Addition of Benzyne to Bicyclo[4.2.1]nona-2,4,7-trien-9-one and 1,6-Methano[10]annulene

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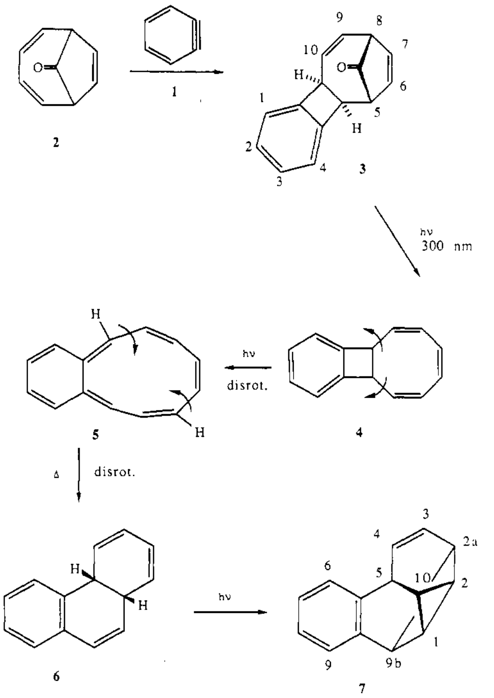
As part of our continuing interest in the products from the reaction of benzyne **1** with unsaturated and aromatic substrates,[1] we have examined the title reactions. Thermal decomposition of benzenediazonium-2-carboxylate in the presence of bicyclo[4.2.1]nona-2,4,7-trien-9-one (**2**) afforded, after chromatography, the 2 + 2 cycloadduct **3** in 8% yield. The structure of **3** follows from its spectral properties. The ^{13}C NMR spectrum, recorded at 75.5 MHz, showed discrete signals for all 15 carbon atoms, ruling out a symmetrical structure, which would have resulted from either 2 + 4 cycloaddition involving the diene moiety of **2** or 2 + 2 cycloaddition with participation of the etheno bridge. In the ^1H NMR spectrum, all nonaromatic proton resonances could be assigned with the aid of spin-decoupling experiments. We assume that addition of benzyne to **2** has occurred from the less hindered exo face; exo addition is also observed, for example, during the cyclopropanation of **2**.[2]

When the bridged ketone **3** was irradiated at 300 nm through silica, smooth photochemical decarbonylation was induced, and the strained polycyclic hydrocarbon **7** was formed as the sole product. Hydrocarbon **7** has previously been isolated by Vedejs and co-workers from the irradiation of *cis*-4b,8a-dihydrophenanthrene,[3] and the ^1H NMR spectral data for our product are in reasonable agreement with those reported. We provided further confirmation for the structure by simulating the richly structured nonaromatic region of the 300-MHz ^1H NMR spectrum of **7** by using the program PANIC. The spin system involves eight chemical shifts and 15 coupling constants, and the values that gave good agreement between the simulated and observed spectrum are summarized in Table I. It is noteworthy that H10 experiences long-range couplings of 1.8 Hz to both H2a and H9b. Molecular models reveal that the latter two protons are both oriented in a planar *W* configuration with respect to H10, which is known to favor coupling across four single bonds.[4] Two other small long-range couplings, $J_{3,9b} = 0.5$ and $J_{1,3} = 0.4$ Hz are also present. Chemical proof for the structure **7** was provided by conversion into phenanthrene on treatment with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in refluxing benzene. Under these conditions **7** presumably reverts to *cis*-4b,8a-dihydrophenanthrene (**6**),[3] which then suffers dehydrogenation.

Table I. Chemical Shifts and Coupling Constants for the Simulated 300-MHz ^1H NMR Spectrum of Hydrocarbon 7

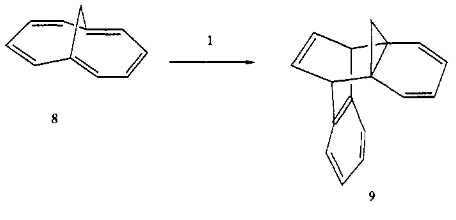
proton	chemical shift (Hz)	coupling constant (Hz)
H10	496.1	$J_{10,1} = 5.25$, $J_{10,2} = 5.32$, $J_{10,2a} = 1.83$, $J_{10,9b} = 1.77$, $J_{10,5} = 7.40$
H1	531.3	$J_{1,10} = 5.25$, $J_{1,2} = 3.62$, $J_{1,9b} = 3.49$, $J_{1,3} = 0.40$
H2	563.9	$J_{2,10} = 5.32$, $J_{2,1} = 3.62$, $J_{2,2a} = 3.65$
H2a	1016.2	$J_{2a,9b} = 8.12$, $J_{2a,3} = 7.23$, $J_{2a,2} = 3.65$, $J_{2a,4} = 1.06$, $J_{2a,10} = 1.83$
H9b	1123.4	$J_{9b,2a} = 8.12$, $J_{9b,1} = 3.49$, $J_{9b,10} = 1.77$, $J_{9b,3} = 0.50$
H5	1135.7	$J_{5,10} = 7.40$, $J_{5,4} = 6.94$
H3	1658.5	$J_{3,4} = 8.42$, $J_{3,2a} = 7.23$, $J_{3,9b} = 0.50$, $J_{3,1} = 0.40$
H4	1905.7	$J_{4,3} = 8.42$, $J_{4,5} = 6.94$, $J_{4,2a} = 1.06$

Scheme I



The formation of hydrocarbon **7** from the photolysis of ketone **3** can be rationalized in terms of decarbonylation to yield **4**, which then undergoes photochemical disrotatory ring opening to afford **5**. Thermal disrotatory ring closure would give **6**, which is known to afford **7** on irradiation.[3] When the photolysis of **3** was monitored by TLC, or interrupted before all of **3** was consumed, only **3** and **7** could be detected. All of the postulated intermediates in Scheme I are thus unstable under the reaction conditions. The photochemical decarbonylation of **3** therefore provides a further entry into the benzo($C_{10}H_{10}$) hydrocarbon pool.[3,5]

The addition of benzyne **1** to 1,6-methano[10]annulene **8** afforded the Diels–Alder adduct **9** in 18% yield. The structure of **9** is evident from its spectroscopic properties, and we assign the stereochemistry shown on the basis that reactive dienophiles such as 4-phenyl-1,2,4-triazolin-3,5-dione also attack **8** from the less hindered face (anti to the methano bridge).[6] Although bicyclo[4.2.1]nona-2,4,7-trien-9-one (**2**) and 1,6-methano[10]annulene (**8**) have similar structural features in that both molecules possess



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[1] Cresp, T. M.; Wege, D. *Tetrahedron* **1986**, *24*, 6713 and references therein.

[2] Takasis, I. M.; Agosta, W. C. *J. Org. Chem.* **1979**, *44*, 1294.

[3] Vedejs, E.; Steiner, R. P.; Wu, E. S. C. *J. Am. Chem. Soc.* **1974**, *96*, 4040.

[4] Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: Oxford, **1969**; p 334.

[5] Paquette, L. A.; Kukla, M. J.; Stowell, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 4920.

[6] Ashkenazi, P.; Ginsburg, D.; Vogel, E. *Tetrahedron* **1977**, *33*, 1169.

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a conjugated diene moiety (albeit part of a delocalized aromatic system in the case of **8**) incorporated in a 4-carbon atom bridge, their behavior toward benzyne is quite different. Ketone **2** affords a 2 + 2 adduct, while hydrocarbon **8** yields a 4 + 2 adduct. The propensity of benzyne to give 2 + 2 cycloadducts with some conjugated dienes, notably 1,3-cycloheptadiene and 1,3,5-cycloheptatriene, is well documented.[7] In these cases the formation of 2 + 2 adducts has been attributed to deviation of the diene system from planarity, especially in the case of 1,3,5-cycloheptatriene, where no 4 + 2 cycloadduct is formed. The more rigid structures **2** and **8** possess essentially planar diene systems, and the failure of ketone **2** to provide any 4 + 2 cycloadduct is probably a consequence of an increased distance between C2 and C5 of the diene moiety in **2** relative to **8**. The short span of the etheno bridge and the presence of the trigonal center at C9 in **2** imparts rigidity, which would maintain the original C2–C5 distance in the transition state of a hypothetical 4 + 2 cycloaddition with benzyne. In the case of **8** however, the C2–C5 distance is probably more suited to concerted 4 + 2 cycloaddition, particularly if the transition state possesses substantial bisnorcaradiene character, or if indeed **8** reacts via the bisnorcaradiene valence isomer.

The addition of benzyne **1** to **2** and **8** thus further illustrates the delicate balance that exists in the reaction of **1** with dienes: subtle structural differences in the diene can favor the 2 + 2 pathway with exclusion of the normal 4 + 2 addition mode.[8]

Experimental Section

NMR spectra were recorded with Bruker WP80 and Bruker AM300 instruments using $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were obtained by using a Hewlett-Packard 5986 instrument, operating in the GC–MS mode. Benzenediazonium-2-carboxylate,[9] bicyclo[4.2.1]nona-2,4,7-trien-9-one,[10] and 1,6-methano[10]annulene[11] were prepared as described in the literature.

Addition of Benzyne to Bicyclo[4.2.1]nona-2,4,7-trien-9-one (2). Benzenediazonium-2-carboxylate derived from anthranilic acid (13.7 g, 0.1 mol) was decomposed during 2 h in a reluxing solution of ketone **2** (6.6 g, 0.05 mol) in 1,2-dichloroethane (120 mL). The solvent was evaporated, and the dark residue was chromatographed on neutral alumina (400 g). Elution with 5% ether–hexane gave unchanged **2** (2.45 g). Elution with 10% ether–hexane afforded 4b,5,8,10a-tetrahydro-5,8-methanobenzo-[3,4]cyclobuta[1,2]cycloocten-11-one (**3**) as a colorless solid (0.85 g, 8%), which crystallized from pentane as needles: mp 101–3 °C; MS, *m/z* 208 (M, 28), 207 (31), 180 (33), 179 (100), 178 (100), 176 (18), 166 (11), 165 (65), 152 (30), 151 (15), 128 (30), 115 (46), 102 (38), 89 (24), 76 (11); ^{13}C NMR (75.5 MHz, all d except where noted) δ 208.2 (s), 145.5 (s), 142.9 (s), 134.7, 131.0, 130.8, 128.0, 127.7, 124.8, 122.0, 121.0, 54.7, 52.5, 50.1, 48.1; ^1H NMR (300 MHz) δ 7.27–7.15 (m, 3 H, aryl), 7.02 (dd, J = 6.8, 1.0, 1 H, aryl), 6.29 (ddd, $J_{7,6} = 6.9$, $J_{7,8} = 2.5$, $J_{7,5} = 0.7$, 1 H, H7), 6.24 (ddd, $J_{6,7} = 6.9$, $J_{6,5} = 2.5$, $J_{6,8} = 0.9$, 1 H, H6), 5.95 (dd, $J_{10,9} = 11.0$, $J_{10,10a} = 4.8$, 1 H, H10), 5.82 (ddd, $J_{9,10} = 11.0$, $J_{9,10a} = 2.0$, $J_{9,8} = 8.9$, 1 H, H9), 4.37 (ddd, $J_{10a,4b} = 4.8$, $J_{10a,10} = 4.8$, $J_{10a,9} = 2.0$, 1 H, H10a), 3.95 (dd, $J_{4b,10a} = 4.8$, $J_{4b,5} = 2.5$, 1 H, H4b), 3.61 (ddd, $J_{5,4b} = 2.5$, $J_{5,6} = 2.5$, $J_{5,7} = 0.7$, 1 H, H5), 3.33 (dd, $J_{8,9} = 8.9$, $J_{8,7} = 2.5$, 1 H, H8); ν_{max} ($CHCl_3$) 1770 cm^{-1}; λ_{max} (cyclohexane) 207 (log ϵ 4.48), 260 (3.51), 267 (3.66), 273 (3.66). Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.56; H, 5.95.

Photolysis of Ketone 3. A solution of **3** (300 mg) in deoxygenated 2-propanol (50 mL) was placed in a silica tube and irradiated for 12 h under a nitrogen atmosphere in a Rayonet photochemical reactor using 300-nm lamps. The solvent was evaporated, and the residue was filtered through a plug of alumina in pentane to remove polymeric material. Evaporation of the pentane gave 2,2a,5,9b-tetrahydro-1,2,5-metheno-1*H*-benzo[*a*]-cyclobuta[*c*]cycloheptene (**7**) as a colorless oil (170 mg, 65%). The GC trace in the GC–MS showed two peaks in the ratio 71:29, presumably reflecting rearrangement of **7** to **6**. The fragmentation patterns of the two components were virtually identical: *m/z* 180 (M, 69%), 179 (100), 178 (84), 177 (12), 176 (16), 165 (53), 152 (21), 151 (11), 89 (17); ^{13}C NMR (75.5 MHz, all d except where noted) δ 144.3 (s), 138.4 (s), 137.6, 127.4, 127.2, 126.5, 126.4, 125.3, 40.3, 36.2, 34.7, 19.9, 18.6, 17.5; ^1H NMR (300 MHz) δ 7.18 (dd, J = 7.0, 1.8, 1 H, aryl), 7.14 (ddd, J = 7.0, 7.0, 1.8, 1 H, aryl), 7.08 (ddd, J = 7.0, 7.0, 1.8, 1 H, aryl), 6.98 (dd, J = 7.0, 1.8, 1 H, aryl), 6.35 (ddd, 1 H, H4), 5.53 (dddd, 1 H, H3), 3.79 (dd, 1 H, H5), 3.74 (dddd, 1 H, H9b), 3.39 (ddddd, 1 H, H2a), 1.88 (ddd, 1 H, H2), 1.77 (dddd, 1 H, H1), 1.65 (ddddd, 1 H, H10); see also Table I.

In a separate experiment, ketone **3** (225 mg) in 2-propanol (90 mL) was irradiated as above, and the reaction was monitored by TLC. Only ketone **3** and hydrocarbon **7** were detected. After 6 h the photolysis was interrupted, and **7** (72 mg) and **3** (66 mg) were isolated by flash chromatography on silica gel.

Conversion of 7 into Phenanthrene. A solution of hydrocarbon **7** (61 mg, 0.34 mmol) and DDQ (80 mg, 0.35 mmol) in benzene (5 mL) was refluxed for 4 h. The mixture was filtered through silica gel in hexane, and the filtrate was evaporated to afford pure phenanthrene (42 mg, 70%), mp and mixed mp 99–100 °C.

Addition of Benzyne to 1,6-Methano[10]annulene (8). Benzenediazonium-2-carboxylate, prepared from anthranilic acid (1.40 g, 10.2 mmol), was added to a solution of **8** (1.45 g, 10.2 mmol) in 1,2-dichloroethane (30 mL). The mixture was stirred under reflux until gas evolution ceased and all the solid had decomposed (30 min). The solvent was evaporated, and the residue was adsorbed onto silica gel and submitted to flash chromatography. Elution with 5% dichloromethane–hexane gave **8** (720 mg) in the early fractions. This was followed by 4a,9,9a,10-tetrahydro-9,10-etheno-4a,9a-methanoanthracene (**9**) as pale yellow crystals (401 mg, 18%): mp 118.5–119.5 °C; MS *m/z* 217 (M − 1, 26), 202 (100), 191 (13), 102 (52); ^{13}C NMR (20.1 MHz) δ 147.2 (s), 133.3 (d), 129.7 (d), 124.4 (d), 123.7 (d), 120.7 (d), 47.2 (d), 35.6 (s), 19.2 (dd); ^1H NMR (80 MHz) δ 7.10–6.83 (m, 4 H, aryl), 6.32 (AA′ part of AA′XX′, 2 H, vinyl H11 and H12), 6.05–5.52 (AA′BB′, 4 H, H1-H4), 3.99 (XX′ part of AA′XX′, 2 H, bridgehead H9 and H10), 2.39 (d, J = 4.7, 1 H, H13), −0.09 (d, J = 4.7, 1 H, H13). Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.51; H, 6.40.

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Supplementary Material Available: The observed and simulated 300-MHz ^1H NMR spectrum of hydrocarbon **7** (2 pages). Ordering information is given on any current masthead page.

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[7] Lombardo, L.; Wege, D. *Tetrahedron* **1974**, *30*, 3945. Crews, P.; Beard, J. *J. Org. Chem.* **1973**, *38*, 522.

[8] The addition of 1 to bicyclo[4.1.1]octa-2,4-diene also unexpectedly gives only 2 + 2 cycloadduct: Yin, T.-K.; Lee, J. G.; Borden, W. T. *J. Org. Chem.* **1985**, *50*, 531.

[9] Logullo, F. M.; Seitz, A. H.; Friedman, L. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. IV, p 54.

[10] Antkowiak, T. A.; Sanders, D. C.; Trimitsis, G. B.; Press, J. B.; Schechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 5366.

[11] Vogel, E.; Klug, W.; Breuer, A. *Org. Synth.* **1974**, *54*, 11.

Stereochemical Aspects of the Reaction of Lithio(1-methyl-2-propenyl)diphenylphosphine Oxide with β-Substituted Aldehydes. Short Syntheses of (−)-α-Selinene and (+)-α-Helmiscapene[1]

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Yamamoto and co-workers have reported that the reaction of the Wittig–Horner reagent, lithio(1-methyl-2-

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