7i (R_S,S,S) as a colorless oil: IR ($CDCl_3$) 1058 cm^{-1} ($\nu_{S=O}$); ^1H NMR ($CDCl_3$) δ 0.94 (s, 3 H), 0.95 (s, 3 H), 1.10 (d, 3 H, J = 6 Hz), 1.10–1.35 (masked m, 2 H), 1.53 (s, 2 H), 1.85–2.40 (m; 1 H), 2.51 (s, 3 H), 3.57 (d, 1 H, J = 2 Hz); (C_6D_6) δ 0.62 (s, 3 H), 0.69 (s, 3 H), 0.75–1.0 (masked m, 2 H), 1.22 (s, 2 H), 2.10 (s, 3 H), 3.47 (d, 1 H, J = 2 Hz); ^{13}C NMR δ 17.9, 25.9, 26.4, 29.7, 31.1, 32.4, 36.4, 39.8, 59.3, 73.0. Anal. Calcd for $C_{10}H_{18}O_2S$: C, 59.36; H, 8.97; O, 15.82. Found: C, 59.36; H, 9.12; O, 15.62.

Characterization of the Intermediate α-(Methylthio) Epoxide 2i. The reaction of 3,5,5-Trimethyl-1-(methylthio)-cyclohexene (**1i**) with 1 molar equiv of ozone in chloroform, according to the above general procedure (method A), was monitored by ^1H NMR as follows: at the end of the reaction, a crude sample was transferred from reaction vessel into the NMR tube. Its spectrum was immediately recorded at −80 °C. Then, from −80 °C to room temperature, NMR spectra were taken regularly. The characteristic signal for the epoxidic proton of **2i** (doublet at 3.2 ppm) disappeared near 0 °C, giving way to new signals of the corresponding allylic alcohol **3i**.

1,2-Epoxy-3,5,5-trimethylcyclohexyl methyl sulfide (2i): ^1H NMR ($CDCl_3$, −78 → 0 °C) δ 0.85–1.2 (m, 14 H), 1.85 (s, 2 H), 2.15 (s, 3 H), 3.24 (d, 1 H, J = 2 Hz).

Solvent and Temperature Effects. When the reactions of **1g** and **1i** with ozone (method A) were conducted in pentane or anhydrous ether with or without pyridine, at −78 °C, there were no significative differences between the ^1H NMR spectra of the crude concentrated mixtures. In these runs, allylic alcohols **3g** and **3i** were obtained as major products (~85% yields). Nevertheless, pyridine was still effective as a reducing agent since ozonide formation could occur to some extent.

Temperature effects were found to be more pronounced. When **1d** (1.2 g, 6 mmol) was allowed to react with 1 equiv of ozone in CH_2Cl_2 above 0 °C, the expected allylic alcohol **3d** was formed in 60% yield together with epoxy sulfoxides **6d** and **7d** (10–15%) and the ozonolysis compound **5d** (15% in isolated yield). Under the same conditions, with more hindered vinyl sulfides **1g** and **1i**, 25% of the corresponding vinyl sulfoxides were produced along with the allylic alcohols (about 50%). In the former case, besides some unreacted vinyl sulfide **1g**, also isolated was 2,3-epoxy-4,4,6,6-tetramethyl-2-(methylsulfinyl)cyclohexanol[5] (10%).

Pyrolysis and Photolysis of 6,7-Diazatricyclo[3.2.2.1^{2,4}]dec-6-ene

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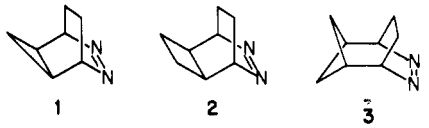
Pyrolysis at 200 °C and direct and sensitized photolysis of the title compound (**3a**) produced only *cis*-1,3-divinylcyclobutane (**6a**) and tricyclo[4.1.1.0^{2,5}]octane (**7a**). The latter hydrocarbon was prepared by an independent synthesis, which involved photochemical ring closure of bicyclo[4.1.1]octa-2,4-diene (**8**) to tricyclo[4.1.1.0^{2,5}]oct-3-ene (**9**), followed by hydrogenation of **9**. The ratio of **6a** to **7a** was 2.4:1 in the pyrolysis reaction, 3.3:1 in the direct photolysis, and >50:1 when the photolysis of **3a** was photosensitized. The kinetics of nitrogen loss from **3a** were measured at three different temperatures to yield log k (s^{-1}) = 15.0 ± 1.0 − (38 300 ± 2200)/2.3RT, with R in cal/mol·K. The stereochemistry of product formation was determined by preparation of the deuterium labeled azo compound **3b**. The **6** that resulted from pyrolysis and direct and sensitized photolysis of **3b** contained a 1:1 mixture of vinyl groups with E and Z stereochemistry. The ratio of **7b** to **7c** was 1.2:1 in the pyrolysis reaction and 1:2.4 in the direct photolysis, indicating 10% excess double retention of configuration in the former reaction and 40% excess double inversion in the latter. These results are discussed, and it is concluded that the high-lying filled orbitals of the 1,3-bridged cyclobutane ring of **3** have no apparent effect on its deazetation.

The bent bonds of suitably oriented cyclopropane rings have been shown to participate in concerted, $_\sigma2_s + _\sigma2_s + _\sigma2_s$ extrusion of nitrogen from azo compounds.[1] For example, the cyclopropane ring in **1** accelerates the rate of nitrogen loss from **1** dramatically compared to that from 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO).[2,3] The activation enthalpy of 21.5 kcal/mol for **1**[4] is less than half that of 43.5–45.0 kcal/mol for DBO.[5] Moreover, the only organic product formed in the thermally induced loss of nitrogen from **1** is 1,4-cycloheptadiene,[2,3] which is the product expected from cleavage of the participating cyclopropane ring bond.



1 **2** **3**

Edge participation by cyclobutane in nitrogen extrusion reactions is less well established. For example, although the enthalpy of activation of 38.5 kcal/mol for nitrogen loss from **2**[3] is lower than that for DBO, the energy lowering may simply reflect greater strain relief in the transition state for deazetation of **2**.[6] Evidence against edge participation by cyclobutane in the transition state for nitrogen loss from **2** comes from the observation that, in addition to 1,5-cyclooctadiene, small amounts of *anti*-tricyclo[4.2.0.0^{2,5}]octane are formed.[6] Of course, the two products could be generated by separate pathways, the major involving edge participation by cyclobutane and the minor one diradical formation; and it has been argued that cyclobutane edge participation is a borderline situation.[7,8]

Azo compounds like **3**, containing a 1,3-bridged cyclobutane ring, have not been studied. Although edge participation of the cyclobutane ring in the transition state for deazetation of such an azo compound is impossible, the high-lying filled orbitals of the four-membered ring[9] can interact strongly with the orbitals that comprise the bonds between the bridgehead carbons and the departing nitrogen molecule. Interactions between the orbitals of cyclobutane and unsaturated 1,3-bridging groups have been

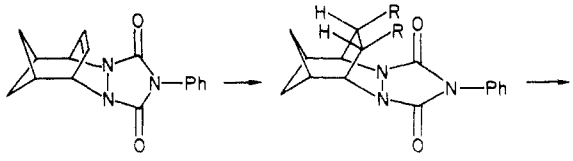
(1) For an excellent review of azo chemistry, see: Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.
(2) Martin, M.; Roth, W. *Chem. Ber.* **1969**, *102*, 811.
(3) Allred, E. L.; Hinshaw, J. C. *J. Chem. Soc., Chem. Commun.* **1969**, 1021.
(4) Snyder, J. P.; Harpp, D. N. *J. Am. Chem. Soc.* **1976**, *98*, 7821.
(5) (a) Cohen, S. G.; Zand, R. *J. Am. Chem. Soc.* **1962**, *84*, 586. (b) Engel, P. S.; Hayes, R. A.; Kiefer, L.; Szilagyi, S.; Timberlake, J. W. *Ibid.* **1978**, *100*, 1876.
(6) Allred, E. A.; Hinshaw, J. C. *Tetrahedron Lett.* **1972**, 387.
(7) Berson, J. A.; Olin, S. S.; Petrillo, E. W.; Bickart, P. *Tetrahedron*, **1974**, *30*, 1639.
(8) Martin, H.-D.; Heiser, B.; Kunze, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 696.
(9) Hoffman, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699.

0022-3263/86/1951-2285$01.50/0

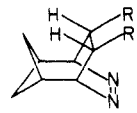
shown to have both spectroscopic[10] and chemical[11,12] consequences. Therefore, it was of some interest to determine how the presence of the four-membered ring in **3** might affect its deazetation.

Results

The preparation of **3** was made possible by our discovery that, unlike its 7,7-dimethyl derivative,[13] the parent bicyclo[4.1.1]octa-2,4-diene[14] reacts with phenyltriazolinedione (PTAD) to form the Diels–Alder adduct **4**.[15] Hydrogenation of **4** to **5a**, followed by hydrolysis and air oxidation, afforded **3a** in 45% yield from **4**, after purification by flash chromatography and sublimation.

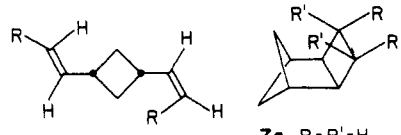


4 **5a**, R = H; **b**, R = D



3a, R = H; **b**, R = D

Pyrolysis of **3a** at 200 °C led to the formation of two hydrocarbons in a ratio of 2.4:1, as determined by capillary GLC. The hydrocarbons were separated by preparative GLC, and each was shown to be stable to the reaction conditions. The IR and ^{1}H NMR spectra of the major product proved identical with those of *cis*-1,3-divinylcyclobutane (**6a**).[16] The minor product was identified as tricyclo[4.1.1.0^{2,5}]octane (**7a**) by its spectra.

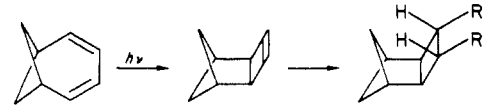


6a, R = H; **b**, R = D

7a, R = R' = H; **b**, R = D, R' = H; **c**, R = H, R' = D

Confirmation of this structural assignment was obtained by independent synthesis of **7a**. Direct photolysis of bicyclo[4.1.1]octa-2,4-diene (**8**) resulted in electrocyclic ring closure to afford tricyclo[4.1.1.0^{2,5}]oct-3-ene (**9**). The photochemical behavior of the parent diene differs from that of its 7,7-dimethyl derivative, which, instead of cyclobutene ring closure, undergoes [1,5]sigmatropic shift of C-7.[17]

Presumably, in the latter diene the two methyl groups attached to this carbon accelerate electronically the rate of C–C bond cleavage at C-7 and also disfavor sterically cyclobutene ring closure syn to C-7. However, in the absence of the methyls at C-7, disrotatory cyclobutene ring closure to **9** is the reaction pathway favored by diene **8** on photolysis. Catalytic hydrogenation of **9** gave **7a**, which proved indistinguishable, both spectroscopically and chromatographically, from the minor product formed in the pyrolysis of **3a**.



8 **9** **7a**, R = H; **b**, R = D

The kinetics of the disappearance of **3a** were followed by GLC at three different temperatures. At each temperature a plot of the log of the concentration of **3a** vs. time was found to be linear through at least one half-life. The first order rate constants were obtained by least-squares fitting. In units of 10^{-4} s^{-1}, they were 2.00 ± 0.21 at 173.5 °C, 6.39 ± 0.84 at 185.0 °C, and 21.6 ± 3.3 at 200.0 °C. From least-squares fitting the temperature dependence of the rate constants was found to be $\log k$ (s^{-1}) = 15.0 ± 1.0 − (38300 ± 2200)/2.3RT, giving $\Delta H^{\ddagger}$ = 37.4 ± 2.2 kcal/mol and $\Delta S^{\ddagger}$ = 7.4 ± 4.6 cal/mol·K.

The direct and sensitized photolyses of **3a** were also investigated. In both photoreactions **6a** and **7a** were again the only two products formed in appreciable (>1%) amounts. The ratio of the two products was 3.3:1 in the direct photolysis, which increased to >50:1 when benzophenone was added as a sensitizer. The small amount of **7a** formed in the sensitized reaction may well come from population of the excited singlet state of **3a**; since, despite the fact that a large excess of benzophenone was used, a few percent of the incident light was absorbed by **3a**.

In order to determine the stereochemistry of product formation, the stereospecifically labeled zero compound **3b** was prepared. It was synthesized by carrying out the reduction of **4** using diimide-d_2.[18] The stereochemistry of the deuterium thus introduced into **3** was established by assigning the protons in the 500-MHz ^{1}H NMR spectrum of **3a** through decoupling and NOE experiments.

The two endo protons on the four-membered ring were easily identified, since each appeared as a triplet. Apparently, the long-range coupling constant between these two protons has almost exactly the same magnitude as the geminal coupling constants to the exo protons. Models show that the dihedral angle between the endo and the bridgehead protons is close to 90°, which is why no coupling to the bridgehead protons is observed. One of the endo protons is shielded by the N–N double bond and so appears at δ 0.68, while the other endo proton appears at δ 1.67, very close to the exo protons at δ 1.70 and 1.74.

The four protons on the two-carbon bridge in **3a** appear as an AA′XX′ pattern at 500 MHZ, one-half of which is centered at δ 1.49 and the other half at δ 1.87. When the two protons at δ 1.87 are irradiated, a large NOE is seen for the endo proton at δ 1.67. However, irradiation at δ

(10) (a) Meinwald, J.; Uno, F. *J. Am. Chem. Soc.* **1968**, *90*, 800. (b) Robin, M. B.; Basch, H.; Keubler, N. A.; Kaplan, B. E.; Meinwald, J. *J. Chem. Phys.* **1968**, *48*, 5037. (c) Meinwald, J.; Tsuruta, H. *J. Am. Chem. Soc.* **1970**, *92*, 2579. (d) Gleiter, R.; Kobayashi, T. *Helv. Chim. Acta* **1971**, *54*, 1081. (e) Bischof, P.; Gleiter, R.; Kukla, M. J.; Paquette, L. A. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *4*, 177. (f) Gleiter, R.; Bischof, P.; Volz, W. E.; Paquette, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 8. (g) Borden, W. T.; Young, S. D.; Frost, D. C.; Westwood, N. P. C.; Jorgensen, W. L. *J. Org. Chem.* **1979**, *44*, 737.

(11) See; for a summary: Borden, W. T.; Gold, A.; Jorgensen, W. L. *J. Org. Chem.* **1978**, *43*, 491.

(12) It has recently been found [Wiberg, K. B.; Wasserman, D. J.; Martin, E. J.; Murcko, M. A. *J. Am. Chem. Soc.* **1985**, *107*, 6019] that the enthalpy of addition of trifluoroacetic acid to bicyclo[2.1.1]hexene is 14.6 and 8.4 kcal/mol more exothermic than the corresponding additions to respectively cyclopentene and norbornene. At least part of the greater reaction exothermicity of bicyclo[2.1.1]hexene is probably due to relief of destabilizing interactions between the π orbital of the double bond and the HOMO of the 1,3-bridged cyclobutane ring in this hydrocarbon.[11]

(13) Borden, W. T.; Young, S. D. *Tetrahedron Lett.* **1976**, 4019. Young, S. D., Ph.D. Thesis, University of Washington, 1979.

(14) First prepared by Volz and Paquette[10f] and subsequently by Yin, Lee, and Borden.[15]

(15) Yin, T.-K.; Lee, J. G.; Borden, W. T. *J. Org. Chem.* **1985**, *50*, 531.

(16) Trautman, W.; Musso, H. *Chem. Ber.* **1981**, *114*, 982.

(17) Young, S. D., Borden, W. T. *J. Org. Chem.* **1980**, *45*, 724. Borden, W. T.; Lee, J. G.; Young, S. D. *J. Am. Chem. Soc.* **1980**, 102, 4841.

(18) Prepared by using the procedure of: Berson, J. A.; Poonian, M. S.; Libbey, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 5567.

1.49 produces no NOE at δ 1.67. These NOE experiments establish that the protons δ 1.87 are spatially proximate to the endo proton at δ 1.67. The proximity of the protons at δ 1.49 to the π cloud of the N–N double bond is presumably responsible for their appearance at higher field.

When the reduction of **4** was performed with N_2D_2, the relative area of the signal at δ 1.49 in the resulting azo compound was reduced to about 15% of that in **3a**. The only peak in the ^{2}H NMR spectrum corresponded to the ^{1}H NMR peak with this chemical shift, indicating that all the deuterium had been incorporated syn to the azo group, as depicted in **3b**. The 1,3-bridged cyclobutane ring is obviously quite effective in blocking the opposite face of the double bond from attack by diimide. The small peak at δ 1.49 in the ^{1}H NMR spectrum of **3b** comes from competitive reduction of **4** by N_2HD, as shown by the mass spectrum, which revealed 70% d_2 species and 30% d_1.

Decoupling experiments established that the resonances at δ 1.42 and 2.11 correspond to the protons on the two-atom bridge in **7a**. Deazetation of **3b** decreased the integrals of both peaks, consistent with this assignment. The stereochemistry of these protons was determined by reducing **9** with N_2D_2, which led to the disappearance of the resonance at δ 2.11 in **7a**. Since the endo face of the double bond in **9** is blocked by the one-carbon bridge that is syn to it, reaction of **9** with N_2D_2 should lead to the formation of **7b**. Thus, a peak at δ 2.11 in the ^{2}H NMR spectrum of the tricyclic hydrocarbon formed from **3b** signals the presence of **7b**, while a peak at δ 1.42 indicates the formation of **7c**.

From integration of these two peaks in the ^{2}H NMR spectrum, the ratio of **7b**, the product of double retention, to **7c**, the product of double inversion, was established. This ratio was 1.2:1 in the pyrolysis of **3b**; but double retention became disfavored compared to double inversion by a ratio of 1:2.4 in the direct photolysis of **3b**.

The vinyl groups of the *cis*-1,3-divinylcyclobutane that was formed in the pyrolysis and in the direct and sensitized photolysis of **3b** showed a 1:1 mixture of *E* and *Z* stereochemistries by both ^{1}H and ^{2}H NMR. However, the spectra do not allow one to distinguish between *E,Z* molecules (**6b**), a 1:1 mixture of *E,E* and *Z,Z* molecules, or a combination of these two possibilities.

Discussion

Despite the fact that our kinetic data show rather larger error limits than we would have liked, they are, nevertheless, sufficiently accurate to establish that the kinetic parameters for deazetation of **3** are similar to those for **2** (at 175 °C, $k = 4.92 \times 10^{-4}$ s^{-1}, $\Delta H^{\ddagger} = 38.5$ kcal/mol, $\Delta S^{\ddagger} = 11$ cal/mol·K).[3] It seems likely that some relief of van der Waals repulsions between bridges in the transition state for nitrogen loss from **2** and **3** is responsible for the fact that both reactions have values of $\Delta H^{\ddagger}$ that are approximately, 5 kcal/mol lower than that for deazetation of DBO. However, if this is the case, it is somewhat surprising that the value of $\Delta H^{\ddagger}$ for nitrogen loss is so similar for **2** and **3**, since molecular mechanics calculations suggest that there is significantly greater strain relief attending the loss of nitrogen from **3** than from **2**.

MM2 calculations[19] were performed on the hydrocarbons corresponding to **2** and **3**. The strain energies computed were, respectively, 47.2 and 62.9 kcal/mol. The diradicals formed from **2** and **3** by nitrogen loss were modeled respectively by bicyclo[4.2.0]- and bicyclo[4.1.1]octa-2,4-diene. Their strain energies were calculated to be respectively 33.8 and 37.1 kcal/mol. Although the results of these model calculations obviously have no quantitative significance, they do suggest stronger van der Waals repulsions between the four-membered ring and the two-atom bridges in **3** than in **2**. Indeed, we have attributed the reluctance of bicyclo[4.1.1]octa-2,4-dienes to enter into Diels–Alder reactions to the development of such repulsions in the transition states for these cycloadditions.[15]

The very similar values of $\Delta H^{\ddagger}$ for **2** and **3** suggest that only a small fraction of the van der Waals repulsions are relieved in the transition states for their decomposition. Initial cleavage of just one C–N bond to form a diazenyl diradical[1,20] in each reaction could accomodate this result. However, Engel has found that the presence of fused rings syn to nitrogen in the DBO skeleton retards the rate of nitrogen extrusion.[20c] Thus, it is also possible that the presence of the one-carbon bridge syn to nitrogen in **3** actually serves to slow the rate of nitrogen loss from this azo compound and makes this rate comparable to that in **2**.

The major product formed in the deazetation of **3**, both thermally and by direct and sensitized photolysis, is *cis*-1,3-divinylcyclobutane (**6**). As discussed above, the NMR spectra of the **6** formed in all three reactions of **3b** is consistent with the product being the *E,Z* isomer (**6b**), an equal mixture of *E,E* and *Z,Z*, or any combinations of these two possibilities. However, the data does exclude formation of **6** occuring by a $_{\sigma}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s$ process, in which C–C bond cleavage is concerted with loss of nitrogen and which produces unequal amounts of the *E,E* and *Z,Z* isomers.

It is tempting to conjecture that the *E,Z* isomer **6b** is the major product, since this would imply that C–C bond cleavage takes place predominantly from a chair geometry of the diradical formed from **3b**. Stereochemical studies, using methyl groups as probes, have found C–C bond cleavage from a chair geometry to be the dominant reaction pathway in the thermolysis of DBO.[21] This is also the preferred pathway in the photolysis of **2**, which yields *cis,trans*-1,5-cyclooctadiene as the major product in several solvents.[8]

Models suggest that a chair geometry should be favored for the putative diradical formed from **3**. From this geometry cleavage of **6** should be preferred to closure to **7**, since formation of the latter product requires a boat geometry. If the triplet diradical lives long enough to adopt the chair conformation, so that intersystem crossing to the singlet occurs at this geometry, this would explain the large ratio of **6** to **7** in the sensitized photolysis of **3**. A similar rationale has been proposed by Engel for the increase in cleavage to closure that is generally observed when the photolysis of other DBO derivatives is sensitized.[22]

The stereochemistry with which **7** is formed is also worthy of comment. Studies of the stereochemistry of formation of bicyclo[2.1.0]pentanes in the deazetation of 2,3-diazabicyclo[2.2.1]heptenes have shown this reaction to occur with predominant double inversion of configuration, both thermally and photochemically.[23] Thus, the roughly 10% excess of double retention found in the

(19) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. We thank Dr. George Renzoni for his assistance in carrying out the MM2 calculations.

(20) (a) Dannenberg, J. J.; Rocklin, D. *J. Org. Chem.* **1982**, *47*, 4529. (b) Engel, P. S.; Gerth, D. B. *J. Am. Chem. Soc.* **1983**, *105*, 6849. (c) Engel, P. S.; Nalepa, C. J.; Horsey, D. W.; Keys, D. E.; Grow, R. T. *Ibid.* **1983**, 7103. (d) Chang, M. H.; Jain, R.; Dougherty, D. A. *Ibid.* **1984**, *106*, 4211. (e) Holt, P. L.; McCurdy, J. S.; Adams, J. S.; Burton, K. A.; Weisman, R. B.; Engel, P. S. *Ibid.* **1985**, *107*, 2180.

(21) Roth, W.; Martin, M. *Tetrahedron Lett.* **1967**, 3865.

(22) Engel, P. S.; Horsey, D. W.; Keys, D. E.; Nalepa, C. J.; Soltero, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 7108.

(23) (a) Roth, W. R.; Martin, M. *Ann.* **1967**, *702*, 1. (b) Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1969**, *91*, 6766. (c) Adam, W.; Oppenlander, T.; Zang, G. *J. Org. Chem.* **1985**, *50*, 3303.

thermal decomposition of **3b** is noteworthy. It is interesting that thermolysis of 2,3-diazabicyclo[2.1.1]hexene in solution also fails to show predominant double inversion.[20d] Bicyclobutane is formed with equal amounts of double retention and double inversion, although a 10% excess of the latter pathway is observed in the gas phase.

In the photolysis of 2,3-diazabicyclo[2.1.1]hexene, bicyclobutane is formed with 47% excess double inversion of configuration.[24] Similarly, the direct photolysis of **3b** results in formation a 1:2.4 mixture of **7b** and **7c**, roughly a 40% excess of the product formed by double inversion. It is not clear why photolysis of these two azo compounds gives substantially greater amounts of double inversion product than does pyrolysis, since this is not the case with 2,3-diazabicyclo[2.2.1]heptenes.[23]

Also noteworthy is the absence of any clear indication of participation of the orbitals of the 1,3-bridged cyclobutane ring in the deazetation of **3**. The lower activation enthalpy for nitrogen extrusion from **3** than from DBO can be easily explained by greater relief of van der Waals repulsions between the bridges in the transition state for nitrogen loss from **3**. In fact, as discussed above, the similar activation enthalpies for deazetation of **2** and **3** are actually somewhat surprising, since the amount of strain relief possible is computed to be considerably larger in **3** than in **2**.

From our results it would appear that electron donation from the high-lying filled, cyclobutane orbitals in **3** is relatively unimportant in the transition state for nitrogen loss. In this connection it is significant that substitution of methyl[5b] or cyclopropane[20c] for hydrogen at both bridgehead positions of DBO results in only very modest rate accelerations. Taken together these results suggest that electron donation to the bridgehead carbons has but a small effect on the rate of deazetation of DBO derivatives.

Experimental Section

^{1}H NMR spectra were obtained with a Bruker WM-500 spectrometer, and ^{2}H and ^{13}C NMR spectra were recorded on a Bruker CXP-200 spectrometer. The NMR spectra were obtained on chloroform solutions with chemical shifts reported in ppm downfield from tetramethylsilane as an internal reference. For the ^{2}H NMR spectra, $CDCl_3$ served as the internal reference. IR spectra were recorded with a Beckmann Acculab 4 spectrometer on chloroform solutions, and UV spectra were obtained with a Hewlett-Packard HP8450A spectrometer on methylene chloride solutions. Mass spectra were measured with a Hewlett-Packard 5985A GC/MS system, equipped with a fused silica capillary column and operating in the electron impact mode with an ionizing energy of 70 eV. Exact masses were determined with a VG 7070 GC/MS and associated 2035 F/B data system operating in the electron impact mode. GLC analyses were performed on a Hewlett-Packard 5790A instrument, equipped with a 25-m ultraperformance capillary column of cross-linked 5% phenylmethylsilicone and a flame ionization detector. For preparative GLC a Varian Model 920 chromatograph was used with a 12 ft $\times$ $^3/_8$ in. column of 20% Carbowax 20M on Chromasorb W and a He flow rate of 50 mL/min. Solvents were stirred over and then distilled from appropriate drying agents under an inert atmosphere.

Hydrogenation of the Phenyltriazolinedione Adduct 4 to 5a. A solution of 281 mg (0.10 mmol) of **4** in 15 mL of ethyl acetate was hydrogenated over 50 mg of 5% Pd/C. After 30 min hydrogen uptake ceased, and the solution was filtered through a pad of Celite to remove the catalyst. Removal of the solvent under reduced pressure gave 273 mg of a white, crystalline solid, mp 180 °C dec, which was used without purification: ^{1}H NMR δ 1.1–2.4 (m, 8 H), 3.05 (m, 2 H), 4.95 (m, 2 H), 7.6 (m, 5 H).

6,7-Diazatricyclo[3.2.2.1^{2,4}]dec-6-ene (3a). In a 10-mL flask were placed 100 mg of **5a** (0.35 mmol), 4.3 g of potassium hydroxide, 2 mL of ethylene glycol, and 2 mL of water. After the mixture was degassed under pump vacuum for 0.5 h, argon was admitted to the reaction vessel, which was heated at 160 °C for 1.5 h. After cooling to room temperature, the reaction mixture was extracted three times with 10-mL portions of ether. The combined ether extracts were washed with water and saturated sodium chloride solution, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel, using 3:1 ether–pentane as the solvent. Sublimation at 45–50 °C and 0.5 mm of pressure gave 23 mg (48%) of the azo compound as a glassy solid, mp 145–175 °C dec, which was pure by analytical GLC: ^{1}H NMR δ 0.68 (t, 1 H, J = 9.9 Hz), 1.49 (apparent d, 2 H, J = 8.6 Hz), 1.67 (t, 1 H, J = 9.9 Hz), 1.70 (d of t, H, J = 9.9 and 5.0 Hz), 1.74 (d of t, 1 H, J = 9.9 and 5.0), 1.87 (apparent d, 2 H, J = 8.6 Hz) 2.49 (m, 2 H), 5.42 (m, 2 H); ^{13}C NMR δ 21.45, 28.10, 32.34, 34.65, 65.97; IR (cm^{-1}) 3000, 2960, 2910, 2860, 1540, 1515, 1475, 1465, 1310, 1290, 1240; UV (nm) 388 (ϵ 107), 379 (83); exact mass calcd for $C_8H_{12}N_2$ 136.1000, found 136.0989.

Pyrolysis of 3a. In a Pyrex tube were placed 20 mg of **3a** and 2 mL of chloroform. The solution was degassed by repeated freeze–pump–thaw cycles, and the tube was sealed and placed in an oil bath at 200 °C. After 25 min the tube was removed, opened, and analyzed by GLC. Only two products were detected; they were present in a 2.4:1 ratio. The two products were separated by preparative GLC at 60 °C. The major product, with a retention time of 20 min, was identified as *cis*-1,3-divinylcyclobutane by comparison of its ^{1}H NMR and IR spectra with those reported in the literature for this hydrocarbon.[16] The minor product, with a retention time of 36 min, was identified as tricyclo[4.1.1.0^{2,5}]octane on the basis of the following data: ^{1}H NMR δ 0.74 (d of d, 1 H, J = 10.3 and 6.9 Hz), 1.42 (m, 2 H), 1.53 (m, 1 H), 1.62 (m, 2 H), 2.11 (m, 2 H), 2.33 (m, 2 H), 2.58 (m, 5 H); ^{13}C NMR δ 22.70, 29.30, 30.69, 37.50, 41.52; exact mass calcd for C_8H_{12} 108.0939, found 108.0926. Each of the products was shown to be stable to the conditions of the pyrolysis reaction.

Photolysis of Bicyclo[4.1.1]octa-2,4-diene (8) To Form Tricyclo[4.1.1.0^{2,5}]oct-3-ene (9). In a Pyrex tube was placed a solution of 15 mg of **8** dissolved in 4 mL of pentane. The contents of the tube were degassed and irradiated under a nitrogen atmosphere for 40 min with a 550-W, high-pressure, Hanovia mercury lamp. Analytical GLC revealed formation of one major (89%) and three minor products. The major product was separated by preparation GLC (retention time, 36 min at 90 °C) and identified as tricyclo[4.1.1.0^{2,5}]oct-3-ene (**9**) by its ^{1}H NMR spectrum: δ 1.22 (d of d, 1 H, J = 10.3 and 6.0 Hz), 1.37 (d of d, 1 H, J = 10.3 and 7.7 Hz), 1.50 (d of t, 1 H, J = 7.7 and 2.6 Hz), 2.07 (d of t, 1 H, J = 6.0 and 2.6 Hz), 2.14 (br s, 2 H), 3.06 (s, 2 H), 6.06 (s, 2 H).

Hydrogenation of 9 to Tricyclo[4.1.1.0^{2,5}]octane (7a). To 5 mL of ethanol were added 12 mg of **9** and 10 mg of 5% Pd/C. After hydrogen uptake ceased, the reaction mixture was filtered through a pad of Celite and extracted with pentane. The pentane solution was washed with water, dried over $MgSO_4$, and most of the pentane was removed by distillation. Final separation of the hydrogenation product from residual pentane was achieved by preparative GLC at 60 °C, which afforded 9.8 mg of **7a**. This hydrocarbon proved identical in all respects with the saturated hydrocarbon that was isolated from the pyrolysis of **3a**.

Kinetics of the Pyrolysis of 3a. A 10-mg sample of **3a** was dissolved in 1 mL of chloroform, and 5 μL of diethyl succinate was added as an internal standard. The solution was equally divided among five 3 mm i.d. Pyrex tubes, which were degassed by repeated freeze–pump–thaw cycles. The tubes were then sealed and immersed in an electrically heated, well-stirred, oil bath, which had been preequilibrated at one of three temperatures (173.5, 185.0, or 200.0 °C). These temperatures were constant to ±0.5 °C during each kinetic run. The tubes were removed from the oil bath at intervals and analyzed by GLC (injector at 175 °C, column at 130 °C). The amount of **3a** remaining was determined by electronic integration of peaks of **3a** and the diethyl succinate reference. The reaction kinetics were followed for at least one half-life, and the rate constants given in the text were obtained

(24) Chang, M. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 2333.

by linear least-squares fitting of the data.

Direct Photolysis of 3a. In 2 mL of degassed methylene chloride in a Pyrex tube was dissolved 1 mg of **3a**. The contents of the tube were irradiated under a nitrogen atmosphere with the light from a 550-W, high-pressure, Hanovia mercury lamp, which was passed through a Pyrex filter. After 20 min **3a** was completely decomposed. Analytical GLC showed that the only two products formed in >1% yield were **6a** and **7a**, which were present in a ratio of 3.3:1. Both products were shown to be stable to the reaction conditions.

Sensitized Photolysis of 3a. A mixture of 0.5 mg of **3a** and 15 mg benzophenone in 1 mL of degassed methylene chloride was irradiated as described above. Analytical GLC showed the major product (>98%) to be **6a**. A small amount (<2%) of **7a** was also formed.

Reduction of 4 to 5b with Diimide-d_2. To a 250-mL, three-necked flask, fitted with a condenser and a dropping funnel, were added 310 mg of **4** (1.1 mmol), 5.7 g of dipotassium azocarboxylate,[18] and 40 mL of 99.5% methanol-*O*-*d*. The reaction mixture was placed under a nitrogen atmosphere, and 2.5 mL of 98% acetic acid-*O*-*d* was added dropwise over 10 min. The reaction mixture was stirred for 45 min. Reduction proved very inefficient, and additional portions of 4.4 g dipotassium azocarboxylate and 2 mL of acetic acid-*O*-*d* were added five times as 45-min intervals. The reaction mixture was stirred overnight, and water was then added until all the solid dissolved. The mixture was extracted three times with 50-mL portions of methylene chloride, and the combined methylene chloride extracts were washed twice with 25-mL portions of 5% $NaHCO_3$ and dried over $MgSO_4$. Removal of the solvent under vacuum afforded 295 mg (95%) of a crystalline solid, which was used without purification.

Synthesis of 3b. The synthesis was carried out, starting with **5b**, in a manner identical with that described above for the preparation of **3a** from **5a**. The ^1H NMR spectrum of the product was similar to that of **3a**; but the resonance at δ 1.49 was reduced to 15% of its size in **3a**, the peak at δ 1.87 appeared as a singlet, and the resonance at δ 5.42 was a doublet with J = 6.0 Hz. The ^2H NMR spectrum displayed a resonance at δ 1.49, and the IR spectrum showed new bands at 2200, 2190, and 2180 cm^{-1}. The mass spectrum showed the product to consist of 70% d_2 molecules and 30% d_1: exact mass calcd for $C_8H_{10}D_2N_2$ 138.1126, found 138.1123; exact mass calcd for $C_8H_{11}DN_2$ 137.1063, found 137.1061.

Reduction of 9 to 7b with Diimide-d_2. In a 25-mL flask was placed 11 mg (0.1 mmol) of tricyclo[4.1.1.$0^{2,5}$]oct-3-ene (**9**), 250 mg (1.28 mmol) of dipotassium azodicarboxylate,[18] and 4 mL of 99.5% methanol-*O*-*d*. The reaction mixture was placed under an atmosphere of nitrogen, and 0.11 mL 98% acetic acid-*O*-*d* was added dropwise by syringe. The reaction mixture was stirred for 1 h and recharged once with 250 mg of dipotassium azodicarboxylate and 0.11 mL of acetic acid-*O*-*d*. The mixture was then stirred overnight at room temperature. Water was added slowly to dissolve the solid, and the resulting mixture was extracted with pentane. The pentane extracts were washed with 5% $NaHCO_3$ and dried over $MgSO_4$. Most of the pentane was removed by distillation, and 5.2 mg (47%) of **7b** was isolated by preparative GLC. The ^1H NMR spectrum of the product was the same as that described above for **7a**, except that the resonance at δ 1.42 appeared as a doublet, with J = 1.6 Hz, and the peak at δ 2.11 was nearly absent. The mass spectrum showed 90% d_2 molecules and 10% d_1.

Product Analysis in the Pyrolysis and Photolysis of 3b. These reactions were performed and the products separated as described above for **3a**. The vinyl hydrogens in **6b** were easily assigned on the basis of their coupling constants to the vinyl proton. Thus, the proton at δ 4.87 with J = 10.3 Hz was assigned as cis, while that at δ 4.92 with J = 17.2 Hz was assigned as trans. Both the ^1H and ^2H NMR spectra showed the ratio of these two resonances to be equal within experimental uncertainty. The ratios of **7b** to **7c** were determined by integrating the resonances at δ 1.42 and 2.11 in the ^2H NMR spectra of the mixture. The ratios corresponded closely to those obtained from integration of the ^1H NMR spectra, after correction of the latter for the presence of 30% of d_1 material. The ratios of **7b** to **7c** obtained for the pyrolysis and direct photolysis of **3b** are given in the text. So little **7** was formed in the sensitized photolysis that no attempt was made to assess its deuterium stereochemistry, especially since it seemed likely that this material resulted from some light absorption by the azo compound instead of by the sensitizer.

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Synthetic Studies on the Indole Alkaloid Vinoxine. Synthesis of 19,20-Dihydro-16-epivinoxine

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The synthesis of vinoxine analogues having the C-16 methoxycarbonyl substituent present in the alkaloid is reported. The key step in this synthesis is the mercuric acetate oxidation of appropriate methyl α-4-piperidyl-1-indoleacetates, which were prepared from 1-(4-pyridylmethyl)indoles through a three-step sequence involving methoxycarbonylation of the interannular methylene carbon, alkylation of the piperidine nitrogen, and hydrogenation of the resulting 4-alkylidene-1,4-dihydropyridine. The stereochemical aspects of 3-ethylpiperidines **13** and the vinoxine analogues **5**, **15**, and **16**, especially in regard to the relative configuration of the methine carbon α to the methoxycarbonyl group, are discussed.

Vinoxine is a minor indole alkaloid isolated[1] in 1967 from *Vinca minor* L. Its unusual planar structure, lacking the characteristic tryptamine unit present in the greater part of indole alkaloids and having, as its pentacyclic analogue pleiocarpamine,[2,3] a C-16[4] methoxycarbonyl group and a

(1) Mokrý, J.; Kompiš, I.; Spiteller, G. *Collect. Czech. Chem. Commun.* **1967**, *32*, 2523.

(2) Hesse, M.; Philipsborn, W. v.; Schumann, D.; Spiteller, G.; Spiteller-Friedmann, M.; Taylor, W. I.; Schmid, H.; Karrer, P. *Helv. Chim. Acta* **1964**, *47*, 878.

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