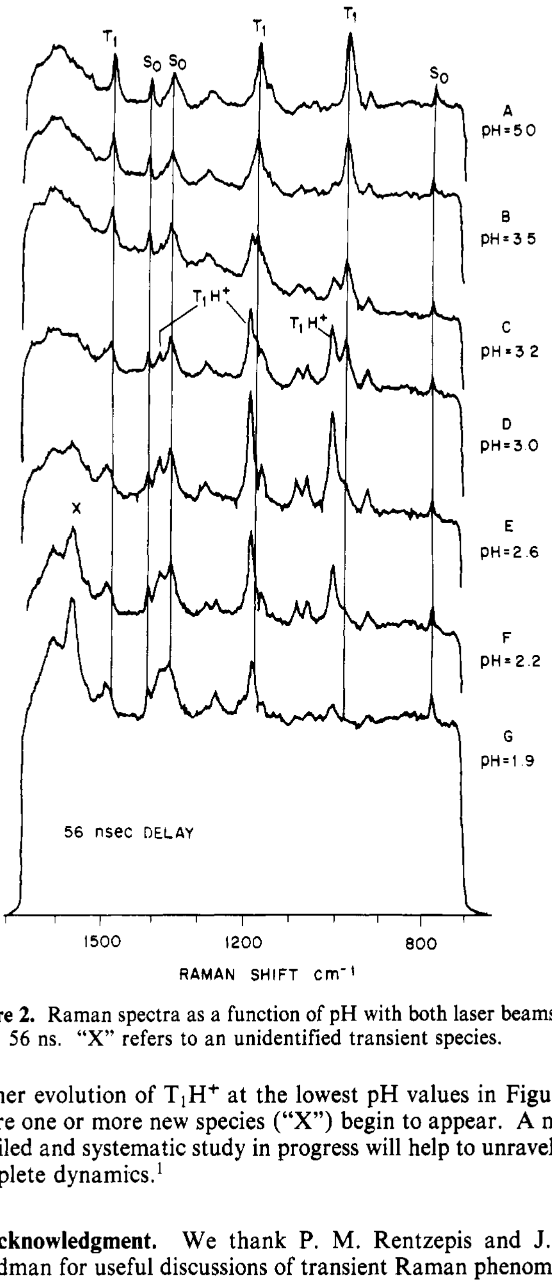

Figure 2. Raman spectra as a function of pH with both laser beams and Δt = 56 ns. "X" refers to an unidentified transient species.

further evolution of T_1H^+ at the lowest pH values in Figure 2 where one or more new species ("X") begin to appear. A more detailed and systematic study in progress will help to unravel the complete dynamics.[1]

Acknowledgment. We thank P. M. Rentzepis and J. M. Friedman for useful discussions of transient Raman phenomena.

Anomalous Cycloaddition Reactions of Distorted Cyclohexa-1,4-dienes. Cycloaddition of *N*-Phenyltriazolinedione to (i,o)-Bicyclo[*n*.2.2]alkadienes

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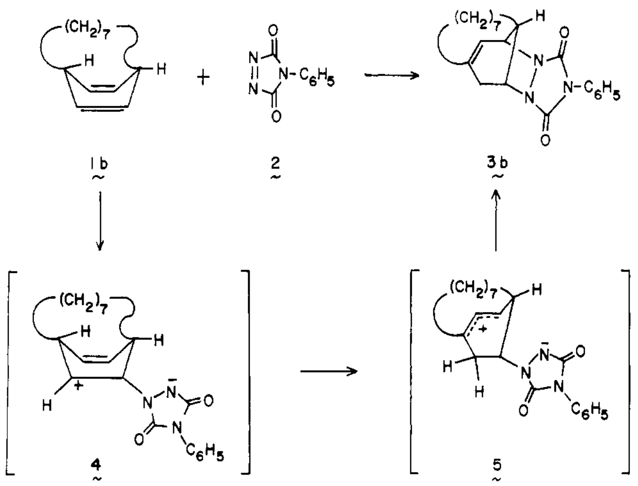
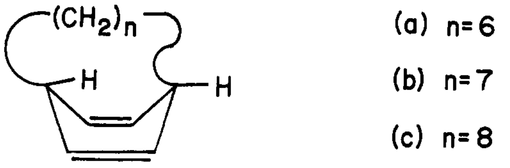
Bridged 1,4-cyclohexadiene derivatives are known to undergo a wide range of cycloaddition reactions. Among the most studied is bicyclo[2.2.1]hepta-2,5-diene which undergoes a homo-Diels–Alder reaction with a wide variety of dienophiles.[1] In the case of highly polarized dienophiles, it has been suggested that zwitterionic intermediates are involved.[2] Similar cycloaddition reactions have been observed with bicyclo[2.2.0]hexa-2,5-dienes,[3] bicyclo[2.2.2]octa-2,5-dienes,[4,5] and bicyclo[3.2.2]nona-6,8-dienes.[4] In contrast, 1,4-cyclohexadiene reacts with diethyl azodicarboxylate, dimethyl acetylenedicarboxylate, tetracyanoethylene, and *N*-phenyl-1,2,4-triazoline-3,5-dione (PTAD) to yield, as primary intermediates, ene type products.[1,6] In view of the difference between 1,4-cyclohexadiene and its bridged derivatives, we decided to explore the reactions of (i,o)-bicyclo[*n*.2.2]alkadienes of general formula **1** with dienophiles. We now wish to report unprecedented cycloaddition reactions of *N*-phenyl-1,2,4-triazoline-3,5-dione (**2**) with **1**.

Scheme I





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Stirring of a chloroform solution of **1b**[7] with **2** at 25 °C for 12 h gave a crystalline 1:1 adduct (**3b**), mp 146–148 °C, in 86% yield.[8] The initial structural assignment was based on a combination of ^{1}H and ^{13}C NMR; ^{1}H NMR (benzene-d_6) δ 7.72 (1 H, m), 7.20–6.85 (4 H, aromatic), 5.38 (H_4, d, $J_{3,4}$ = 6 Hz), 4.09 (H_3, d of d, $J_{3,4}$ = 6 Hz, $J_{2,3}$ = 4 Hz), 3.90 (H_1, m) 2.61 (H_6, $J_{5,6}$ = 18 Hz),[9] 1.85 (2 H, H_2,[10] H_5, $J_{5,6}$ = 18 Hz,[9] $J_{1,5}$ = 4 Hz), and 1.70–0.38 (14 H, br m). Irradiation at δ 2.2 removed all coupling

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(1) Ullman, E. F. *Chem. Ind.* (*London*) **1958**, 1173. Blomquist, A. T.; Meinwald, Y. C. *J. Am. Chem. Soc.* **1959**, *81*, 667. Hall, H. K. *J. Org. chem.* **1960**, *25*, 42. Kobuke, Y.; Sugimoto, T.; Furakawa, J.; Tueno, T. *J. Am. Chem. Soc.* **1972**, *94*, 3633. Krespan, C. G.; McKusick, B. C.; Cairns, T. L. *Ibid* **1961**, *83*, 3428. Cookson, R. C.; Dance, J. *Tetrahedron Lett.* **1962**, 879. Heuber, C. F.; Donoghue, E.; Dorfman, L.; Stuber, E. A.; Danielli, N.; Wenkert, E. *Ibid.* **1966**, 1185. Schrauzer, G. N.; Glockner, P. *Chem. Ber.* **1964**, *97*, 2451. Tabushi, I.; Yamamura, K.; Yoshida, Y.; Togashi, A. *Bull. Chem. Soc. Jap.* **1975**, *48*, 2922; Gillis, B. T.; Hagarty, J. D. *J. Org.Chem.* **1967**, *32*, 330.

(2) Sasaki, T.; Eguchi, S.; Sugimoto, M.; Hibi, F. *J. Org. Chem.* **1972**, *37*, 2317.

(3) Iwamura, H.; Tanabe, Y.; Kobayashi, H. *Tetrahedron Lett.* **1976**, 1987.

(4) Fickes, G. N.; Metz, T. E. *J. Org. Chem.* **1978**, *43*, 1057.

(5) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1964**, *86*, 1434.

(6) Longone, D. T.; Smith, G. L. *Tetrahedron Lett.* **1962**, 205. Jacobson, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 886.

(7) Gassman, P. G.; Bailey, T. F.; Hoye, R. C. *J. Org. Chem.* **1980**, *45*, 2923.

(8) Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds.

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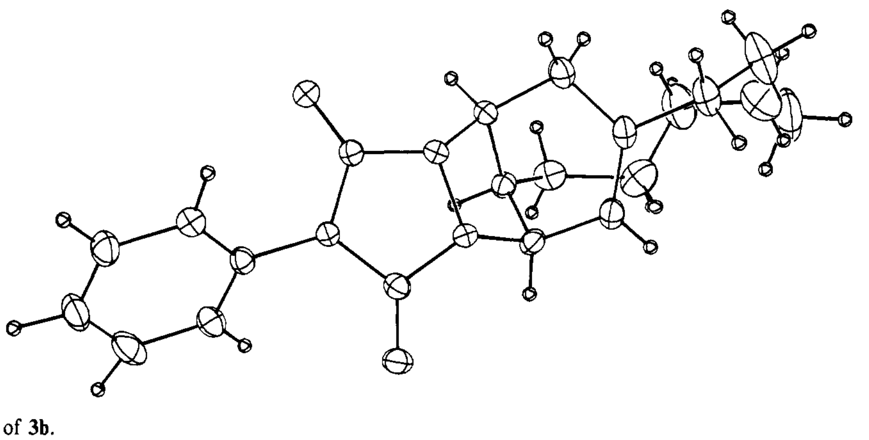
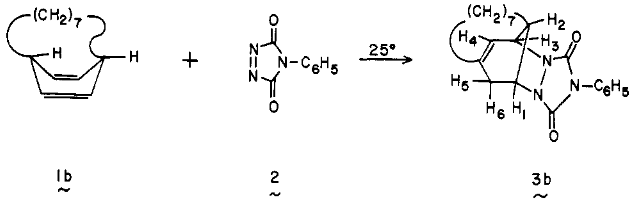


Figure 1. ORTEP drawing of **3b**.

Table I. Second-Order Rate Constants for the Reaction of (i,o)-Bicyclo[7.2.2]trideca-10,12-diene (**1b**) with *N*-Phenyl-1,2,4-triazoline-3,5-dione (**2**) at 40.16 ± 0.02 °C

solvent	dielectric constant	rate, L/mol/s	k_{rel}
benzene	2.27	2.73 ± 0.12	5.4
ethyl acetate	6.03	0.51 ± 0.02	1
acetonitrile	37.5	1.12 ± 0.04	2.2



to H_2, H_5, and H_6, resulting in considerable simplification of the spectrum with both H_3 and H_4 appearing as sharp doublets while H_1 collapsed to a sharp singlet. The ^{13}C NMR ($CDCl_3$) spectra showed δ 155.17, 154.80, 139.51, 131.89, 129.01, 128.02, 125.56, 121.33, 56.91, 54.13, 42.73, 35.50, 31.82, 26.55, 26.36 (2C), 22.17, and 22.03. Confirmation of the structure was provided by a single-crystal X-ray analysis.[11] Figure 1 is an ORTEP drawing of **3b**. Tables of bond lengths, bond angles, and atomic coordinates of all the atoms are included in the supplementary material.

Because of the unique nature of this cycloaddition, the mechanistic path of the reaction was of interest. An obvious possibility involved the ionic mechanism depicted in Scheme I. Initial ionic addition would generate the zwitterion **4**, which on 1,2-hydride shift would yield the allylic cation–amide anion combination **5**. Collapse of this dipolar intermediate would then produce **3b**. In order to test this hypothesis, a study of the effect of solvent on the rate of reaction of **1b** with **2** was carried out. Benzene, ethyl acetate, and acetonitrile were chosen as solvents because their dielectric constants ranged from 2.27 to 37.5.[12] It has been well established[13] that, if a zwitterionic intermediate was involved, this range of polarities would result in a rate change of 10^3–10^5.

Scheme II

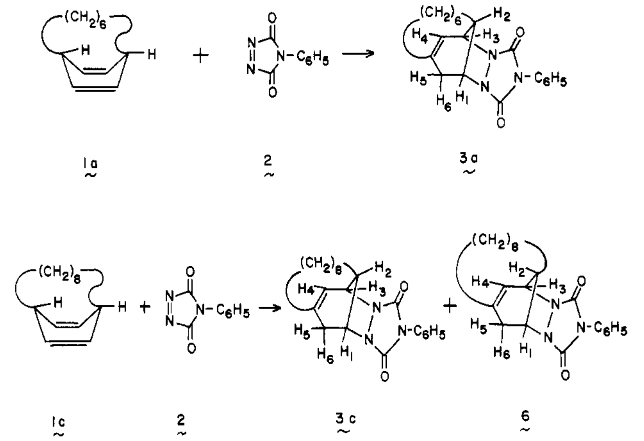


Table I lists the second-order rate constants for the reaction of **1b** with **2**. As can be seen from the data, solvent polarity had little effect on the second-order rate constants. In fact, the rate was fastest in the least polar solvent, benzene. These kinetic results completely ruled out any further consideration of a zwitterionic mechanism. Thus it would appear that the formation of **3** involved either a diradical or a concerted process.

In order to test the generality of the reaction, we added **2** to **1a**[14] and **1c** (Scheme II). Addition to **1a** gave a 37% yield of **3a**, mp 184–187 °C. The ^1H NMR spectrum (C_6D_6) showed δ 7.62 (1 H, m), 7.25–6.65 (4 H, m, aromatic), 5.52 (H_4, d, $J_{3,4}$ = 6 Hz), 4.00 (H_3, d of d, $J_{3,4}$ = 6 Hz, $J_{2,3}$ = 4 Hz), 3.95 (H_1, m), 2.36 (H_6, $J_{5,6}$ = 18 Hz), 2.12 (H_5, $J_{5,6}$ = 18 Hz, $J_{1,5}$ = 4 Hz), 1.95 (H_2, m), and 1.80–0.32 (12 H, br m). The correspondence of this spectrum to that of **3b** established the structure.

The addition of **2** to **1c**[7] in chloroform at 50 °C for 4 h resulted in the formation of two adducts. The major adduct, which was obtained in 54% yield (mp 194–197 °C), showed an ^1H NMR spectrum (C_6D_6) which coincided extremely well with that of **3** and **6**: δ 7.72 (1 H, m), 7.20–6.82 (4 H, m, aromatic), 5.38 (H_4, d, $J_{3,4}$ = 7 Hz), 4.13 (H_3, d of d, $J_{3,4}$ = 7 Hz, $J_{2,3}$ = 4 Hz), 3.92 (H_1, m), 2.31 (H_6, $J_{5,6}$ = 18 Hz), 1.99 (H_5, $J_{1,5}$, = 4 Hz, $J_{5,6}$ = 18 Hz), 1.95 (H_2, m), and 1.77–0.57 (16 H, br m). On the basis of this comparison, the major adduct was assigned structure **3c**.

The minor adduct, which was obtained in 8% yield, was extremely unstable and became intractable on attempted rigorous

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(9) Protons H_5 and H_6 appeared as an AB quartet centered at δ 2.23. The upfield half of the AB quartet exhibited further coupling and appeared as a doublet of doublets. The upfield portion of the AB pattern was assigned to H_5 based on an examination of Dreiding models which indicated the angle between H_1 and H_5 should be ca. 40° while that between H^1 and H^6 should be ca. 80°.

(10) The bridgehead proton, H_2, appeared as a broad multiplet at ca. δ 2.0. Irradiation at δ 4.0 resulted in the decoupling of H_1 and H_3 with H_2 and H_2 then appeared as a triplet (J = 8 Hz).

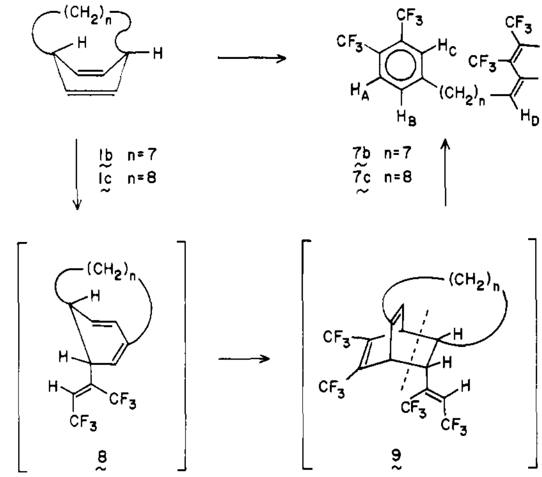
(11) The white crystals of $C_{21}H_{25}N_3O_2$ belonged to the monoclinic space group $P2_1/c$. The measured cell constants, a = 12.335 (3), b = 6.893 (2), c = 22.033 (6) Å and β = 101.17 (2)°, gave a calculated density of 1.270 g/cc for four molecules in the unit cell at ambient temperature. Data were collected on a fully automated Enraf–Nonius CAD4 Diffractometer by using a variable rate ω–2θ scan technique and graphite monochromatized Cu Kα radiation (λ = 1.54184 Å). After Lorentz–polarization corrections, 1941 of 3125 unique reflections (62%) with 2θ = 0–130° were observed for $[F_o > 2\sigma(F_o)^2]$. A combination of direct methods and difference Fourier synthesis was used to locate all nonhydrogen atoms. Thermal anisotropic refinement was applied to all nonhydrogen atoms. The positions of all hydrogen atoms were calculated and refined by full-matrix least-squares analysis. The R factor for the structure was 0.069. All calculations were carried out on a PDP 11/34 computer using the Enraf–Nonius SDP programs. This crystallographic computing package is described by: Frentz, B. A. In "Computing in Crystallography"; Schenck, H., Olthof-Hazekamp, R., van Konigweld, H., Bassie, G. S., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

(12) Reichardt, C. *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 29.

(13) Williams, J. K.; Wiley, D. W.; McKusick, B. C. *J. Am. Chem. Soc.* **1962**, *84*, 2210. Stewart, C. A., Jr. *Ibid.* **1962**, *84*, 117. Proskow, S.; Simmons, H. E.; Cairns, T. L. *Ibid.* **1966**, *88*, 5254.

(14) For the preparation of **1a** see: Gassman, P. G.; Hoye, R. C. *J. Am. Chem. Soc.*, **1981**, *103*, 215.

Scheme III



purification. Its exact M_r (calcd for $C_{22}H_{27}N_3O_2$ 365.208; found: 365.209) confirmed the 1:1 nature of the adduct. The ^{13}C NMR and mass spectral fragmentation patterns were very similar to those of **3c**, while the ^1H NMR differed considerably from **3c**, both in the positions and splitting patterns of H_2, H_3, H_5, and H_6. In view of this data, the minor adduct has been *tentatively* assigned structure **6**.

Addition of perfluoro-2-butyne to **1b** and **1c** appeared to occur in a more precedented fashion. As shown in Scheme III, heating of **1b** with perfluoro-2-butyne for 58 h at 140 °C gave 70% of **7b**, while **7c** was formed from **1c** in 66% yield after 6 days under the same conditions. The structures were readily determined from their NMR spectra. Mechanistically, we believe **1** underwent an initial ene reaction to give **8** which then added a second equivalent of perfluoro-2-butyne to produce **9**. A reverse Diels-Alder reaction of **9** would give **7**.[15]

In summary, distortion of a 1,4-cyclohexadiene through "trans" bridging as in **1** results in a complete change in the reactions with potent dienophiles. The unique products which resulted from these cycloaddition reactions required that our distortion of the 1,4-cyclohexadiene moiety provide the impetus for mechanistically new reaction paths.

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE78-10231, which supported this investigation, and Grant CHE77-28505 which aided in the purchase of an Enraf-Nonius X-ray diffractometer. We thank Mr. M. McGuiggan and Professors L. Pignolet and J. Z. Gougoutas for their help in the X-ray study.

Supplementary Material Available: Tables of bond distances, bond angles, thermal parameters, and atom coordinates (4 pages). Ordering information is given on any current masthead page.

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(15) Surprisingly, **1b** and **1c** failed to react with either dicyanoacetylene or dimethyl acetylenedicarboxylate on heating at 140–170 °C for 6 days.

Synthesis, Structure, and Reactivity of the (i,o)-Diazabicyclo[*n*.2.2]alkene Skeleton. Extremely Facile Cleavage of a C–N Bond

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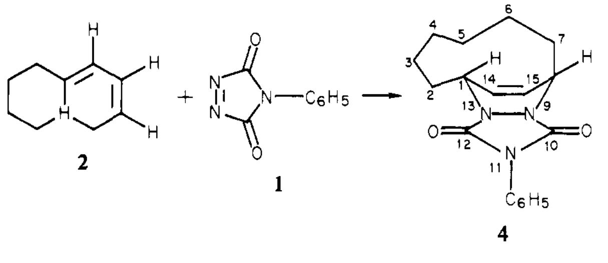
Our interest in the synthesis and reactivity of bicyclic molecules with inverted bridgeheads[1] has prompted us to explore the addition of the very reactive dienophile, *N*-phenyl-1,2,4-triazoline-3,5-dione (**1**) to relatively small, cyclic, *cis,trans*-1,3-dienes. Recently, we demonstrated that maleic anhydride can be added to *cis,trans*-cyclodeca-1,3-diene (**2**) to give the (i,o)-bicyclo[6.2.2]dodecene system, albeit in very low yield.[1d] We now wish to report that **1** adds to **2** in excellent yield and *cis,trans*-cyclonona-1,3-diene (**3**) in acceptable yield to produce (1i,8o)-11-phenyl-9,11,13-triazatricyclo[$6.5.2.0^{9,13}$]pentadec-14-ene-10,12-dione (**4**) and (1i,7o)-4-phenyl-2,4,6-triazatricyclo[$5.5.2.0^{2,6}$]tetradec-13-ene-3,5-dione (**5**), respectively.[2] Single-crystal X-ray structure determination for both **4** and **5** indicated large distortions from normal bonding parameters. These distortions were reflected in the thermal rearrangement of **5** at 50 °C.

When a chloroform solution of molar equivalents of **1**[3] and **2**[4] was stirred at 25 °C for 30 min, an 80% yield of **4**[5] was obtained as a white solid, mp 177–179 °C; ^1H NMR ($CDCl_3$) δ 7.60–7.04 (5 H, m), 6.52–6.20 (2 H, m), 5.07 (1 H, d of t, J = 4 and 5 Hz), 4.63 (1 H, m), and 3.08–0.87 (12 H, br m). The structural assignment was rigorously established through single-crystal X-ray analysis.[6,7] Figure 1 shows an ORTEP stereoview of **4** and Table I lists the bond lengths and bond angles. The structural characteristics of **4** and **6**[1d] were very similar. The C_1–C_2–C_3 angle of **4** was contracted to 105.5° (vs. 107.8° for **6**) as it is "pulled" back. The C_6–C_7–C_8 angle of **4** was expanded to 123.2° (vs. 123.9° for **6**) as it was bent to minimize the nonbonded interaction with the hydrogen at C_1. The other four C–C–C bond angles in



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(1) (a) Gassman, P. G.; Korn, S. R.; Thummel, R. P. *J. Am. Chem. Soc.* **1974**, *96*, 6948. (b) Gassman, P. G.; Korn, S. R.; Bailey, T. F.; Johnson, T. H.; Finer, J.; Clardy, J. *Tetrahedron Lett.* **1979**, 3401. (c) Gassman, P. G.; Bailey, T. F.; Hoye, R. C. *J. Org. Chem.* **1980**, *45*, 2923. (d) Gassman, P. G.; Hoye, R. C. *J. Am. Chem. Soc.* **1981**, preceding paper in this issue. (e) Gassman, P. G.; Hoye, R. C., submitted for publication.

(2) For a discussion of nomenclature in these systems, see ref 1a. Also see: Simmons, H. E.; Park, C. H.; Uyeda, R. T.; Habib, M. F. *Trans. N.Y. Acad. Sci.* **1970**, *32*, 521. The i term has been assigned to that bridgehead carbon having a hydrogen or other nonbridging substituent which resides inside the bicyclic (polycyclic) cavity. The o term has been allocated to that bridgehead carbon having a hydrogen or nonbridging substituent which resides outside the bicyclic (polycyclic) cavity. The i bridgehead has been assigned numbering position 1. Standard IUPAC numbering for the remainder of the bicyclic (or polycyclic) system has then been used. A detailed discussion of nomenclature in these systems and of the problems which occur will be presented in a full paper on this subject.

(3) For the preparation of **1**, see: Cookson, R. C.; Gupta, S. S.; Stevens, I. D. R.; Watts, C. T. *Org. Synth.* **1971**, *51*, 121. See also: Stickler, J. C.; Pirkle, W. H. *J. Org. Chem.* **1966**, *31*, 3444.

(4) For the preparation of **3**, see: Blomquist, A. T.; Goldstein, A. *J. Am. Chem. Soc.* **1955**, *77*, 1001.

(5) Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds except **10**, which was analyzed as its acetylated derivative.

(6) The white crystals of $C_{18}H_{21}N_3O_2$ belonged to the triclinic space group $P\bar{1}$. The measured cell constants a = 8.101 (2), b = 9.921 (2), c = 10.304 (2) Å; α = 93.00 (2), β = 100.02 (2), and γ = 104.80 (1)° gave a calculated density of 1.33 g/cc for four molecules in the unit cell at ambient temperature. Data were collected on a fully automated Enraf–Nonius CAD4 diffractometer by using a variable rate ω–2θ scan technique and graphite monochromatized Cu Kα radiation (λ = 1.54184 Å). After Lorentz–polarization corrections, 2267 of 2993 unique reflections (76%) with 2θ = 0–140° were observed for $[F_o > 2\sigma(F_o)^2]$. A combination of direct methods and difference Fourier synthesis was used to locate all nonhydrogen atoms.[7] The positions for all hydrogen atoms were calculated and refined by full-matrix least-squares analysis. The R factor for the structure was 0.049.

(7) All calculations were carried out on a PDP 11/34 computer by using the Enraf–Nonius SDP programs. This crystallographic computing package is described by Frentz, B. A. In "Computing in Crystallography"; Schenck, H., Olthof-Hazekamp, R., van Konigweld, H., Bassie, G. S., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

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