Electronic Control of Stereoselectivity. 7. Stereospecificity of *N*-Methyltriazolinedione Cycloaddition to Tricyclo[5.2.1.$0^{2,6}$]deca-2,5-diene, Tricyclo[5.2.1.$0^{2,6}$]deca-2,5,8-triene, and Tricyclo[5.2.2.$0^{2,6}$]undeca-2,5,8-triene[1]

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The Diels–Alder reactions of the title compounds (**1–3**) with *N*-methyltriazolinedione (MTAD) were investigated and determined to proceed with endo stereospecificity. Stereochemical assignment to the adduct derived from **3**, viz., **4**, was arrived at by a three-dimensional X-ray crystal structure analysis. In the case of **9**, the cycloadduct derived from **2**, reliance was placed upon diimide redution of its more reactive internal double bond from the exo direction to give **10**, hydrolysis–oxidation of which delivered the azo compound **12**. Direct irradiation of this substance afforded cage compound **13**, thereby demonstrating the close spatial proximity of C=C and N=N in the precursor molecule. The stereochemistry of the third and final adduct **14** was deduced by chemical interconversion with **9** and **11**. The heightened reactivity of MTAD results in the development of early transition states where prevailing electronic factors are magnified. The overwhelming preference for endo stereoselection is attributed to important electronic effects which are present in strained bicyclo systems and can make themselves recognized at more distant sites in fused cyclopentadiene rings.

Recent studies of the stereoselection which operates in [4 + 2]π cycloadditions to cyclopentadiene rings fused at C_2,C_3 to bridged bicyclic systems are playing an important role in our development of a deeper understanding of the electronic character of norbornane, norbornene, and bicyclo[2.2.2]octene frameworks.[3-5] Discovery of kinetically overwhelming stereospecific endo capture by **1** and **2** of

1 **2** **3**

a number of moderately reactive dienophiles has led to the postulate that interaction of σ electrons located in the norbornane and norbornene part structures with the π_s diene orbital induces a disrotatory tilt of the terminal π orbitals. As a consequence, a considerably smaller antibonding contribution materializes during endo attack relative to the exo option. In the case of **3**, the additions were seen to be stereoselective only, with exo attack now being somewhat more favored. Theoretical analysis of the electronic character of **3** by INDO and SPINDO methods proved to be in full agreement with this reduction in stereoselectivity, although a slight preference for attack on the side of the etheno bridge was indicated.[1]

To achieve reasonable rates of reaction, the cycloadditions of **1–3** with dienophiles typified by methyl acrylate, methyl propiolate, *p*-benzoquinone, and phenyl vinyl sulfone were conducted above 0 °C and more often at temperatures in excess of 25 °C. Nonetheless, these reactions are considered to proceed under the "normal" Diels–Alder frontier orbital guidelines where the dienophile LUMO and diene HOMO orbital energies comprise the dominant interaction.[6,7] Perturbation theory clearly denotes that the earlier the transition state, the more successful will be the application of molecular orbital analysis.[8] For concerted Diels–Alder reactions, early transition states are thought to resemble most closely a two-plane orientation complex of the reactant pair. Furthermore, when such conditions prevail, the major portion of the $\Delta G^{\ddagger}$ term is normally due to entropy, the small $\Delta H^{\ddagger}$ contribution signifying that little alteration in bond energies has materialized to that point.[9,10] As a consequence, the electronic features peculiar to any given diene should be most clearly manifested during reactions which occur rapidly at low temperatures.

For these reasons, we were led to investigate the stereochemical facets of the Diels–Alder reactions involving **1–3** and the highly reactive *N*-methyltriazolinedione molecule. This selection was predicated upon the well-known high reactivity of triazolinedione derivatives and the knowledge that the LUMO of this dienophile (electron affinity is unknown; IP = 11.23 eV)[11] does not differ substantially from those of the less reactive dienophiles examined previously (e.g., the IP of methyl acrylate which is seen at 10.72 eV).[12] The various ionization potentials for **1–3** were reported earlier.[3b] This last precondition stems from our desire not to change Diels–Alder reaction type[6] while simultaneously enhancing reactivity.

The definitive experimental results to be described in this paper show that complete endo stereospecificity now operates in all three examples. The unambiguous structural assignments indicate that **3**, like **1** and **2**, does indeed prefer to enter into [4 + 2]π cycloaddition from the direction of its etheno bridge, as predicted earlier by theo-

(1) Part 6: Paquette, L. A.; Bellamy, F; Böhm M. C.; Gleiter, R. *J. Org. Chem.*, preceding paper in this issue.
(2) (a) The Ohio State University. (b) Hoffmann-La Roche, Inc.
(3) (a) Paquette, L. Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186. (b) Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *J. Am. Chem. Soc.*, in press. (c) Paquette, L. A.; Carr, R. V. C.; Arnold, E.; Clardy, J. *J. Org. Chem.*, accompanying paper in this issue.
(4) Sugimoto, T.; Kobuke, Y.; Furukawa, J. *J. Org. Chem.* **1976**, *41*, 1457. For an earlier assessment of the response of **1** to select dienophiles, see: Alder, K.; Flock, F. H.; Janssen, P. *Chem. Ber.* **1956**, *89*, 2689.
(5) The Diels–Alder reactivity of 2,3-dimethylenenorbornanes is being actively investigated by Professor Pierre Vogel and his co-workers. Consult: Pilet, O.; Chollet, A.; Vogel, P. *Helv. Chim. Acta* **1979**, *62*, 2341 and earlier references cited therein.
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(7) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.
(8) Sustmann, R; Trill, H. *Agnew Chem., Int. Ed. Engl.* **1972**, *11*, 838. Sustmann, R.; Schubert, R. *ibid.* **1972**, *11*, 840. Sustmann, R. *Pure Appl. Chem.* **1974**, *40*, 569.
(9) See, for example: Kiselev, V. D.; Miller, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 4036.
(10) Huisgen, R.; Schug, R. *J. Am. Chem. Soc.* **1976**, *98*, 7819.
(11) Gleiter, R., private communication.
(12) Houk, K. N.; Munchhausen, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 937.

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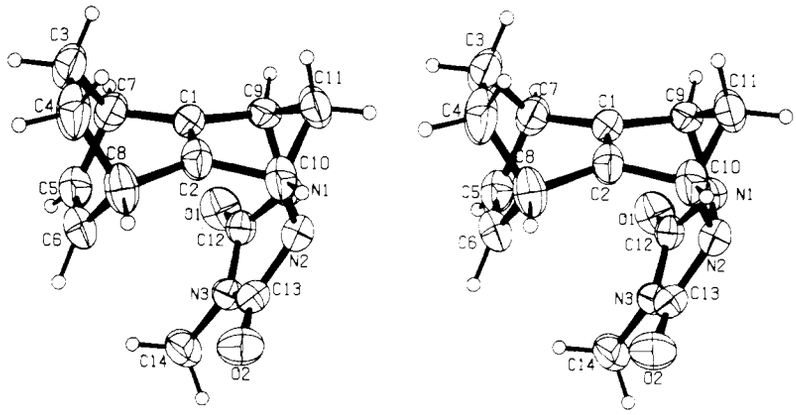


Figure 1. Three-dimensional view of **4** as determined by X-ray analysis.

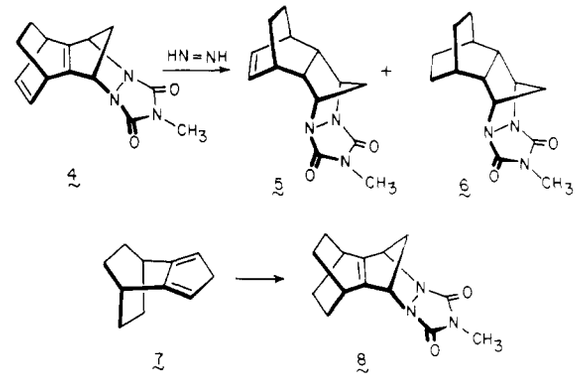
ry,[3a,b] when conditions most proper for examining this phenomenon are employed.

Results

Tricyclo[5.2.2.0^{2,6}]undeca-2,5,8-triene (3). The reaction of *N*-methyltriazolinedione (MTAD) with **3** proceeded very rapidly (instantaneous fading of the red dienophile color) in the temperature range −80 to +40 °C, and a single product was formed in high yield on every occasion. When the progress of the cycloaddition was closely followed in the cold (−80 °C) probe of a 90-MHz NMR spectrometer, only direct conversion to the same [4 + 2] adduct was observed. The protons of the ethano bridge of the colorless crystalline solid appear as a broadened singlet of area 4 at δ 1.38. The absence of a marked chemical shift difference between the "inside" and "outside" pairs of protons suggested that the endo configuration **4** may well be the correct one. The alternative exo adduct would necessarily have the urazole moiety positioned significantly closer to the "inside" pair, and through-space anisotropy effects might be anticipated. However, the possibility remained that the shielding generated by the two double bonds contained within the adduct could be dominant in dictating chemical shift. To gain information on this point, we subjected **4** to controlled diimide reduction. This reagent saturates the reactive central double bond more rapidly than the peripheral one and makes possible the isolation of **5**. Diimide is believed to approach the central region of **4** from the less hindered surface (exo to the diazanorbornene part structure; see Scheme I) to give **5**, whose ensuing reduction leads to **6**. In the case of **5**, the four ethano protons are again seen as a very narrow multiplet centered at δ 1.37. Also, the chemical shift of its two olefinic protons (δ 5.93) was not significantly altered from that exhibited by **4** (δ 6.08).

Because reservations concerning the correctness of our structural assignment to **4** persisted, attention was directed to the reaction of MTAD with tricyclo[5.2.2.0^{2,6}]undeca-2,5-diene (**7**),[13] a molecule whose symmetry negates any difference between exo and endo approach. From a series of multiplets of relative area 8 which appear at δ 1.77–0.62 in the ^{1}H NMR spectrum of **8**, it was made clear that the "inside" and "outside" ethano protons are differently shielded in this particular structural arrangement. Nevertheless, our ignorance over the combined shielding effects of two flaking double bonds as present uniquely in **4** persisted. Therefore, recourse was ultimately made to X-ray crystal structure analysis.

Scheme I



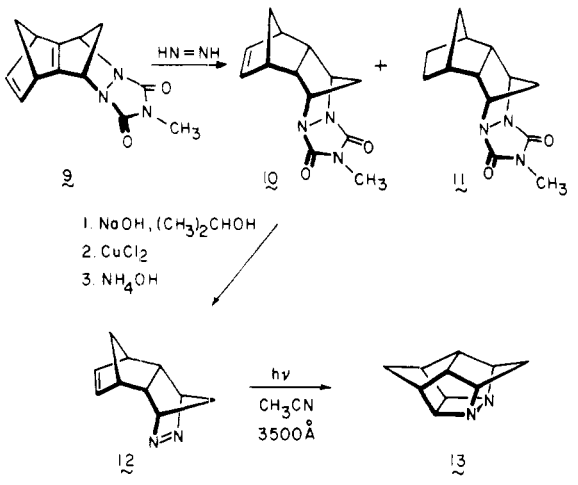
The crystals of **4** proved to be triclinic and of space group P$\bar{1}$, with a = 7.34 (1) Å, b = 7.960 (1) Å, c = 11.737 (2) Å, α = 81.90 (1)°, β = 86.53 (1)°, γ = 66.87 (1)°, and d_{calcd} = 1.388 g cm^{-3} for Z = 2 ($C_{14}H_{15}N_3O_2$, M_r = 257.29). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). A crystal measuring approximately 0.2 × 0.3 × 0.4 mm was used for the data collection. A total of 1661 reflections were measured for $\theta < 57°$, of which 1579 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure[14] and was refined by full-matrix least-squares methods. Ten low θ reflections which were strongly affected by extinction were excluded from the final refinement and final difference map. In the final refinement, anisotropic thermal parameters were used for the heavier atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are R = 0.050 and R_w = 0.074 for the remaining 1569 observed reflections. The final difference map has no peaks greater than ±0.3 e A^{-3}. The three-dimensional structure of **4**, which clearly shows that endo capture of MTAD has indeed taken place, is reproduced in Figure 1. Tables I–IV, which contain data concerning final atomic and anisotropic thermal parameters, bond lengths, and bond angles, are provided as supplementary material.

Tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene (2). The reaction of **2** with MTAD also proceeds very rapidly in ethyl acetate solution at −35 °C. The sole cycloadduct **9** could be selectively reduced to dihydro derivative **10** with diimide (Scheme II). The overreduction of **10** to **11** also gains importance since this fully saturated urazole later serves

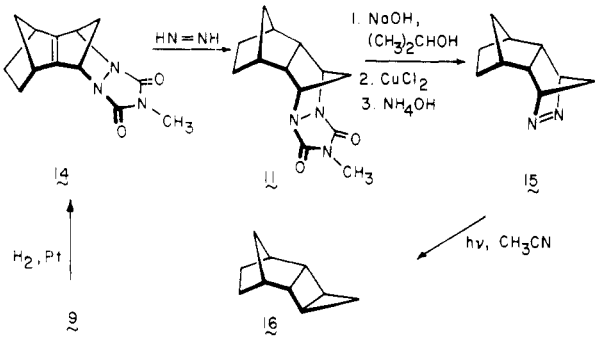
(13) Scroggins, R. T.; Rettig, R. F.; Wing, R. M. *Inorg. Chem.* **1976**, *15*, 1381.

(14) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

Scheme II

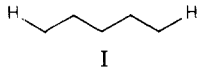


Scheme III



as a relay. Two fundamental stereochemical questions were now resolved simultaneously by hydrolysis–oxidation of **10** to the unsaturated azo compound **12** and its photocyclization to **13**. The n–π^* absorption of **12** [λ_{max} 356 nm (ϵ 386)] indicates the azo group to be in spatial proximity to the olefinic π bond [compare **15**, γ_{max} 341 nm (ϵ 231)]. The excited-state intramolecular [$_\pi2_s + _\pi2_s$] cycloaddition of **12** is only the second example of azo involvement in such a reaction and is, in fact, modeled upon the precedent-setting observation of Berning and Hünig.[15]

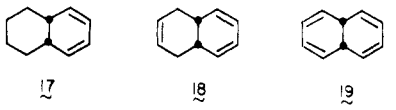
Tricyclo[5.2.1.0^{2,6}]deca-2,5-diene (1). MTAD addition to **1** at −20 °C gave adduct **14** exclusively. Stereochemistry was assigned to the colorless crystalline solid on the basis of its independent preparation by catalytic hydrogenation of **9** and its conversion in the presence of diimide to **11** (Scheme III). Additional structural proof was derived from the conversion of **11** to the known hydrocarbon **16**.[16] Thus, hydrolysis–oxidation of **11** afforded azo compound **15**, the photolysis of which in acetonitrile or acetone solution resulted in nitrogen photoextrusion. The endo,anti configuration of **16** rests upon a remarkably large ^6J coupling of 1 Hz across a rigid geometric arrangement of type I and direct comparison with an authentic sample.[16]



I

Discussion

In 1973, Jacobson reported that Diels–Alder reactions of **17**–**19** with *N*-phenyltriazolinedione, tetracyanoethylene,



17 18 19

and diethyl fumarate proceed with a preference for attack on the less hindered face in all cases.[17] This selectivity was attributed to steric effects, and the conclusion was reached that secondary orbital interaction with a neighboring nonconjugated double bond was not an important determinant of stereochemical control.

A better substrate for evaluating stereoelectronic control in cycloaddition reactions to 1,3-cyclohexadienes was investigated in 1977 by Feast and co-workers, who described their findings involving the perfluorinated triene **20**.[18]

20 21

Thermally promoted condensations involving ethylene (210 °C), 2-butyne (125 °C), and dimethyl acetylenedicarboxylate (125 °C) as coreagents delivered pairs of isomeric [4 + 2] adducts in high yield. The relative amounts of cycloaddition occurring from the same side as the CF_2CF_2 bridge were 50, 75, and 83%, respectively. These product ratios were also unfortunately interpreted in terms of the absence of secondary orbital interactions within the bicyclo[2.2.2]octenyl framework.

Curiously, the selectivity of addition observed for **20** is reversed in the lower cyclopentadienyl analogue **21**.[19] This triene adds 2-butyne (120 °C) and propyne (115 °C) chiefly from the endo surface (77 and 55%, respectively).

The stereochemical response of **3** was shown earlier by us to differ from that of its fluorocarbon analogue **21** in that capture of dimethyl acetylenedicarboxylate (25 °C), methyl propiolate (42 °C), and benzyne (85 °C) is preferred from the exo direction (86, 79, and 81%, respectively) under kinetically controlled conditions.[1,3]

While we are not prepared at this time to comment on the ground-state electronic features of **20** and **21**, Böhm and Gleiter have determined by INDO and SPINDO methods that the subjacent π_s orbital of the diene component in **3** admixes to a substantial degree with the precanonical (PCMO) molecular orbital of the π bridge and σ_s.[3b] Although this interaction does not reach the intensity uncovered in bicyclo[2.2.1]heptyl systems such as **1** and **2**, it remains adequate to tilt the terminal diene π orbitals disrotatorily toward the ethano bridge. The advantage to endo attack then materializes as a direct result of a reduction in the level of antibonding interaction as the surface having the *lesser* electron density is approached by the dienophile. As alluded to earlier, the lowering in $\Delta H^\ddagger$ which appears available to endo attack, small as it might be, is likely to become increasingly dominant as the transition state arrives earlier. Under these conditions, the activated complex is more reactant like, and the possible differences in orbital energetics become more magnified. The high Diels–Alder reactivity of MTAD has allowed us to probe the electronic features of the early transition states for [4 + 2]π bonding to **1**–**3** and to uncover that endo stereospecificity operates. The origin of this

(15) Borning, W.; Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 777.
(16) Baldwin, J. E.; Pinschmidt, R. K., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 5247.
(17) Jacobson, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 2579.
(18) Feast, W. J.; Hughes, R. R.; Musgrave, W. K. R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 152.
(19) Feast, W. J.; Musgrave, W. K. R.; Preston, W. E *J. Chem. Soc., Perkin Trans. 1* **1972**, 1830.

stereochemical control lies in the heretofore incompletely appreciated electronic character of strained bicyclic frameworks.

Experimental Section

Melting points are uncorrected. Proton magnetic resonance spectra were obtained with Varian T-60 and Bruker HX-90 spectrometers; apparent splittings are given in all cases. Carbon spectra were recorded on the Bruker unit. Infrared and mass spectra, the latter at an ionization potential of 70 eV, were determined on Perkin-Elmer Model 467 and AEI-MS9 spectrometers, respectively. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory.

***N*-Methyltriazolinedione Addition to 3.** A solution of **3** (137 mg, 0.95 mmol) in chloroform (1 mL) was cooled to −35 °C under argon, and 100 mg (0.88 mmol) of MTAD in 2 mL of chloroform was added via syringe during 5 min (instant decolorization). The solvent was evaporated under reduced pressure, and the residue was place under a vacuum of 0.5 torr for 45 min to remove the excess **3**. There was obtained 218 mg (96%) of **4** as a colorless solid: mp 128 °C dec (from ethyl acetate–hexane, 5:1); ^{1}H NMR ($CDCl_3$) δ 6.08 (m, 2 H), 5.00 (t with fine splitting, J = 2.5 Hz, 2 H), 2.69 (s, 3 H), 2.08 (dt, J = 8.5, 2.5 Hz, 1 H), 1.75 (dt, J = 8.5, 2.5 Hz, 1 H), 1.38 (br s, 4 H); ^{13}C NMR ($CDCl_3$) 151.1 (s), 146.7 (s), 134.8 (d), 66.1 (d), 49.4 (t), 36.6 (d), 25.4 (q), 25.2 (t) ppm; mass spectrum, m/e calcd 257.1164, obsd 257.1169.

Anal. Calcd for $C_{14}H_{15}N_3O_2$: C, 65.36; H, 5.88. Found: C, 65.27; H, 5.89.

Generalized Diimide Reduction Procedure. Into a three-necked round-bottomed flask equipped with a dropping funnel, alcohol thermometer, gas outlet, and magnetic stirring bar was placed the ethanol solution of the urazole to be reduced. This solution was cooled to 0 °C, and the appropriate amount of anhydrous (97%) hydrazine was added. With vigorous stirring, 30% hydrogen peroxide was added in small aliquots (0 ± 5 °C maintained throughout). The solution was allowed to stir at 0 °C for 30 min and was then warmed to room temperature. Diisopropyl ether (peroxide free) was added, and the aqueous layer was drawn off and back-extracted with diisopropyl ether. The combined organic phases were washed once with water, dried, and evaporated at reduced pressure to give the reduction product(s).

By use of this procedure, 510 mg (1.98 mmol) of **4** dissolved in 40 mL of ethanol was reduced with 1.9 g (59 mmol; 14.9 equiv per double bond) of hydrazine and 2.8 mL of hydrogen peroxide. The peroxide addition required 25 min, and stirring at room temperature was maintained for 4 h. The crude material weighed 183 mg and contained **5** and **6** in the approximate ratio of 28:72. This mixture was separated by preparative layer chromatography on silica gel (elution with ethyl acetate–hexane, 3:2) to give 34 mg of **5** and 94 mg of **6**.

For **5**: colorless solid; mp 114–115 °C (from ethyl acetate–hexane); IR (CCl_4) 3060, 2955, 1772, 1713, 1448, 1392, 1198, 1010 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.93 (dd, J = 4.0, 3.5 Hz, 2 H), 4.40 (m, 2 H), 3.02 (s, 3 H), 2.72 (m, 2 H), 2.22 (m, 2 H), 1.60 (m, 2 H), 1.37 (m, 4 H); ^{13}C NMR ($CDCl_3$) 128.6, 62.3, 46.3, 39.5, 30.9, 25.7, 25.6 ppm; mass spectrum, m/e calcd 259.1321, obsd 259.1327.

For **6**: colorless solid; mp 128.5–130 °C (from ethyl acetate–hexane, 1:3); IR (CCl_4) 2978, 2945, 2905, 2855, 1773, 1713, 1448, 1394, 1198, 1010 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.55 (m, 2 H), 3.02 (s, 3 H), 2.58–0.62 (series of m, 14 H); ^{13}C NMR ($CDCl_3$) 159.7, 64.3, 42.1, 40.1, 29.2, 26.6, 25.7, 21.7 ppm; mass spectrum, m/e calcd 261.1477, obsd 261.1482.

Anal. Calcd for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33. Found: C, 64.29; H, 7.38.

***N*-Methyltriazolinedione Addition to Tricyclo[5.2.2.0^{2,6}]-undeca-2,5-diene (7).** A soltuion of **7** (574 mg, 3.99 mmol) in ethyl acetate (4 mL) cooled to −25 °C was treated with a solution of MTAD (413 mg, 3.65 mmol) in 6 mL of the same solvent. Workup as previously described gave 915 mg (97%) of a beige solid which was homogeneous by ^{13}C NMR analysis. Recrystallization from ethyl acetate–hexane (1:3) afforded **8** as a transparent solid: mp 120–122 °C dec; IR (CCl_4) 3020, 2955, 2868, 1780, 1720, 1448, 1388 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.04 (t, J = 1.0 Hz, 2 H), 2.86 (s, 3 H), 2.86 (m, 2 H), 2.23 (dt, J = 8.5, 1.0 Hz, 1 H), 1.92 (dt, J = 8.5, 1.0 Hz, 1 H), 1.77–0.62 (series of m, 8 H); ^{13}C NMR ($CDCl_3$) 160.7 (s), 145.1 (s), 67.4 (d), 51.4 (t), 30.0 (d), 26.3 (t), 26.0 (t), 25.0 (q) ppm; mass spectrum, m/e calcd 259.1321, obsd 259.1325.

Anal. Calcd for $C_{14}H_{17}N_3O_2$: C, 64.85; H, 6.61. Found: C, 64.75; H, 6.74.

***N*-Methyltriazolinedione Addition to 2.** A solution of MTAD (350 mg, 3.10 mmol) in ethyl acetate (10 mL) was added under a nitrogen atmosphere during 10 min to a magnetically stirred cold (−35 °C) solution of **2** (410 mg, 3.15 mmol) in the same solvent (3 mL). Instant decolorization was seen, and a light tan precipitate was deposited. The solid was dissolved by warming the mixture briefly to 40 °C, and warm hexane (10 mL) was added. After the mixture was cooled and filtered, there was isolated 645 mg (86%) of **9** as transparent prisms: mp 111 °C dec; IR (CCl_4) 3010, 2945, 2865, 1780, 1720, 1448, 1385 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.52 (dd, J = 1.9, 1.9 Hz, 2 H), 5.19 (t, J = 1.3 Hz, 2 H), 3.61 (m, 2 H), 2.79 (s, 3 H), 2.32–219 (m, 3 H), 2.11 (dt, J = 11.3, 1.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 160.3 (s), 144.5 (s), 142.5 (d), 74.5 (t), 63.5 (d), 50.3 (d), 48.3 (t), 25.1 (q) ppm; mass spectrum, m/e calcd 243.1008, obsd 243.1016.

Anal. Calcd for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39. Found: C, 64.21; H, 5.42.

Diimide Reduction of 9. By use of the standard reduction procedure, 4.2 g (17.3 mmol) of **9** in 75 mL of ethanol was treated with 2.9 g (87.9 mmol; 5.1 equiv per double bond) of hydrazine and 4.0 mL of hydrogen peroxide. There was obtained 478 mg (11.4%) of a viscous yellow oil determined to be a 78:11:11 mixture of **10**, **11**, and unreacted **9**. Preparative thin-layer chromatography on silica gel (elution with ethyl acetate–hexane, 3:1) afforded 365 mg of **10**: mp 130–131 °C (from ether–hexane); IR (CCl_4) 3060, 2958, 2859, 1763, 1705, 1445, 1205, 1105, 1010 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.88 (m, 2 H), 4.37 (m, 2 H), 2.95 (s, 3 H), 2.72 (m, 4 H), 1.68 (m, 4 H); ^{13}C NMR ($CDCl_3$) 158.3 (s), 131.0 (d), 60.9 (d), 56.5 (t), 47.9 (d), 44.4 (t), 43.2 (d), 25.5 (q) ppm; mass spectrum, m/e calcd 245.1164, obsd 245.1170.

Anal. Calcd for $C_{13}H_{15}N_3O_2$: C, 63.66; H, 6.15. Found: C, 63.66; H, 6.20.

The sample of **11** which was isolated (25 mg) proved to be spectroscopically identical with the sample isolated and characterized below.

***syn*-4,5-Diazatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (12).** A mixture of sodium hydroxide (0.55 g, 13.74 mmol) and isopropyl alcohol (30 mL) was heated to reflux with stirring, and a solution of urazole **10** (280 mg, 1.14 mmol) in the same solvent (5 mL) was added. The resultant mixture was heated at reflux under nitrogen for 3 h (all of the urazole was consumed after 2 h by TLC), cooled in an ice bath, and treated with 3 N hydrochloric acid (4 mL) followed by a solution of cupric chloride (7.5 g) in water (200 mL). The mixture was stirred at room temperature for 2 h. Concentrated ammonium hydroxide was introduced until a deep blue color persited. An ether–pentane mixture (1:1, 200 mL) was added, and the organic phase was separated. This process was repeated, and the combined organic layers were washed with water, dried, and evaporated to give 150 mg (82%) of the crude product. Recrystallization of this material from pentane yielded 40 mg (22%) of **12** as colorless crystals, mp 96–97 °C. The analytical sample was prepared by sublimation [43–48 °C (0.1 torr)]: ^{1}H NMR ($CDCl_3$) δ 5.26 (s, 2 H), 4.92 (s, 2 H), 2.74 (s, 4 H), 1.50–1.40 (m, 4 H); ^{13}C NMR (CD_3CN) 129.95, 78.93, 55.87, 49.22, 44.46, 41.16 ppm; mass spectrum, m/e calcd 160.1000, obsd 160.1004.

Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55. Found: C, 74.86; H, 7.49.

Photocyclization of 12. A thin-wall NMR tube containing azo compound **12** (30 mg) in CD_3CN (1 mL) was placed in close proximity to a long-wavelength UV lamp (desk-top model used for TLC analysis). The irradiation required 5.5 h (monitored by NMR) to proceed to completion. The solvent was evaporated to give **13** as a light brown mobile oil: 27 mg (90%); ^{1}H NMR (CD_3CN) δ 4.20 (m, 2 H), 3.50 (m, 2 H), 2.86–2.60 (m, 4 H), 2.20 (m, 2 H), 1.63–1.17 (m, 2 H); ^{13}C NMR (CD_3CN) 70.38, 68.25, 54.12, 46.60, 41.21, 28.25 ppm; mass spectrum, m/e calcd 160.1000, obsd 160.1004.

The picrate salt of **13** was obtained as a yellow crystalline solid, mp 219–222 °C dec (from ethanol).

Anal. Calcd for $C_{16}H_{15}N_5O_7$: C, 49.36; H, 3.88. Found: C, 48.83; H, 3.99.

N-Methyltriazolinedione Addition to 1. Reaction of MTAD (630 mg, 4.57 mmol) with isodicyclopentadiene (740 mg, 5.60 mmol) in 15 mL of ethyl acetate at -35 °C as before gave 1.2 g (88%) of **14** as transparent prisms: mp 129 °C dec; IR (CCl_4) 2960, 1785, 1728, 1448, 1182, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.00 (dd, J = 2.0, 1.5 Hz, 2 H), 2.98 (m, 2 H), 2.88 (s, 3 H), 2.47-0.92 (m, 8 H); ^{13}C NMR ($CDCl_3$) 161.3 (s), 151.0 (s), 64.7 (d), 55.4 (t), 54.9 (t), 41.3 (d), 25.7 25.4 ppm; mass spectrum, m/e calcd 245.1164, obsd 245.1170.

Anal. Calcd for $C_{13}H_{15}N_3O_2$: C, 63.66; H, 6.16. Found: C, 63.63; H, 6.17.

Catalytic Hydrogenation of 9 to 14. A 14-mg sample of platinum oxide in 1 mL of ethyl acetate was prehydrogenated, and the slurry was cooled to -20 °C. A solution of **9** (105 mg, 0.43 mmol) in 4 mL of ethyl acetate was introduced, and hydrogenation was resumed until ca. 9 mL of hydrogen was taken up. The mixture was filtered through Celite, and the filtrate was evaporated to give 103 mg (97%) of **14** whose spectra were superimposable upon those of the substance prepared above.

Diimide Reduction of 14. Following the standard procedure, 1.5 g (6.12 mmol) of **14** in 45 mL of ethanol was reduced with 4.3 g (134 mmol) of hydrazine and 6.2 mL of hydrogen peroxide. Workup gave 235 mg (15.6%) of **11**, a colorless solid: mp 157-158 °C (from ethyl acetate-hexane); ^1H NMR ($CDCl_3$) δ 4.45 (pseudo s, 2 H), 3.03 (s, 3 H), 2.52-137 (series of m, 12 H); ^{13}C NMR ($CDCl_3$) 158.2 (s), 60.4 (d), 47.8 (d), 42.3 (t), 39.4 (d), 35.7 (t), 25.6 (q), 24.3 (t) ppm; mass spectrum, m/e calcd 247.1321, obsd 247.1327.

Anal. Calcd for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93. Found: C, 63.02; H, 6.98.

***syn*-4,5-Diazatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (15).** A solution of sodium hydroxide (0.8 g, 20 mmol) and **11** (420 mg, 1.70 mmol) in 40 mL of isopropyl alcohol was heated at reflux for 4 h, cooled in ice, and acidified with 6 mL of 3 N hydrochloric acid. The mixture was added to 300 mL of water containing 12 g of cupric chloride, and stirring was maintained for 2 h. Ammonium hydroxide was added until a deep blue color persited, and 400 mL of a 1:1 pentane-ether mixture was added. After thorough shaking, the organic phase was separated, washed with water and brine, and dried. Solvent evaporation furnished 175 mg (63.5%) of **15** as a colorless waxy solid which was sublimed 70 °C (0.4 torr): mp 101-102 °C; IR (CCl_4) 2990, 2950, 2875, 1480, 1450, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.87 (m, 2 H), 2.20 (m, 2 H), 1.67-0.85 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 76.6 (d), 45.0 (t), 40.7 (d), 37.9 (d), 34.4 (t), 24.4 (t) ppm; mass spectrum, m/e calcd 134.1095, obsd 134.1099 ($M^+ - N_2$).

Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70. Found: C, 74.08; H, 8.63.

***endo,anti*-Tetracyclo[5.2.1.0^{2,6}.0^{3,5}]decane (16).** A solution of **15** (85 mg, 0.52 mmol) in 12 mL of acetone was irradiated at 3500 Å in a Rayonet reactor for 2 h. The solvent was carefully evaporated, and the residue was passed through a short column of alumina (pentane elution). Pentane was removed by distillation to leave 41 mg (59%) of **16** as a colorless mobile oil: ^1H NMR ($CDCl_3$) δ 2.38-0.95 (series of m, 13 H), 0.75 (m, 1 H); ^{13}C ($CDCl_3$) 45.1, 40.9, 38.1, 24.65, 18.7, 18.3 ppm.

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Supplementary Material Available: Table I, final atomic parameters for **4**; Table II, final anisotropic thermal parameters for **4**; Table III, bond lengths in **4**; Table IV, bond angles in **4** (4 pages). Ordering information is given on any current masthead page.

Palladium-Catalyzed Triethylammonium Formate Reductions. 4.[1] Reduction of Acetylenes to Cis Monoenes and Hydrogenolysis of Tertiary Allylic Amines

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Eight phenyl-conjugated and double bond conjugated acetylenes were reduced with triethylammonium formate and a palladium on carbon catalyst. Cis olefins were obtained in good yields in five examples. 4-Nitrodiphenylacetylene gave only 4-aminodibenzyl and (*Z*)-methyl non-2-en-4-ynoate gave mainly the *E,Z* dienoate. 1-Phenyl-3-methylbut-3-en-1-yne gave the cis diene initially, but it isomerized partially under the reaction conditions. Five tertiary allylic amines were shown to undergo hydrogenolysis with the same reducing agent and catalyst to give mixtures of two isomeric olefins in moderate to good yields.

Palladium-catalyzed triethylammonium formate reduction of aromatic halides,[2] mono-[2] and dinitro[1] compounds, α,β-unsaturated carbonyl compounds,[3] conjugated dienes,[3] and acetylenes[3] has been reported. Only three simple acetylenes were studied previously, diphenylacetylene, 3-hexyne, and 1-hexyne.[3] We thought it would be useful to investigate the selective reduction of more complex acetylenes and to better define the usefulness of this reaction. Since a major advantage of the reduction with triethylammonium formate over reduction with hydrogen is the ease of precisely measuring the amount of reductant needed, we have looked for other types of compounds which may be selectively reduced, as well as the acetylenes, to find possible new applications for this reagent. With this in mind, we investigated hydrogenolysis of benzylic and allylic oxygen and nitrogen derivatives. Useful reductions were obtained with tertiary allylic amines. This reduction has proved to be useful for selectively removing morpholino and piperidino groups from the tertiary amines obtained in the recently discovered palladium-catalyzed reaction of vinylic halides with olefins and morpholine or piperidine.[4]

(1) Paper III in the series: J. R. Weir and R. F. Heck, *J. Org. Chem.*, companion paper in this issue.
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