Thermal Retrograde [2 + 2] Aromatization of Caged Bicyclo[4.2.0]octa-2,4-diene Derivatives

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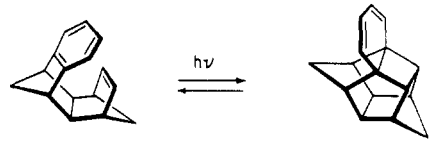
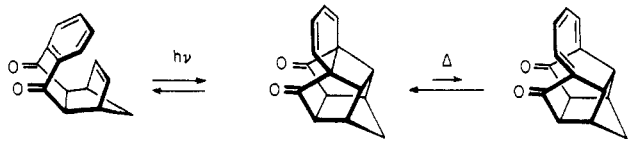
The question of the thermal frangibility of bicyclo[4.2.0]octa-2-diene moieties located within strained caged molecules is examined. For this purpose, the urazoles **6**, **10**, **14**, and **17** were prepared and individually converted by halogenation–dehydrohalogenation into their more highly oxidized counterparts **7**, **11**, **15**, and (presumably) **19**, respectively. All four compounds were observed to undergo relatively facile retrograde [2 + 2] fragmentation and resultant aromatization. These findings agree with the earlier expectation that a portion of the large potential exothermicity available to this reaction pathway may operate to facilitate the nonconcerted two-band scission, but contrast with the behavior of caged diketone **4**. This dichotomy in chemical reactivity is briefly discussed.

Excited-state [6 + 2] cycloadditions of benzene rings to double bonds are well documented reactions.[3] Intramolecular variants of this process,[4] exemplified by **1**[5] and **3**,[6] are also known. The photoisomerizations of **1** to **2**, carried out under conditions of acetone sensitization, and of **3** to **4** (benzene or cyclohexane solution) expectedly lead to



1 **2**

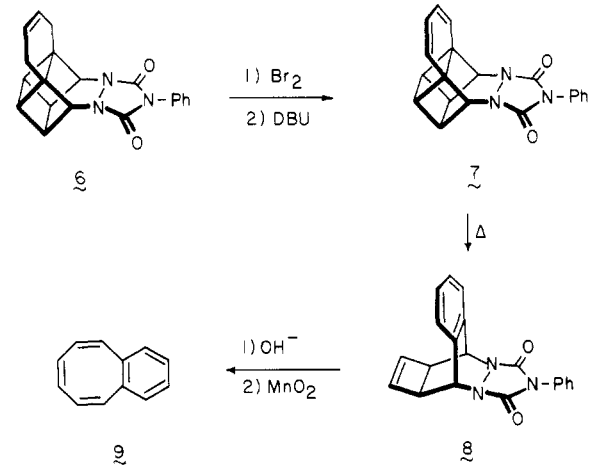


3 **4** **5**

photostationary mixtures of the individual components. Because the bicyclo[4.2.0]octa-2,4-diene part structures within **2** and **4** form part of highly strained cage structures, such processes have attracted attention as possible methods for the photochemical conversion of solar energy.[7] However, dione **4** has been shown to be thermally stable to temperatures above 150 °C[7,8] and to resist catalytic reversion to **3**. The reluctance of **4** to experience retrograde [2 + 2] aromatization despite a large potential exothermicity has been attributed to adverse inductive and steric substituent effects.[7] More recently, however, Mehta and co-workers have demonstrated that **4** equilibrates readily with triene **5** in refluxing toluene[9] and in the presence of acids.[8] Since such behavior could deprive **4** of the opportunity to revert to **3** upon heating, further investigation of the propensity of strained bicyclo[4.2.0]octa-2,4-dienes for thermal aromatization appeared in order. Molecules such as **2** and **4** are geometrically constrained to $[{}_{g}2_{s} + {}_{\sigma}2_{s}]$ fragmentation and resultant nonconcertedness.[3] Nonetheless, we now show that thermal reactions of this type can occur under relatively mild conditions.

Results and Discussion

Urazole **6**, an intermediate prepared earlier in these laboratories,[10] was quantitatively transformed into the corresponding dibromide by reaction with elemental bromine. Subsequent dehydrobromination with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in anhydrous tetrahydrofuran yielded the desired diene **7**. The first clue to the thermal instability of **7** materialized during its attempted recrystallization from isopropyl alcohol. In the time required to dissolve the rather insoluble solid, almost complete conversion to **8** took place. Kinetic measurements made on solutions of **7** in C_6D_6–C_5H_5N (1:1) established the half-life of the diene under these conditions to be only 20 min at 76.6 °C. The structural assignment to **7** follows from spectral data (see Experimental Section) and its conversion through hydrolysis–oxidation[11] to benzocyclooctatetraene (**9**).[12]



6 **7** **8** **9**

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(2) Proctor and Gamble Co. Fellow, 1974–1975.
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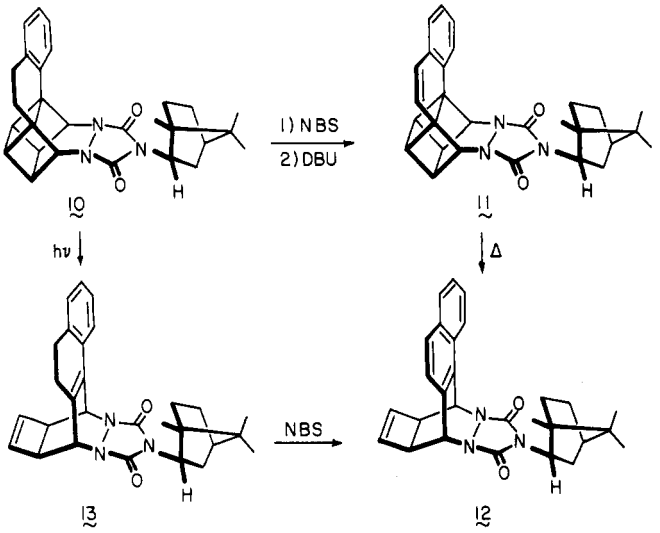
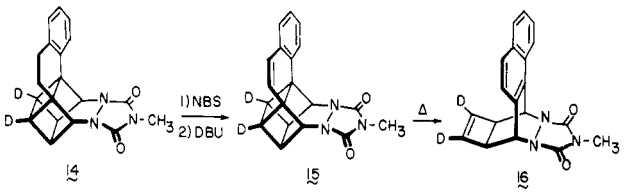
At this junction, our attention was directed to the pair of angular tetralin derivatives **10** and **14**.[13,14] Access to **10** rests upon the efficient Diels–Alder cycloaddition of (–)-*endo*-bornyltriazolinedione[15] to 2,3-benzo[4.4.2]propella-2,7,9,11-tetraene[13] and triplet-sensitized [2 + 2] photocyclization of the adduct (the absolute configuration of diastereomerically pure **10–13** is presently the subject of an X-ray crystal structure study). Benzylic bromination of this urazole followed by treatment with DBU (C_6H_6–THF solution, 25 °C, 18 h) afforded **11** in 40% overall yield (based upon recovered **10**). Heating of **11** in carbon tetrachloride gave **12** cleanly. An authentic sample of **12** was prepared by irradiation of **10** to achieve photofragmentation[14] to **13** and dehydrogenation of this compound with *N*-bromosuccinimide (NBS) in dichloromethane solution.

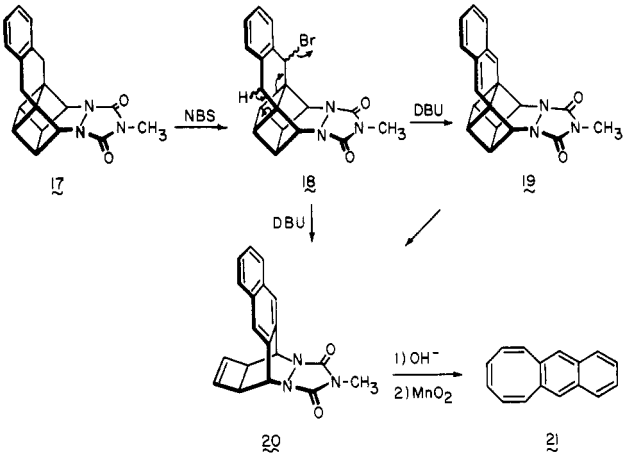


A similar sequence of chemical events was noted when **14** was analogously brominated with NBS. Introduction of the double bond was again achieved with DBU at room temperature (24 h). Heating of **15** in ethyl acetate as before delivered **16** (34% overall yield).



The availability of **17**[13] led us to consider another aspect of these aromatization reactions. While bromide **18** should be available without difficulty, subsequent elimination of the elements of HBr cannot give rise to a styrene part structure as before. The transient generation of *o*-xylylene **19** appeared feasible. A more fascinating possibility was the direct eliminative fragmentation of **18** to **20** (see arrows). In actuality, **18** was converted cleanly to **20** (59% isolated) when exposed to DBU in benzene–tetrahydrofuran (3:1) at room temperature for 24 h. The hydrolysis–oxidation of **20** afforded the known naphthocyclooctatetraene **21**.[16]

Clearly, the [2 + 2] cleavage–aromatization of **7**, **11**, **15**, and perhaps **19** occurs readily. The fragmentation of one framework bond in **7** would result in the generation of a



biradical species of which one radical center is a delocalized pentadienyl radical. The resonance energy of such a species must be greater than that of an allyl (11.6–14.0 kcal/mol) or benzyl radical (~13.5 kcal/mol). Thus, **7**, **11**, and **15** are all capable of forming biradical intermediates possessing roughly the same amount of stabilization. The 1,8-bishomocubane nucleus of the urazoles is without doubt more strained than the secohomopentaprismane ring system present in **4**, and the recalcitrancy of **4** must be due in large part to diminished ring strain which results in a lower energy of the starting state. A particularly interesting difference would also seem to be the tendency of **4** to isomerize to trienedione **5**, a phenomenon which would be less likely in the urazole examples because of the more adverse strain consequences of this valence isomerization in a 1,8-bishomocubane (Bredt-type distortion) and the absence of potentially conjugative carbonyl groups.

Experimental Section

Proton magentic resonance spectra were obtained with a Varian EM-360 spectrometer except were noted; apparent splittings are given in all cases. ^{13}C NMR spectra were recorded on a Bruker WP-80 spectrometer and infrared spectra were determined on a Perkin-Elmer Model 467 instrument. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The optical rotations were obtained on a Perkin-Elmer Model 241 polarimeter and are expressed in milligrams/milliliter.

Bromination–Dehydrobromination of 6. A magnetically stirred cold (–78 °C) solution of **6**[10] (0.50 g, 1.51 mmol) in 100 mL of dichloromethane was treated dropwise with 4.9 mL of a 0.33 M solution of bromine in carbon tetrachloride (1.62 mmol). The reaction mixture was stirred at –78 °C for 15 min and allowed to warm to room temperature where it was kept for 30 min. Removal of the solvent in vacuo afforded a quantitative yield of dibromide as a white solid: IR ($CHCl_3$) 3010, 1760, 1695, 1505, 1420 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.65–7.25 (m, 5 H), 4.72 (m, 2 H), 4.55 (m, 2 H), 3.80–3.35 (br m, 2 H), 2.55, 2.38, and 2.20 (pseudo t, 2 H).

A solution of the dibromide in anhydrous tetrahydrofuran (125 mL) was treated in one portion with DBU (2.00 g, 13.2 mmol) and stirred at room temperature for 18 h. Addition of water (50 mL) dissolved a light precipitate which had formed. The reaction mixture was diluted with dichloromethane and the layers were separated. The aqueous phase was extracted with dichloromethane and the organic layers were combined. After being washed with water (2 × 150 mL), 10% hydrochloric acid (150 mL), 10% sodium carbonate solution (150 mL), and brine, the solution was dried, filtered, and evaporated to dryness (no heat was applied). The resulting white solid was shown by ^1H NMR to be a mixture of dibromide, diene **7**, and fragmentation product **8**, with **7** predominating widely; ^1H NMR ($CDCl_3$) δ 7.5–7.1 (m, 5 H), 5.7–5.1 (AA'BB', 4 H), 4.60 (t, J = 3.5 Hz, 2 H), 3.8–3.3 (m, 4 H).

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Retrograde Fission of 7 to 8. The substance obtained above was recrystallized three times from isopropyl alcohol to give 8 as colorless crystals: mp 218–218.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.5–7.1 (m, 9 H), 5.74 (s, 2 H), 5.49 (m, 2 H), 3.56 (d, J = 4 Hz, 2 H); m/e calcd 329.1169.

Anal. Calcd for $C_{20}H_{15}N_3O_2$: C, 72.94; H, 4.59; N, 12.80. Found: C, 72.66; H, 4.79; N, 12.80.

Benzocyclooctatetraene (9). A suspension of 8 (430 mg, 1.30 mmol) and 85% potassium hydroxide (850 mg, 15.0 mmol) in 20 mL of 2-propanol was heated at the reflux temperature under a nitrogen atmosphere for 2.25 h. The reaction mixture was cooled in ice and 10% hydrochloric acid was added until the pH measured 2. This mixture was stirred for 5 min and 3 N ammonium hydroxide was added to bring the pH to 7–8. Pentane (15 mL) was added, followed by 2.60 g of manganese dioxide on activated carbon (slow addition at first to allow for gas evolution). The black suspension was stirred for 30 min at 0 °C and for 1 h at room temperature. The organic layer was separated by decantation and the remaining solid was slurried several times with pentane. The organic fractions (50 mL) were combined, washed with water (2 × 50 mL) and brine (50 mL), and dried. The aqueous washes were extracted with pentane and treated analogously. The combined organic solutions were filtered and concentrated by distillation at atmospheric pressure through a 100-mm vacuum-jacketed Claisen–Vigreux head. The product (83 mg, 42%) was purified by preparative VPC (6 ft × 0.25 in. 5% SF-96 on Chromosorb G, 120 °C). The ^{1}H NMR spectrum was identical with that of an authentic specimen.[12]

Kinetic Study of the 7 → 8 Aromatization. Samples of freshly prepared 7 were dissolved in a 1:1 C_6D_6–C_5H_5N solvent system. Aliquots were sealed in NMR tubes under house vacuum and stored at −70 °C until use. Since the spectrum of 7 [δ 7.94–7.4 (m, 5 H), 5.82–5.45 (AA′BB′, 4 H), 4.98 (t, J = 3.5 Hz, 2 H), 3.7–3.6 (m, 4 H)] was found to differ drom that of 8 [δ 7.60–7.42 (m, 9 H), 5.80 (pseudo t, J = 3.5 Hz, 4 H), 3.60 (J = 3.5 Hz, 2 H)] in certain key regions, it was possible to follow the decreasing concentration of 7 by monitoring the area of the δ 4.98 signal vs. that of the constant intensity peak at δ 3.60. Spectra were recorded with a Jeolco MH-100 instrument at a probe temperature of 76.6 °C. A least-squares analysis of plots of ln (δ 4.98 area/δ 3.60 area) vs. times was employed to obtain the rate constant. A pair of kinetic runs was carried out and the averaged rate constant was 5.85×10^{-4} s^{-1} or a $t_{1/2}$ of 20 min.

Diels–Alder Addition of (−)-*endo*-Bornyltriazolinedione to 2,3-Benzo[4.4.2]propella-2,7,9,11-tetraene. A cold (−78 °C), magnetically stirred solution of 2,3-benzo[4.4.2]propella-2,7,9,11-tetraene[13] (4.36 g, 21.1 mmol) in pentane–ethyl acetate (4:1, 150 mL) was treated dropwise with a solution of (−)-*endo*-bornyltriazolinedione[15] (4.97 g, 21.1 mmol) in 30 mL of the same solvent. The reaction mixture was stirred for 1 h at room temperature and the precipitate which had formed was collected to give 3.40 g of colorless, crystalline adduct, $[\alpha]^{23}_{578}$ −243° (c 10.9, benzene). The filtrate was diluted with more pentane to precipitate an additional 3.73 g (total 77%) of product, $[\alpha]^{23}_{578}$ 169° (c 14.0, benzene). One pure diastereoisomer was obtained by two recrystallizations of the first precipitate from chloroform–ethyl acetate: mp 260–260.5 °C; $[\alpha]^{23}_{D}$ −231° (c 12.8, benzene); IR (KBr) 3080–2800, 1765, 1700, 1420, 1390, 780, 755 cm^{-1}; UV (C_2H_5OH) 258 nm (ε 3.9×10^3), 215 (9.7×10^3); ^{1}H NMR ($CDCl_3$) δ 7.53–7.20 (m, 4 H), 6.34–6.29 (m, 2 H), 6.02 (d, J = 2.8 Hz, 1 H), 5.75 (d, J = 2.8 Hz, 1 H), 5.53–5.50 (m, 1 H), 4.73–4.70 (m, 1 H), 4.23–4.10 (m, 1 H), 2.90–1.11 (series of m, 11 H), 0.92 (s, 3 H), 0.84 (s, 3 H), 0.71 (s, 3 H); ^{13}C NMR ($CDCl_3$) 160.0, 159.4, 139.3, 138.4, 134.4, 129.0, 127.7, 127.2 (2 C), 126.7, 125.5, 59.4, 59.1, 57.0, 51.6, 51.0, 49.7, 47.8, 45.5, 29.6, 28.1, 272, 26.7, 25.8, 19.7, 18.7, 14.0 ppm; m/e calcd 441.2416, obsd 441.2425.

Anal. Calcd for $C_{28}H_{31}N_3O_2$: C, 76.16; H, 7.08; N, 9.52. Found: C, 75.80; H, 7.08; N, 9.49.

Photocyclization–Rearrangement of the Urazole Adduct. A solution of the preceding urazole adduct (1.0 g, 2.26 mmol) in benzene–acetone (1:1, 400 mL) was irradiated through Corex under a nitrogen atmosphere with a 450-W Hanovia lamp for 2 h. Three such runs were combined and the solvent was evaporated. The reaction mixture was separated into its two components by high-pressure liquid chromatography on a Waters Prep 500 instrument (silica gel, elution with 25% ethyl acetate in petroleum ether). There was isolated 1.51 g (50%) of 10: colorless crystals; mp 202–202.5 °C (from benzene–hexane); $[\alpha]^{23}_{D}$ −28.9° (c 13.3, chloroform); IR (KBr) 3050–2700, 1740, 1700, 1520, 1410, 1380, 1290, 1280 cm^{-1}; UV (C_2H_5OH) 225 nm (ε 1.4×10^4); ^{1}H NMR ($CDCl_3$) δ 7.42–7.13 (m, 4 H), 5.77–5.39 (m, 1 H), 4.83–4.76 (m, 1 H), 4.33–1.20 (series of m, 16 H), 0.95 (s, 3 H), 0.85 (s, 3 H), 0.77 (s, 3 H); ^{13}C NMR ($CDCl_3$) 152.8, 152.4, 138.8, 134.1, 128.6, 127.1 (2 C), 125.8, 58.8, 53.5, 52.2, 51.7, 51.2, 48.4, 47.8, 45.5, 43.8, 38.5, 38.4, 38.3, 29.4, 28.0, 27.8, 27.2, 26.6, 19.7, 18.8, 13.9 ppm; m/e calcd 441.2416, obsd 441.2425.

Anal. Calcd for $C_{28}H_{31}N_3O_2$: C, 76.16; H, 7.08; N, 9.52. Found: C, 76.12; H, 7.10; N, 9.48.

Urazole 13 was eluted first with 10% ethyl acetate in petroleum ether. There was obtained 600 mg (20%) of this product as a colorless crystalline solid: mp 181–182.5 °C (from hexane); $[\alpha]^{23}_{D}$ 114° (c 9.8, chloroform); IR (KBr) 3100–2800, 1760, 1710, 1420, 1395, 1385, 780 cm^{-1}; UV (C_2H_5OH) 270 nm (ε 2.5×10^4), 225 (5.5×10^5); ^{1}H NMR ($CDCl_3$) δ 7.26–7.12 (m, 4 H), 5.97 (q, J = 2.6 Hz, 2 H), 5.42 (d, J = 4.1 Hz, 1 H), 4.85 (d, J = 4.1 Hz, 1 H), 4.30–1.57 (series of m, 14 H), 0.90 (s, 3 H), 0.82 (s, 3 H), 0.74 (s, 3 H); ^{13}C NMR ($CDCl_3$) 159.7, 159.4, 159.0, 139.6, 139.0, 138.8, 138.6, 135.2, 131.1, 130.4, 129.2, 128.8, 128.0, 127.6, (2 C), 127.3, 127.1, 126.2, 122.5, 122.0, 121.4, 59.3, 59.2, 58.9, 53.9, 53.7, 51.7, 51.6, 47.8, 45.5, 45.4, 41.8, 41.6, 29.2, 28.9, 27.9, 27.1, 26.5, 26.3, 25.6, 19.6, 18.7, 18.6, 14.0 ppm; m/e calcd 441.2416, obsd 441.2425.

Anal. Calcd for $C_{28}H_{31}N_3O_2$: C, 76.16; H, 7.08. Found: C, 76.12; H, 7.08.

Preparation of 11. Retrograde Fission to 12. A mixture of 10 (103 mg, 0.233 mmol), *N*-bromosuccinimide (44.0 mg, 0.247 mmol), and AIBN (2 mg) in dry benzene (20 mL) under argon was irradiated with a sunlamp for 4 h. The reaction mixture was alllowed to cool, treated with a solution of DBU (350 mg, 2.3 mmol) in dry tetrahydrofuran, and stirred overnight under nitrogen at room temperature. The mixture was washed with water (2 × 10 mL), 10% hydrochloric acid (10 mL), 0.5 N sodium hydroxide (10 mL), and sodium chloride solutions (10 mL) before drying. Solvent evaporation left a brown oil which was subjected to preparative layer chromatography on silica gel. Elution with 25% ethyl acetate in hexane afforded 27.6 mg (27%) of 11 and 14.1 mg (13%) of unreacted 10. For 11: ^{1}H NMR ($CDCl_3$) δ 7.4–7.1 (m, 4 H), 6.23 (d, J = 9.9 Hz, 1 H), 5.90 (d, J = 9.9 Hz 1 H), 5.25–5.10 (m, 1 H), 4.83–4.76 (m, 1 H), 4.40–1.10 (series of m, 12 H), 0.95 (s, 3 H), 0.85 (s, 3 H), 0.60 (s, 3 H).

The 11 so obtained was heated at reflux in carbon tetrachloride solution (10 mL) under nitrogen for 19 h. The residue resulting from solvent evaporation was purified by preparative layer chromatography on silica gel (elution with 25% ethyl acetate in hexane) to give 23.2 mg (84%) of 12. Recrystallization from ethyl acetate gave the analytical sample as colorless prisms: mp 217–219 °C; IR (KBr) 3100–2800, 1770, 1715, 1420, 1390, 775 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.2–7.0 (m, 6 H), 6.10 (d, J = 3.9 Hz, 1 H), 5.62 (q, J = 2.4 Hz, 2 H), 5.43 (d, J = 3.9 Hz, 1 H), 4.1–3.3 (m, 2 H), 2.4–0.3 (series of m, 8 H), 0.73 (s, 3 H), 0.68 (s, 3 H), 0.22 (s, 3 H); ^{13}C NMR ($CDCl_3$) 159.1, 159.0, 139.0, 138.7, 133.8, 129.2, 128.9, 128.8, 127.3, 127.1, 126.2, 122.5, 122.1, 59.0 (2 C), 53.8, 51.6, 47.6, 45.4, 41.8, 41.6, 29.1, 26.9, 26.3, 19.5, 18.6, 13.5 ppm; m/e calcd 439.2260, obsd 439.2272.

Anal. Calcd for $C_{28}H_{29}N_3O_2$: C, 76.51; H, 6.65. Found: C, 76.06; H, 6.70.

Independent Synthesis of 12 from 13. A mixture of 13 (514 mg, 1.16 mmol), *N*-bromosuccinimide (209 mg, 1.17 mmol), and AIBN (23 mg) in dichloromethane (400 mL) was irradiated with a DYV tungsten projector lamp for 1.5 h. The reaction mixture was concentrated to a volume of ca. 200 mL and stirred with 40 mL of saturated sodium bicarbonate solution for 30 min. The organic phase was separated and washed with saturated sodium bicarbonate solution (40 mL) and water (2 × 40 mL) before drying. Because ^{1}H NMR analysis of this mixture indicated that substantial amounts of 13 remained, the mixture was taken up in dichloromethane (50 mL) and treated as before with 171 mg (0.961 mmol) of *N*-bromosuccinimide and 20 mg of AIBN. After 8.25 h of irradiation, a similar workup was deployed. The resulting beige foam was passed through a short column of alumina (elution with 25% ethyl acetate in hexane) and then subjected to preparative layer chromatography on silica gel (elution with same solvent system). There was obtained 304 mg (60%) of 12, mp

217-219 °C (from ethyl acetate). The spectral properties of this compound were identical with those of the urazole isolated above.

Conversion of 14 to 16. A mixture of 14[14] (101 mg, 0.316 mmol), *N*-bromosuccinimide (63.7 mg, 0.358 mmol), and a little AIBN in dry carbon tetrachloride (25 mL) was irradiated as before for 4 h. The cooled reaction mixture was filtered, washed with saturated sodium bicarbonate solution (3 × 10 mL), dried, filtered, and evaporated to give a beige foam which was not further purified.

The above solid was dissolved in dry tetrahydrofuran (25 mL), DBU (520 mg, 3.4 mmol) was added, and the reaction mixture was stirred under nitrogen for 24 h. After dilution with dichloromethane (25 mL), water (10 mL) was added and the aqueous phase was removed and extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with 10% hydrochloric acid (2 × 5 mL), 0.5 N sodium hydroxide solution (2 × 5 mL), and water (10 mL) prior to drying and solvent evaporation.

The resultant brown oil (**15**) was heated to reflux in ethyl acetate (25 mL) under nitrogen for 18 h. After solvent removal, the residue was subjected to preparative layer chromatography on silica gel (elution with 15% ethyl acetate in hexane) to give 33.8 mg (34%) of **16** as a white foam: IR ($CDCl_3$) 3100-2820, 1770, 1710, 1460, 1400, 1200, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.33-7.20 (series of m, 6 H), 6.17 (d, J = 3.9 Hz, 1 H), 5.49 (d, J = 3.9 Hz, 1 H), 3.72-3.50 (m, 2 H), 2.76 (s, 3 H); m/e calcd 319.1290, obsd 319.1279.

Conversion of 17 to 20. A mixture of 17[13] (171 mg, 0.535 mmol), *N*-bromosuccinimide (87.5 mg, 0.491 mmol), and a little AIBN in dry benzene (15 mL) was irradiated as before for 1.5 h. The reaction mixture was cooled, treated with DBU (0.75 g, 4.9 mmol) in dry tetrahydrofuran (5 mL), and stirred overnight at room temperature. The reaction mixture was passed through a short silica gel column. Medium-pressure liquid chromatography on silica gel (elution with 45% ethyl acetate in petroleum ether) of the residue after evaporation afforded 99.4 mg (59%) of **20**. The analytical sample was prepared by recrystallization from ethyl acetate: white solid; mp 198-200 °C; IR (KBr) 3100-2800, 1775, 1710, 1460, 1400, 1205, 1135, 880, 780, 765, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97-7.35 (m, 6 H), 5.73 (s, 2 H), 5.60-5.43 (m, 2 H), 3.72-3.55 (m, 2 H), 2.80 (s, 3 H); ^{13}C NMR ($CDCl_3$) 156.6, 138.6, 133.68 129.7, 128.3, 126.6, 123.5, 57.9, 42.3, 25.2 ppm; m/e calcd 317.1164, 317.1171.

Anal. Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76. Found: C, 71.74; H, 4.84.

Hydrolysis-Oxidation of 20 to Naphthocyclooctatetraene 21. A slurry of **20** (29.8 mg, 0.094 mmol) and sodium hydroxide (0.14 g, 3.5 mmol) in 2-propanol was heated at reflux for 1.5 h. The reaction mixture was cooled, made acidic with 10% hydrochloric acid, basified (pH ~9) with ammonium hydroxide solution, and extracted with dichloromethane (4 × 5 mL). The combined organic phases were dried, filtered, and evaporated. The residue was taken up in dichloromethane (10 mL) and Attenburrow manganese dioxide (132 mg) was added. The reaction mixture was stirred overnight under nitrogen and filtered through Celite. The filtrate was evaporated and the residue was chromatographed on silica gel (elution with carbon tetrachloride). There was obtained 16 mg (83%) of **21** as a white solid, mp 91-97 °C. Recrystallization from pentane raised the melting point to 111-113 °C (lit.[16] mp 113-114 °C): IR (KBr) 3100-2800, 890, 760, 730, 680, 640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8-7.25 (m, 6 H), 6.76 (d, J = 5.3 Hz, 2 H), 6.07 (br d, J = 6.8 Hz, 2 H), 5.8-5.7 (m, 2 H); m/e calcd 204.0939, obsd 204.0944.

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Registry No. 6, 38310-36-0; **6** dibromide adduct, 77416-62-7; **7**, 77400-32-9; **8**, 77400-33-0; **9**, 265-49-6; **10**, 77400-34-1; **11**, 77400-35-2; **12**, 77400-36-3; **13**, 77416-63-8; **14**, 77400-37-4; **15**, 77400-38-5; **16**, 77400-39-6; **17**, 63079-33-4; **18**, 77400-40-9; **20**, 77400-41-0; **21**, 262-83-9; 2,3-benzo[4.4.2]propella-2,7,9,11-tetraene, 65140-12-7; (-)-*endo*-bornyltriazolinedione, 73462-83-6; (-)-*endo*-bornyltriazolidine 2,3-benzo[4.4.2]propella-2,7,9,11-tetraene addition product, 77400-42-1.

Kinetics of the Acid-Catalyzed Hydration of Allene and Propyne

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The kinetics of the conversion of allene and propyne to acetone in aqueous sulfuric acid have been measured. The solvent isotope effects k_{H^+}/k_{D^+} and the dependence of the rates on acidity are consistent with the Ad_E2 mechanism of rate-limiting protonation at the terminal carbons leading to the intermediate 2-propenyl cation $CH_3C^+H{=}CH_2$ in each case, followed by hydration to the enol and isomerization to acetone. This route is strongly favored by published theoretical studies.

The hydration of allene to acetone in concentrated sulfuric acid (eq 1) has been known since 1888.[1] However,

$$CH_2{=}C{=}CH_2 \xrightarrow[H_2O]{H_2SO_4} CH_3C(O)CH_3 \qquad (1)$$

even though there has been great interest in electrophilic additions to substituted allenes[2,3] and alkynes,[4,5] including a variety of kinetic studies, there do not appear to have been any rate studies of hydration of allene itself (eq 1). Similarly, there are no published studies on the acid hydration of the isomer propyne, which also gives acetone (eq 2).

$$CH_3C{\equiv}CH \xrightarrow[H_2O]{H_2SO_4} CH_3C(O)CH_3 \qquad (2)$$

Examination of the protonation of allene and propyne in the gas phase[6] led to the conclusion that either of these

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