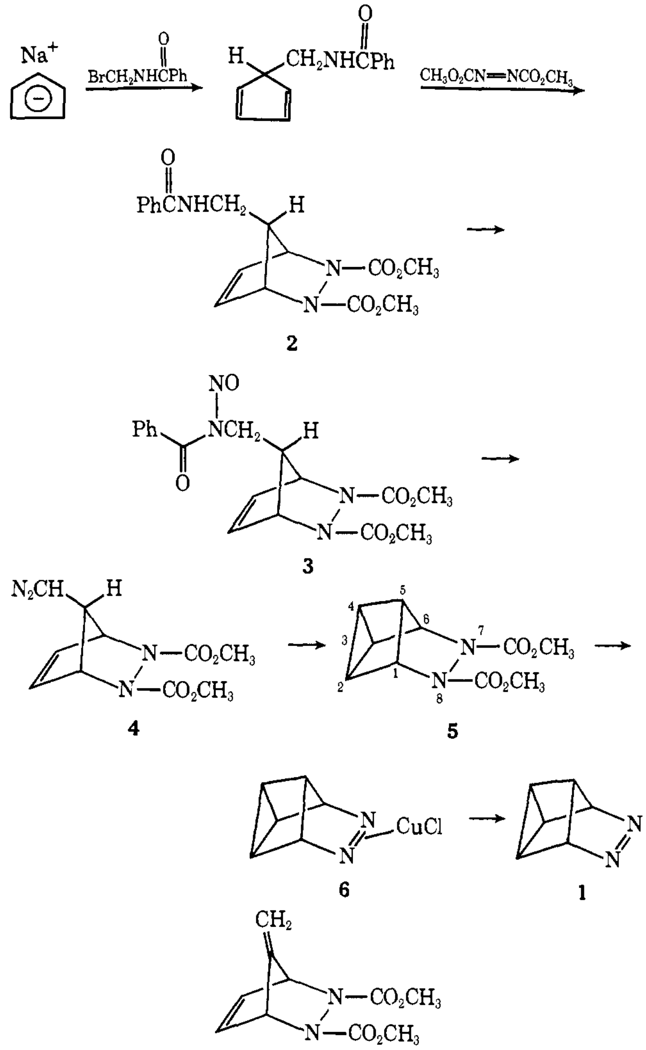
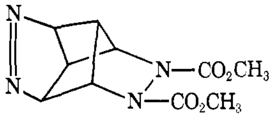
Scheme I. Synthetic Sequence



of dienophile to diene.[6] Independent generation of related compounds in the anti series[7] as well as ultimate success of the synthetic plan confirmed the assignment. Conversion of **2** to nitrosamide **3** using dinitrogen tetroxide in methylene chloride at 0° proceeded in 95% yield. Treatment of **3** with sodium methoxide in tetrahydrofuran at 0° gave a 60% yield of diazo compound **4**: nmr ($CDCl_3$) δ 2.89 (d of m, 1, J = 7 Hz, 7-CH), 3.34 (d, 1, J = 7 Hz, CHN_2), 3.79 (s, 6, OCH_3), 5.02 (m, 2, bridgehead CH), 6.48 (t, 2, J = 2 Hz, vinyl CH); ir (CH_2Cl_2) 2070 cm^{-1}. Irradiation of a crude solution of **4** with a 450-W mercury vapor lamp fitted with a Pyrex filter at −78° generated the desired tetracyclic carbamate ester **5** (28% overall isolated yield based on **3**) in addition to the product of hydrogen migration, **7** (15% overall isolated yield based on **3**). Compound **5** showed the following characteristics:[5] nmr ($CDCl_3$) δ 2.23 (m, 2, J = 5.5, 4.7, 3.3, 2.0, and 1.0 Hz, 2- and 3-CH), 2.53 (t of d, 1, J = 3.3 and 0.8 Hz, 4-CH), 2.96 (t of t of d, 1, J = 4.7, 4.7, and 0.8 Hz, 5-CH), 3.78 (s, 6, OCH_3), 5.00 (d of m, 2, J = 4.7, 2.0, 1.0, and 0.2 Hz, 1- and 6-CH); ir (CCl_4) 1748, 1709 cm^{-1}. Compound **7**[5] was compared to an authentic sample generated independently by the addition of fulvene to dimethyl azodicarboxylate.[8] Saponification of the cyclic carbamate **5** with methanolic potassium hydroxide at 25° followed directly by oxidation of the hydrazine with cupric chloride produced the brick red cuprous chloride complex **6**. Azo compound **1** was released from the complex by treatment with aqueous sodium hydroxide. Recrystallization from pentane at −78° gave a 75% yield (overall yield from **5**) of **1**[5] as a colorless hygroscopic solid: nmr ($CFCl_3$) δ 2.19 (m, 3, cyclopropyl H), 2.79 (m, 1, 5-CH), 5.74 (m, 2, 1- and 6-CH); ir (CCl_4) 1493 cm^{-1} (-N=N-); uv (cyclohexane) λ_{max} (log ϵ) 357 (sh, 2.37), 363 (2.46), 368 (2.46), 372 (2.49), and 381 nm (2.40).[9]

The intramolecular carbene addition to the double bond (conversion of **4** to **5**) is quite interesting in light of Hoffmann's calculations regarding the geometry for singlet carbene additions.[10] These calculations indicate that for a concerted cycloaddition the p orbital of the carbene overlaps in a σ manner *with one end* of the ethylene π bond. This lopsided configuration is unattainable in the carbene derived from **4** without severely distorting the rigid bicyclic framework. In agreement with this hypothesis, attempted thermal decomposition of **4** in the presence of copper salts failed to generate any insertion product **5**. Success of the photolysis may be attributable to the intermediacy of either a triplet carbene or to nitrogen loss from an intermediate 1,3-dipolar adduct **8**.[11]



8

Our approach to 7,8-diazatetracyclo$[3.3.0.0^{2,4}.0^{3,6}]$oct-7-ene is quite flexible and clearly should be applicable to the all-carbon system as well.

Acknowledgment. We wish to express our appreciation to the National Science Foundation for their generous support of our programs.

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[6] In some of the cycloadditions to 5-substituted cyclopentadienes, additions to the more hindered side have been observed. See, for example, (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955); (b) S. McLean and P. Haynes, *Tetrahedron Lett.*, 2313 (1965); (c) K. L. Williamson and Y.-F. L. Hsu, *J. Amer. Chem. Soc.*, **92**, 7385 (1970).

[7] Generated by catalytic hydrogenation of dimethyl 7-alkylidene-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate.[8]

[8] R. M. Cory, unpublished results in these laboratories.

[9] Compare the uv spectrum of 8,9-diazatetracyclo$[4.3.0.0^{2,4}.0^{3,7}]$non-8-ene; R. M. Moriarty, *J. Org. Chem.*, **28**, 2385 (1963).

[10] R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

[11] For an example of this process, see M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).

[12] Henry and Camille Dreyfus Teacher-Scholar Grant Recipient.

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The Thermal and Photochemical Decomposition of 7,8-Diazatetracyclo$[3.3.0.0^{2,4}.0^{3,6}]$oct-7-ene. 1,2-Diazacycloocta-2,4,6,8-tetraene

Sir:

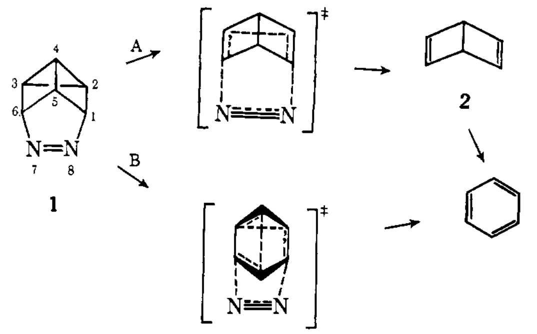
In the preceding communication,[1] we reported the synthesis of 7,8-diazatetracyclo$[3.3.0.0^{2,4}.0^{3,6}]$oct-7-ene

[1] B. M. Trost and R. M. Cory, *J. Amer. Chem. Soc.*, **93**, 5572 (1971).

(1)—a potential precursor of the parent prismane molecule.[2] Studies of its thermal and photochemical decomposition have generated insight regarding the high walls along its reaction pathways created by orbital symmetry and a synthesis of the fascinating 1,2-diazacycloocta-2,4,6,8-tetraene molecule.[3]

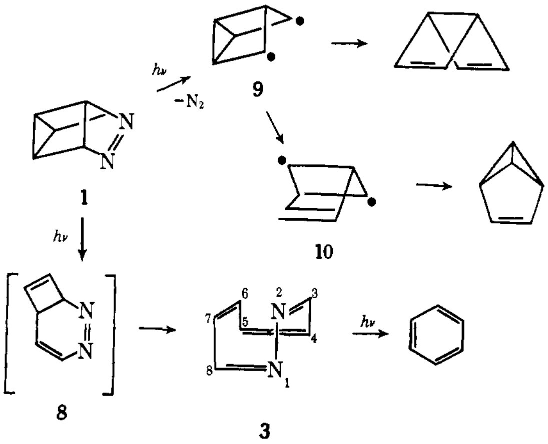
The azo compound 1 was stable up to 160° in hexachlorobutadiene at which temperature it underwent transformation to benzene exclusively. Slow sublimation at 0.2 mm pressure through a column packed with glass helices at 230° produced only benzene in addition to starting material. Two pathways may be envisioned (see Scheme I). Path A represents the symmetry-allowed six-electron process involving Dewar benzene (2) as a discrete intermediate. Conversion of 2 to benzene proceeds rapidly at 90°.[4] Path B depicts a novel eight-electron process providing a direct pathway for highly strained azo compound 1 to the thermodynamic sink benzene. The likelihood that some Dewar benzene should have survived the flow pyrolysis system makes us favor path B at present. The surprisingly high activation energy that must be associated with the thermal decomposition may arise from the poor initial overlap between the C_4–C_5 and C_2–C_3 bonds.[5]

Scheme I. Thermal Decomposition of **1**

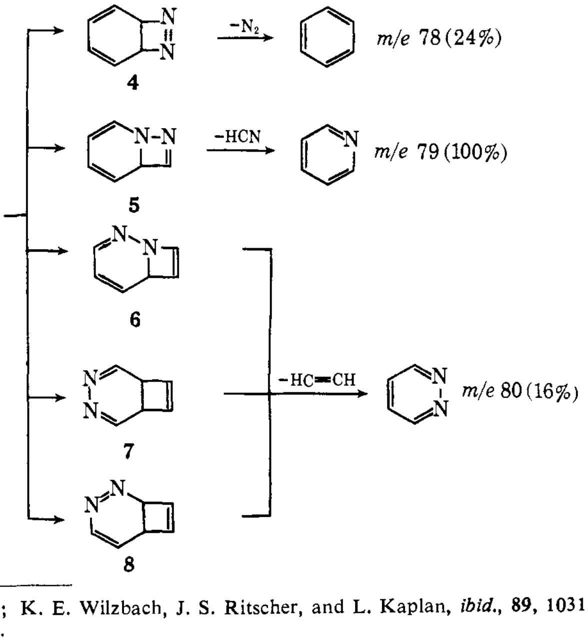


Since paths A and B are photochemically forbidden, it was anticipated that the photoexcited state would dissipate its excess energy mainly by disengagement of molecular nitrogen to a diradical (see Scheme II).[6] Photolysis through Pyrex at −78° with a 450-W mercury vapor lamp produced only small amounts (about 2% each) of the expected $(CH)_6$ isomers Dewar benzene,[4] benzvalene,[7] and benzene. No conclusive evidence for the formation of prismane could be obtained.[8] Furthermore, the amount of benzene increased at the expense of the major photochemical product 3. This product was isolated by thick-layer chromatography on silica gel PF 254 eluting with 1:1 ether-methylene chloride. Mass spectrometry established the molecular formula of 3 as $C_6H_6N_2$ (calcd, 106.05306; found, 106.05222). The nmr spectrum showed two singlets in the ratio 2:1 at δ 6.08 and 6.93.[9] The ultraviolet spectrum shows a λ_{max} 374 nm (log ε ~2.3) in addition to end absorption. Independent photolysis of 3 under the same conditions as for 1 generates a quantitative yield of benzene. This evidence is uniquely in accord with 1,2-diazacycloocta-2,4,6,8-tetraene (3)[10] as the major photoproduct (70% yield). The mass spectrometric fragmentation pattern provides strong confirmation of this structure. The major fragments (Scheme III)

Scheme II. Photolytic Decomposition of **1**



Scheme III. Mass Spectral Fragmentations



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[2] Although substituted prismanes are known, the parent system remains elusive. See K. E. Wilzbach and L. Kaplan, *ibid.*, **87**, 4004 (1965); R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **5**, 519 (1966); D. M. Lemal and J. P. Lokensgard, *J. Amer. Chem. Soc.*, **88**, 5934 (1966).

[3] This ring system with the double bonds depicted in structure 3 is unknown. For related structures in the dibenzo series see W. W. Paudler and A. G. Zeiler, *Chem. Commun.*, 1077 (1967); W. W. Paudler and A. G. Zeiler, *J. Org. Chem.*, **34**, 3237 (1969). A series of highly substituted diazabicyclo[4.2.0]octatrienes, a valence tautomeric system, has been prepared; see G. Maier, U. Heep, M. Wiessler, and M. Strasser, *Chem. Ber.*, **102**, 1928 (1969).

[4] E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963).

[5] The question of orbital symmetry allowedness or forbiddenness associated with this eight-electron process is ambiguous. Application of simple correlation diagrams or rules are unreliable due to the fact that the symmetry plane contains one of the reacting bonds. Extended Hückel calculations (R. Hoffmann, private communiction) seem to indicate noninvolvement of the 4,5 bond. For a careful study of the factors involved in decomposition of tetracyclo[$3.2.1.n^{3,8}.0^{2,4}$]azo compounds see E. L. Allred and A. L. Johnson, *J. Amer. Chem. Soc.*, **93**, 1300 (1971).

[6] R. M. Moriarty, *J. Org. Chem.*, **28**, 2385 (1963). For contrasting results, see R. C. Cookson, S. S. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).

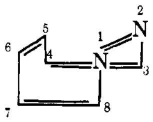
[7] H. R. Ward and J. S. Wishnok, *J. Amer. Chem. Soc.*, **90**, 1085 (1968); K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *ibid.*, **89**, 1031 (1967).

[8] In one of our experiments, a singlet at δ 2.8 appeared at −78° which disappeared after a few hours at −78°. No corroborative evidence to assign the absorption to prismane could be obtained.

[9] Similar characteristics have been noted for 2-methoxy-1-azacyclooctatetraene: L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Philips, *J. Amer. Chem. Soc.*, **93**, 152 (1971).

[10] The fact that the bond-shift isomers of the higher substituted annulenes frequently represent different tautomers (not resonance forms) presents a nomenclature problem. For the present case, differentiation of 3 and 3a may best be indicated by assigning positions to the double bonds. Thus, 3 becomes 1,2-diazacycloocta-2,4,6,8-tetraene and 3a 1,2-diazacycloocta-1,3,5,7-tetraene.

clearly arise by initial valence tautomerization to the bicyclo[4.2.0]octatrienes **4**–**8**, followed by cleavage to the aromatic radical cations of benzene, pyridine, and pyridazine. The formation of pyridine as the major fragment is in accord with energy considerations. Thus, the bond isomer **3** should be greatly preferred to **3a**[11] and it should cyclize preferentially to valence isomer **5**. 1,2-Diazacycloocta-2,4,6,8-tetraene is stable in solution below room temperature and decomposes to tars slowly in solution at room temperature and rapidly in the neat.



3a

The photochemical decomposition of **1** stands in stark contrast to the thermal decomposition. Scheme II provides a rationale for these observations. Note that benzene arises only indirectly as a secondary photolysis product of **3**. Indeed, support for this interpretation arises from consideration of the product ratios as a function of photolysis time (*vide supra*). Formation of benzene as the exclusive photoproduct of **3** demands the intermediacy of the bicyclic isomer **4** which subsequently loses nitrogen presumably also by a photochemical step.[12,13]

Thus the photoexcited state of **1** dissipates energy to only a minor extent by nitrogen disengagement to diradical **9**. This species either collapses to Dewar benzene or diradical **10**, the precursor of benzvalene.[14] The major process for energy dissipation is the allowed 2 + 2 reversion to the diazabicyclo[4.2.0]octatriene (**8**). Even at −78° this compound rearranges to **3** in striking contrast to bicyclo[4.2.0]octa-2,4,7-triene which is quite stable at this temperature.[15] The lower activation energy for the rearrangement of **8** to **3** compared to the all-carbon system presumably reflects the stability gained in terms of bond energies in generating the azine moiety. A concerted pathway is conceivable for the conversion of **1** to the bond shift isomer of **3** (*i.e.*, **3a**); this would be a formal $[{}_{\sigma}2_{s} + {}_{\sigma}2_{a} + {}_{\sigma}2_{a}]$ cycloreversion, photochemically forbidden by orbital symmetry considerations.

Acknowledgment. We wish to express our appreciation to the National Science Foundation for their generous support of our programs.

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(11) Similar behavior has been noted for derivatives of 1,2-diazacycloocta-1,3,7-triene which prefer to exist as 3,4-diazabicyclo[4.2.0]-octa-2,4-dienes: G. Maier and F. Seidler, *Chem. Ber.*, **99**, 1236 (1966).

(12) Compare the photolysis of cyclooctatetraene and bicyclo[4.2.0]-octa-2,4,7-triene to benzene and acetylene: H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc.*, **92**, 2015 (1970), and references therein. For azine photolysis see R. W. Brinkley, *J. Org. Chem.*, **34**, 931 (1969).

(13) $\Delta^{1,2}$-Diazetines have been shown to be remarkably stable thermally: N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *J. Amer. Chem. Soc.*, **91**, 5668 (1969).

(14) This process is comparable to the presumed intermediates in the di-π-methane rearrangement. For a leading reference, see H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267, 6259, 1407, 1409 (1970).

(15) E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964).

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(17) National Science Foundation and National Institutes of Health Predoctoral Fellow.

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Nucleophilic Additions to Allenes. A New Synthesis of α-Pyridones

Sir:

A 1,3-dicarboalkoxyallene might be expected to serve as a powerful receptor toward Michael addition since the resultant anion would be a highly stabilized glutaconate system.[1,2] Surprisingly, the synthetic applications of such allenes[3] have been limited to Diels–Alder reactions.[4] With a total synthesis of camptothecin[5] as our orienting goal, we studied the feasibility and utility of Michael additions to compound I (R = Et).[6–8]

Condensation of equimolar quantities of I with ethyl *trans*-β-aminocrotonate in the presence of 1 equiv of triethylamine gives an adduct which, when heated in 1:1 acetic acid–toluene at 100 for 5 hr, gives pyridone III, mp 128–130°, in 70% overall yield. The structure of III follows from its monohydrolysis product (2 equiv of NaOH ethanol, reflux 3 hr) IV which smoothly decarboxylates at its melting point (195°) to give the known[9] 4,6-dimethyl-5-carbethoxy-α-pyridone (V). Interestingly, treatment of IV with chloromethyl methyl ether in acetic acid gave lactone VI, mp 233–235°,[10,11] in 31% yield. While we have not carried compound VI further, the demonstration of the feasibility of this type of insertion played a crucial role in formulating a strategy for synthesizing camptothecin.[12]

Allene I is also attacked by monoenamines of β-diketones. Thus, condensation of 4-aminopent-3-en-4-one[13] with I using the conditions described above gave VIII, mp 141–143°,[10,11] in 48% yield. This new synthesis of α-pyridones may be executed with preservation of acid-sensitive functionality. Carbomethoxylation of 3,3-diethoxybutanone[14] (sodium hydride–dimethyl carbonate–benzene) gives β-keto ester VIII,[10,11] which is converted in 50% yield to enamine IX. Condensation of the latter with allene I in ethanol containing 1 equiv of triethylamine at room temperature gives pyridone X, mp 123–127°,[10,11,15] in 36% yield. Half-saponi-

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(1) The full stabilization of the glutaconate system at the level of the transition state of addition requires a rotation about the C_2–C_3 bond. This argument has already been set forth in the context of the addition of amines to 1-cyanoallene.[2]

(2) P. M. Greaves and S. R. Landor, *Chem. Commun.*, 322 (1966).

(3) For a most unusual reaction in the addition of 1-morpholinocyclohexane with cyanoallene, see W. Reid and W. Kaepeller, *Justus Liebigs Ann. Chem.*, **687**, 183 (1965).

(4) G. Büchi and J. A. Carlson, *J. Amer. Chem. Soc.*, **90**, 5336 (1968).

(5) M. E. Wall, M. C. Wani, C. E. Cook, K. H. Palmer, A. T. McPhail, and G. A. Simm, *ibid.*, **88**, 3888 (1966).

(6) The correct structures of the parent diacid and dimethyl ester were established by E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 3208 (1954).

(7) The method of preparing I was that of J. C. Craig and M. Moyle, *ibid.*, 5356 (1963).

(8) A new route to derivatives of allenedicarboxylic acid has recently been developed by J. Ficini and J. Pouliquen, *J. Amer. Chem. Soc.*, **93**, 3295 (1971).

(9) J. N. Collie, *J. Chem. Soc.*, 297 (1897).

(10) Molecular formulas were verified by either combustion analyses or in the case of compounds III–VII by high-resolution mass spectrometry.

(11) The assigned structure is consistent with the ir, nmr, and mass spectra of the product.

(12) R. Volkmann, S. Danishefsky, J. Eggler, and D. M. Solomon, *J. Amer. Chem. Soc.*, **93**, 5576 (1971).

(13) For a related reaction of this enamine with dimethyl acetylenedicarboxylate, see: C. Heubner, L. Dorfman, M. M. Robinson, E. Donoghue, and P. Straehen, *J. Org. Chem.*, **28**, 3134 (1963).

(14) For ethoxyalylation, see: H. Muxfeldt, M. Weigele, and V. Rheenen, *ibid.*, **30**, 3573 (1965).

(15) The use of hydroxylic solvent tends to promote one-step cycliza-