioketal function in **12** and **13** with methyl iodide in hot aqueous acetone leads exclusively to enedione **14**, a molecule much more subject to air-oxidation and self-polymerization than its congeners **15** and **16**.

In the context of projected syntheses of the structurally interesting lycopodium alkaloids magellanine (**1**)[1] and paniculatine (**2**),[2] we have concerned ourselves with assembling the central B/C diquinane unit by an annulation scheme that would place both five-membered rings at oxidation levels suitable for subsequent controlled chemical modification. Since an attractive retrosynthetic analysis involved use of a 1,3-dicarbonyl dipole typified by **3** where the two carbonyl groups are suitably differentiated, efforts have presently been made to develop suitable methodology along these lines in a model system.

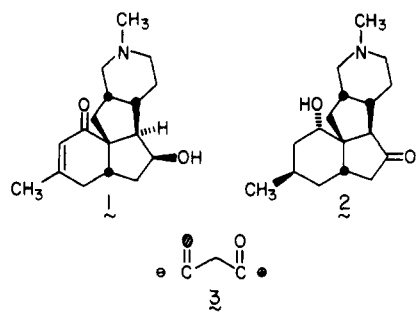

Table I. Product Distributions Arising from Acid-Catalyzed Hydrolysis-Aldolization of 7 (20 °C, Acetone Solution, N_2 Atmosphere)[a]

aqueous HCl, %	reactn time, h	product distribution, % 8	9	10	11
1	144	12.3	5.2	42.8	30.7
5	60	1.3	24.1	20.6	27.5
5	84	0.6	14.4	38.5	33.5
10	20			53.4	32.0

[a] Values represented isolated yields following MPLC on silica gel.

(1) (a) Castillo, M.; Loyola, L. A.; Morales, G.; Singh, I.; Calvo, C.; Holland, H. L.; MacLean, D. B. *Can. J. Chem.* **1976**, *54*, 2893. (b) Loyola, L. A.; Morales, G.; Castillo, M. *Phytochemistry* **1979**, *18*, 1721.

(2) Castillo, M.; Morales, G.; Loyola, A.; Singh, I.; Calvo, C.; Holland, H. L.; MacLean, D. B. *Can. J. Chem.* **1975**, *53*, 2513; **1976**, *54*, 2900.

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