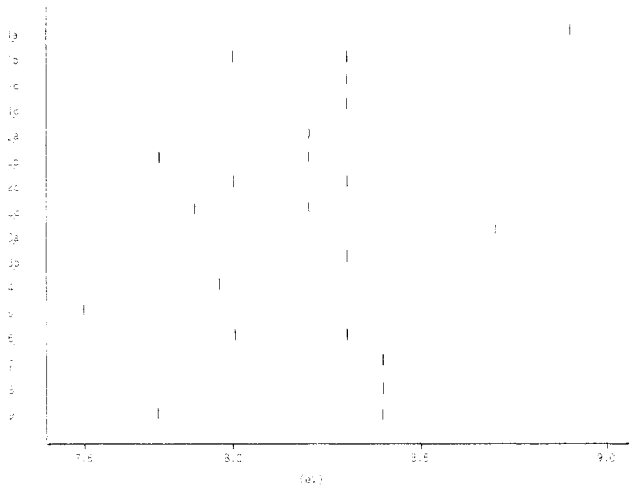

Figure 4. Low IP region of the photoelectron spectra of 1–9.

are only observed in cases of severe steric hindrance (see Figure 4). For thiophenol, the energy difference between the planar and perpendicular forms is only half as large (~1.5 kcal/mol). Presumably, for selenium-substituted aromatics the corresponding energy differences are even smaller. When these electronic factors are coupled with the previously discussed steric factor, the trends reported in this study appear quite reasonable.

In summary, then, it appears that relative peak heights measured from the photoelectron spectra give a reasonable estimation of rotamer populations if distinct features attributable to the different rotamers can be identified. In the compounds examined here, the observation of such distinct features depends on the existence of a significant interaction between the substituent lone pair and the phenyl π orbitals.

Experimental Section

Photoelectron spectra were obtained on a modified Perkin-Elmer PS16 spectrometer.[13] Compounds were either commercially available or synthesized by standard methods.

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Registry No. **1a**, 645-96-5; **1b**, 4346-64-9; **1c**, 17774-38-8; **1d**, 22233-89-2; **2a**, 37773-21-0; **2b**, 1528-88-7; **2c**, 37773-42-5; **2d**, 78805-16-0; **3a**, 78805-17-1; **3b**, 78805-18-2; **4**, 1842-38-2; **5**, 60096-27-7; **6**, 37773-43-6; **7**, 614-71-1; **8**, 496-16-2; **9**, 104-95-0; phenol, 108-95-2; benzenethiol, 108-98-5.

(13) Horozoglu, G. Ph.D. Thesis, City University of New York, 1980.

Cycloaddition of Substituted Bicyclo[3.2.1]octa-2,6-diene with 4-Phenyl-1,2,4-triazoline-3,5-dione

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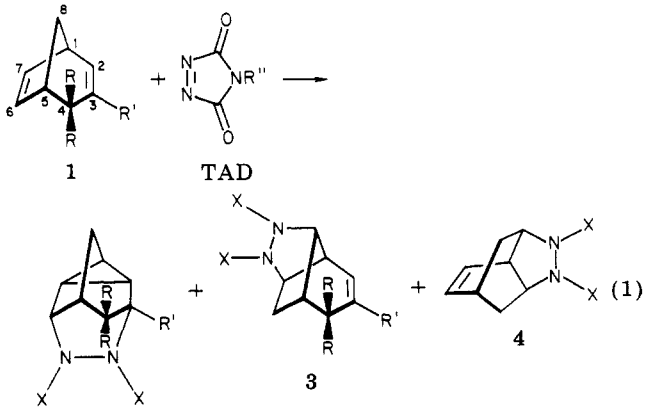
4,4-Dimethylbicyclo[3.2.1]octa-2,6-diene (**1b**) reacts with 4-phenyl-1,2,4-triazoline-3,5-dione to give the rearranged urazole **3b** (via dipolar cycloaddition at the more strained C_6–C_7 double bond) as the only isolable (22% yield) product, while 3-bromobicyclo[3.2.1]octa-2,6-diene (**1c**) affords the ene adduct **7** as the major product (60% yield) together with a 10% yield of the rearranged urazole **3c**. Both dimethyl substitution at the C_4 position and bromo substitution at the C_3 position suppress effectively homocycloaddition and dipolar cycloaddition at the less strained C_2–C_3 double bond. The ene reactivity of the bromo diene **1c** is surprising, since neither the parent diene **1a** nor the dimethyl diene **1b** exhibit this cycloaddition behavior.

Recently we observed[1] that the parent hydrocarbon bicyclo[3.2.1]octa-2,6-diene (**1a**) reacted with 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) to give the urazoles **2**–**4** (eq 1). Urazole **2a** is the product of homocycloaddition at the C_3–C_6 site, while **3a** and **4a** result from dipolar cycloaddition,[2] respectively, at the C_6–C_7 and C_2–C_3 double bonds. The fact that dipolar cycloaddition competed effectively with the usually preferred homocycloaddition[3] is unique for this dienic substrate and stimulated our interest to examine the reaction of substituted derivatives of **1** with TAD. On one hand, we chose the 4,4-dimethyl derivative **1b** in an attempt to suppress the homocycloaddition mode on grounds of steric blocking of homoattack at the C_3–C_6 site; on the other hand, we chose the 3-bromo derivative **1c** to suppress dipolar attack on the C_2–C_3 double bond. We report here on the synthesis of the hitherto unknown diene **1b** and the cycloaddition reactivity of dienes **1b** and **1c** with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD).



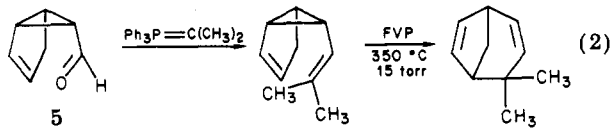
1 TAD **2** **3** **4** (1)

a, R = R = H; b, R = Me, R′ = H; c, R = H, R′ = Br; X + X = -CONR″CO-; R″ = Me, Ph

(1) Adam, W.; De Lucchi, O. *J. Am. Chem. Soc.*, in press.
(2) Adam, W.; De Lucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806.
(3) Adam, W.; De Lucchi, O. *Angew, Chem., Int. Ed. Engl.* **1980**, *19*, 762.

0022-3263/81/1946-4130$01.25/0

The synthesis of **1b** was modeled after that reported for the parent diene **1a**,[4] starting from aldehyde **5** and isopropylidenetriphenylphosphorane (eq 2). Diene **6** was

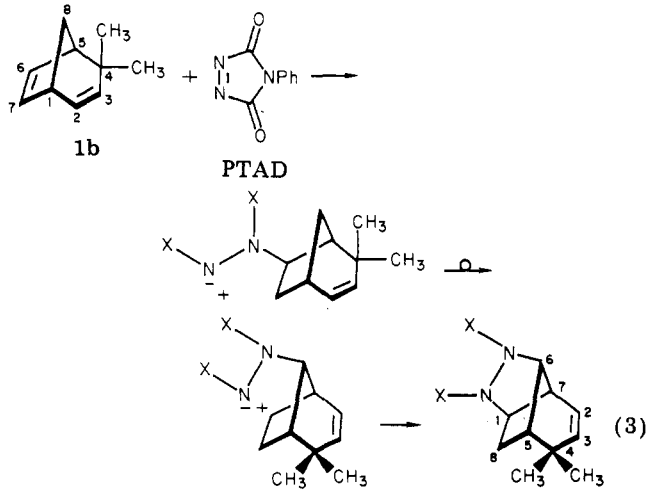


5 6 1b (2)

obtained in 50% yield and exhibited a surprising thermal stability for a *cis*-divinylcyclopropane, i.e., at room temperature it could be preserved for months. In contrast, the unsubstituted diene **6** rearranged in situ during the Wittig reaction to **1a**.[4] Apparently the *gem*-dimethyl group blocks out the usually facile Cope rearrangement. Vacuum pyrolysis (VFP) at 350 °C and 15 torr afforded quantitatively the desired diene **1b**.[5]

Treatment of the bicycloalkadiene **1b** with PTAD in CH_2Cl_2 at 25 °C for 48 h afforded as the only isolable product the rearranged urazole **3b** in 22% yield after silica gel chromatography with CH_2Cl_2. The remainder of the product balance of the reaction of **1b** with PTAD was intractable tar. The urazoles **2b** (homocycloaddition) and **4b** (dipolar cycloaddition at the less strained C_2–C_3 double bond) were not formed. Consequently, the *gem*-dimethyl substitution effectively blocked both of these cycloaddition processes in **1b**, allowing only the dipolar route at the more strained C_6–C_7 double bond to give the rearranged urazole **3b**.

A question arose as to the assignment of the position of the double bond in urazole **3b**. On the basis of mechanistic considerations,[3] we would expect the location of the double bond as proposed in **3b** (eq 3); but it took high-field 400-

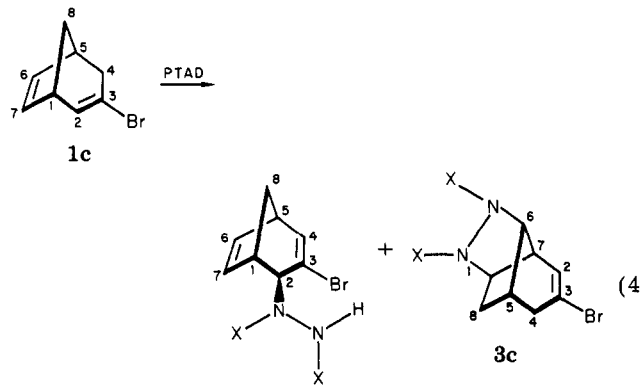


1b PTAD 3b (3)

X + X = -CON(Ph)CO-

MHz ^{1}H NMR with decoupling experiments to confirm this structural feature (cf. Experimental Section for full NMR data). The olefinic region shows the AB part of a ABMX system, where A is only further coupled to M (6 Hz) and B to X (2 Hz). Thus, J_{AM} was assigned to the vicinal coupling $J_{2,7}$ and consequently A (5.53 ppm) was assigned to H_2, B (5.42 ppm) to H_3, M (2.64 ppm) to the bridgehead H_7, and X (2.26 ppm) to the other bridgehead H_5. Furthermore, H_5 is connected by a large coupling of 8 Hz with the proton at 1.81 ppm, which in turn together with the proton at 1.99 ppm must belong to the CH group. Thus, the juxtaposition of H_5 and the CH_2 group is evident and the urazole bridge must be connected between C_1 and C_6 (cf. eq 3).

The bromo diene **1c** gave the ene adduct **7** (eq 4) as



1c 7 3c (4)

X + X = -CON(Ph)CO-

major product (60% yield) together with the rearranged urazole **3c** (10% yield) via dipolar cycloaddition at the more strained C_6–C_7 double bond. The urazoles **2c** and **4c** were not formed in the reaction of the bromo diene **1c** with PTAD. While the 3-bromo substituent was effective in blocking the dipolar attack at the C_2–C_3 double bond, it also suppressed the homocycloaddition route; but more importantly it promoted the ene reactivity of **1c**. This is indeed surprising since the parent diene **1a** gave no ene reaction with TAD. Presumably subtle interplay between electronic and steric factors control the cycloaddition modes of these bicyclic dienic substrates. So far little is known about the mechanistic details of such complex and competitive dienic reactivity.

Experimental Section

Known compounds were prepared and purified according to literature procedures and matched the reported physical constants and spectral data. All new compounds exhibited satisfactory combustion analysis, which were performed in-house. Melting and boiling points are uncorrected. The ^{1}H NMR spectra were recorded on a Varian EM-390 (90 MHz) and an Hitachi R24B (60 MHz) instrument. The 400-MHz was measured on a Bruker WH400 spectrometer. ^{13}C NMR spectra were measured on a Bruker WH90 (in-house) or kindly run for us by Professor Modena's staff (Padua, Italy). Infrared spectra were determined on a Beckman Acculab 4 or on a Perkin-Elmer 157G spectrometer. Unless otherwise stated, rotoevaporation was performed at room temperature (ca. 20 °C) and water aspirator pressure (ca. 10–25 torr).

Preparation of *endo*-6-Isobutenylbicyclo[3.1.0]hex-2-ene (6).[6] Isopropyltriphenylphosphonium bromide (8.2 g, 21 mmol) was placed with ca. 15 mL of dry ether into a three-necked, round-bottomed flask, equipped with magnetic spinbar, N_2 inlet and outlet, and a rubber septum. With stirring, 12.3 mL of a 1.5 N solution of *n*-BuLi in hexane was added dropwise and the resulting red solution was kept at room temperature for 3 h. After the solution was cooled with an ice–water bath, the 6-*endo*-carboxaldehyde bicyclo[3.1.0]hex-2-ene[7] (**5**) (2 g, 18.5 mmol) in

(4) (a) Cupas, C.; Watts, W. E.; Schleyer, P. v. R. *Tetrahedron Lett.* **1964**, 2503. (b) However, cf. Brown, J. M. *J. Chem. Soc., Chem. Commun.* **1967**, *638*, for another example of a reluctant *cis*-divinylcyclopropane rearrangement.

(5) Refluxing a benzene solution of **6** for 48 h gave a mixture of 20% **1b** and 80% 1-(3-cyclopentenyl)-3-methyl-1,3-butadiene by ^{1}H NMR (C_6D_6, Me_4Si) δ 0.50–2.60 (8 H, complex m), 4.65 (2 H, d of m, 9 Hz), 5.37 (2 H, m), 5.90 (2 H, m). The latter was not further characterized.

(6) Brown, J. M.; Occolowitz, J. L. *J. Chem. Soc. B.* **1968**, 411.

(7) Meinwald, J.; Labana, S. S.; Chadha, M. S. *J. Am. Chem. Soc.* **1963**, *85*, 582.

ca. 5 mL of dry ether was added by means of a syringe. The reaction mixture was allowed to reach room temperature and kept there for 1 h. THF was added to replenish the ether that was evaporating on account of the N_2 stream. The reaction mixture was heated in a steam bath until all the ether had been distilled off and refluxed for 1 h. Extraction with pentane and usual workup afforded after rotoevaporation a yellow oil. Pure **6** was obtained after distillation on a 10-cm Vigreaux column, affording 1.23 g (50% yield): bp 63–65 °C (15 torr); n^{21}_D 1.4963; ^{1}H NMR (CCl_4, Me_4Si) δ 1.40–2.70 (5 H, $H_{1,4,5,6}$, complex m), 1.67 (3 H, CH_3, s), 1.65 (3 H, CH_3, s), 4.72 (1 H, *iso*-butenyl H, d, 6.6 Hz), 5.45 and 5.55 (2 H, $H_{2,3}$, complex AB pattern, $J_{2,3}$ = 6 Hz); IR (CCl_4) ν 3020, 2960, 2900, 1440, 1375, 1355, 1160, 1080, 1040, 910, 720 cm^{-1}.

4,4-Dimethylbicyclo[3.2.1]octa-2,6-diene (1b). A home-built, simplified model of the Bonnett–Brown–Smith[8] vacuum flash pyrolysis (VFP) apparatus was used. A sample of *endo*-6-isobutenylbicyclo[3.1.0]hex-2-ene **6** (50 mg, 0.37 mmol) was placed into a 10-mL round-bottomed flask which was connected to the VFP apparatus, consisting of a 25-cm long, heavy-walled (12 mm o.d.) Pyrex tube, which was heated by means of a Nichrome resistance wire at 350 °C. The outlet of the pyrolysis vessel was connected to a liquid nitrogen cold trap, which in turn was connected via a three-way stopcock to a vacuum pump. At 15 torr and 60 °C the diene **6** was volatilized into the pyrolysis vessel. After completion of the pyrolysis, the condensed pyrolysate was recovered from the liquid nitrogen cold trap by dissolving it in CH_2Cl_2. Rotoevaporation of the solvent afforded the product in quantitative yields as colorless oil. An analytical sample (n^{20}_D 1.4854) was obtained by VPC collection on a 15% SE 30 column on Chromosorb P at 150 °C: ^{1}H NMR (CCl_4, Me_4Si) δ 0.85 (3 H, endo CH_3, s), 1.12 (3 H, exo CH_3, s), 1.92 (2 H, H_8, m), 2.35 (1 H, bridgehead, m), 2.52 (1 H, bridgehead, m), 4.90 (1 H, H_3, dd, $J_{2,3}$ = 9.6 Hz, $J_{1,3}$ = 2.1 Hz), 5.70 (1 H, H_6, dd, $J_{6,7}$ = 5.7 Hz, $J_{5,6}$ = 2.9 Hz), 5.88 (1 H, H_2, dd, $J_{1,2}$ = 6 Hz), 6.23 (1 H, H_7, dd, $J_{1,7}$ = 2.9 Hz); IR (CCl_4) ν 3075, 3020, 2960, 2920, 2875, 1475, 1465, 1450, 1370, 1365, 1340, 1040, 940 cm^{-1}.

Reaction of 4,4-Dimethyltricyclo[3.2.1]octa-2,6-diene (1b) with PTAD. The bicycloalkadiene **1b** (180 mg, 1.34 mmol) was dissolved in ca. 10 mL of CH_2Cl_2 and placed into a 25-mL, round-bottomed flask and PTAD (250 mg, 1.43 mmol) was added in one portion. After the mixture was stirred at room temperature overnight, TLC (CH_2Cl_2) revealed no starting material. The red-brown solution was rotoevaporated and chromatographed on 70–230-mesh silica gel (ca. 15:1 weight ratio of adsorbant to substrate) with CH_2Cl_2. Recrystallization from EtOH afforded needles, mp 175–6 °C, 92 mg (22% yield); correct elemental composition by combustion analysis: 400-MHz ^{1}H NMR[10] ($CDCl_3$, Me_4Si) δ 1.00 (3 H, CH_3, s), 1.18 (3 H, CH_3, s), 1.81 (1 H, $H_{8\text{-exo}}$, ddd, $J_{8\text{-endo},8\text{-exo}}$ = 14 Hz, $J_{5,8\text{exo}}$ = 8 Hz, $J_{7,8\text{-exo}}$ = 2 Hz), 1.99 (1 H, $H_{8\text{-endo}}$, br d, $J_{8\text{-endo},8\text{-exo}}$ = 14 Hz), 2.26 (1 H, H_5, br d, $J_{5,8\text{-exo}}$ = 8 Hz), 2.64 (1 H, H_7, dq, $J_{2,7}$ = 6 Hz, $J_{1,7}$, $J_{5,7}$, $J_{6,7}$, $J_{7,8\text{-exo}}$ = 1–2 Hz), 4.55 (1 H, H_6, br s, $J_{2,6}$, $J_{6,7}$ = 0.5–1 Hz); 4.58 (1H, H_1, dd, $J_{1,8\text{-endo}}$ = 4 Hz, $J_{1,7}$ = 2 Hz), 5.42 (1 H, H_3, dd, $J_{2,3}$ = 9.5 Hz, $J_{3,5}$ = 2 Hz), 5.53 (1 H, H_2, dd, $J_{2,3}$ = 9.5 Hz, $J_{2,7}$ = 6 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 24.83, 28.96, 29.87, 40.13, 45.90, 47.11, 62.29, 64.29, 120.27, 139.09, and expected resonances for the phenyl and the CO carbons; IR (KBr) ν 2940, 1765, 1700, 1495, 1400, 1275, 1240, 1125, 1065, 810, 770, 700 cm^{-1}.

Reaction of 3-Bromobicyclo[3.2.1]octa-2,6-diene[9] (1c) with PTAD. A solution of bromooctadiene **1c** (150 mg, 0.81 mmol) and PTAD (200 mg, 1.6 mmol) in 10 mL of CH_2Cl_2, was stirred for 48 h at room temperature. The resulting red-brown reaction mixture was filtered and concentrated by rotoevaporation. Column chromatography on 70–230-mesh silica gel (ca. 20:1 weight ratio of adsorbant to substrate) with CH_2Cl_2 afforded rearranged urazole **3c**, 71 mg (10% yield), as the second fraction, mp 188–9 °C (needles from EtOH); correct elemental composition by combustion analysis: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.73–2.17 (2 H, m), 2.38 (1 H, A part AB system) J_{AB} = 18 Hz), 2.65 (2 H, bridgehead, m), 2.93 (1 H, B part AB system), 4.33 (1 H, CHN, br s), 4.75 (1 H, CHN, br s), 6.03 (1 H, H_2, d, $J_{7,2}$ = 6.3 Hz), 7.50 (5 H, C_6H_5, narrow m); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 33.21, 36.97, 43.89, 47.23, 62.11, 65.99, 123.61, 124.82, and expected resonances for NPh and CO carbons; IR (KBr) ν 3060, 2910, 1720, 1700, 1495, 1400, 1260, 1230, 1130, 835, 685 cm^{-1}. As the third fraction, the ene product **7** was isolated, 410 mg (60% yield), mp 208–9 °C (prisms from EtOH); correct elemental composition by combustion analysis: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.85 (1 H, H_8, m, J_{gem} = 10.5 Hz), 2.03 (1 H, H_8, m), 2.97 (2 H, $H_{1,5}$, m), 4.62 (1 H, H_2, t, 1.5 Hz), 6.08 (1 H, H_7, dd, 5.1 and 3 Hz), 6.52 (1 H, H_6, q, 2.7 Hz), 6.77 (1 H, H_4, d, 7.2 Hz), 7.50 (5 H, C_6H_5, m), 8.30 (1 H, NH, br); IR (KBr) ν 3150, 3060, 2940, 1755, 1690, 1485, 1410, 1285, 1175, 1120, 905, 770, 730, 685 cm^{-1}.

Acknowledgments are made to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the National Institutes of Health, the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the generous financial support. Dr. G. Wolff from Bruker Analytishe Meβtechnik (Forchheim) is gratefully acknowledged for the 400-MHz NMR spectra.

Registry No. 1b, 76487-21-3; **1c**, 51788-41-1; **3b**, 78698-20-1; **3c**, 78698-21-2; **5**, 4729-05-9; **6**, 78698-22-3; **7**, 78698-23-4; isopropyltriphenylphosphonium bromide, 1530-33-2; 1-(3-cyclopentenyl)-3-methyl-1,3-butadiene, 78698-24-5; PTAD, 4233-33-4.

(8) Bonnett, R.; Brown, R. F. C.; Smith, R. *J. Chem. Soc., Perkin Trans.* 1 **1973**, 1432.

(9) Moore, W. R.; Moser, W. R.; LaPrade, J. E. *J. Org. Chem.* **1963**, *28*, 2200.

(10) For convenience, the numbering of the skeleton (**3b**) is that given in eq 3.