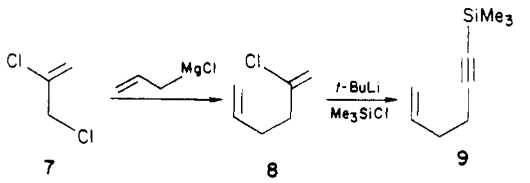
action provides a simple and inexpensive route to **9**, which previously has been prepared by a longer route involving vinyl bromide.[11]



We briefly investigated the reaction of dibromide **1** and its dichloro analogue **7** with *tert*-butyllithium, followed by chlorotrimethylsilane. The dibromide appeared to undergo metal–halogen interchange at the allylic carbon to give a poor yield of 2-bromo-3-(trimethylsilyl)propyne, difficult to separate from solvent. The dichloride gave many components, not studied further.

Experimental Section

2-Bromo-1,5-hexadiene (2) was prepared by adding a solution of allylmagnesium bromide (1 M in ethyl ether, 0.16 mol) by cannula to a dried three-neck flask equipped with a Friedrich condenser and drying tube, septum fitted addition funnel, and thermometer. The condenser temperature was set at −10 °C. 2,3-Dibromopropene (0.12 mol, 24 g) was added to the main flask at a rate which maintained rapid reflux. A vigorous reaction began immediately. After the addition, the solution was maintained at reflux for 2 h. An insoluble salt separated and a brown color developed. The solution was washed with HCl (15 mL, concentrated) in H_2O (90 mL) and was dried overnight over $CaCl_2$. The ether was removed by columm distillation. The desired 2-bromo-1,5-hexadiene (**2**), distilled at 43 °C, 28 torr, 11.4 g (60%). A higher boiling component, possibly 2,5-dibromo-1,5-hexadiene, was discarded. ^1H NMR ($CDCl_3$): δ 5.70 (m, 1, $CH{=}$); 5.58, 5.48 (peaks show small allylic coupling, $CH_2{=}CBr$); 5.10 (m, 2, $=CH_2$); 2.41 (m, 4, CH_2). Anal. Calcd for C_6H_9Br:C, 44.75; H, 5.63. Found: C 44.98; H, 5.62. ^{13}C NMR (CDC_3): δ 133.71 ($=CBr$), 121.06 ($=CH$), 116.74 ($=CH_2$), 115.65 ($=CH_2$), 40.61 (CH_2), 32.07 (CH_2).

2-Chloro-1,5-hexadiene (8) was prepared by a similar procedure using allylmagnesium bromide (1 M, 0.065 mol) and 2,3-dichloropropene (0.045 mol, 5 g). The product was distilled at 52–54 °C, 100 torr. No higher boiling component (cf. preceding preparation) was present. The yield was 4.1 g (78%). ^1H NMR ($CDCl_3$): δ 5.66 (m, 1, $CH{=}$), 5.15 (s, 2, $CCl{=}CH_2$), 5.03 (m, 2, $CH_2{=}$), 2.38 (m, 4, CH_2).

2-Bromo-5,6-epoxy-1-hexene (3). A solution of 2-bromo-1,5-hexadiene (**2**) (4.99 g, 0.031 mol) in methylene chloride was prepared. To it was added (at 150 dp/min) a nominal 35% excess of untitrated *m*-chloroperbenzoic acid (7.20 g, 0.042 mol) in 92 mL of CH_2Cl_2. After reaction overnight a gas chromatogram showed seven area percent of reactant remaining. A nominal 10 mol % of additional MCPBA was added. After 24 h, isolation in the manner described for the conversion of **5** to **6** and distillation through a Vigreaux column gave **3**, 3.47 g, 63%, bp 70–85 °C, 10 torr. ^1H NMR ($CDCl_3$): δ 5.82 and 5.71 (s, 2 H, $=CH_2$), in 2.95 (m, 1 H, HCO), 2.89 (m, 2 H, H_2CO), 2.77 (m, 2 H, CH_2), 1.95 and 1.86 (m, 2 H, CH_2). ^{13}C NMR: δ 133.15 ($=CBr$), 117.19 ($=CH_2$), 50.91 (CHO), 46.95 (CH_2), 37.89 (CH_2), 30.89 (CH_2). Anal. Calcd for C_6H_9Br:C, 40.70; H, 5.12. Found: C, 40.41; H, 5.29.

2-(Trimethylsilyl)-5,6-epoxy-1-hexene (4). A solution of 2-bromo-5,6-epoxy-1-hexene (**3**) (3.01 g, 17 mmol) in a Trapp solvent mixture (tetrahydrofuran/ether/pentane, 4:1:1) was cooled in a bath of methylcyclohexane/liquid N_2 until the bath temperature was below −100 °C. After several minutes *tert*-butyllithium in pentane (20 mL, 1.7 M) was added slowly by syringe. After 3 h at −100 °C, Me_3SiCl (1.83 g, 16.9 mmol) was added. After 10 min the mixture was removed from the cold bath and allowed to warm to room temperature. During this time the solution turned from yellow to clear with precipitation of a solid (presumably LiBr). To the mixture was added brine containing HOAc and CH_2Cl_2. After repeated extractions with brine the CH_2Cl_2 layer was subjected to rotary evaporation and distillation to give 2.04 g, 71%, of **4**, bp 82–86 °C, 18–21 torr. ^1H NMR ($CDCl_3$): δ 5.55 and 5.35 (s, 2 H, $=CH_2$), 2.95 (m, 1 H, CHO), 2.80 and 2.55 (m, 2 H, OCH_2), 2.30 (m, 2 H, CH_2), 1.6 (m, 2 H, CH_2), 0.21 (s, 9 H, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 151.01 ($=CSi$), 124.16 ($=CH_2$), 51.89 (CHO), 47.01 (CH_2O), 31.78 (CH_2), 31.69 (CH_2), −1.61 ($Si\text{-}CH_3$). Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65. Found: C, 63.42; H, 10.99.

2-(Trimethylsilyl)-1,5-hexadiene (5) and Its Epoxidation. A solution of 2-bromo-1,5-hexadiene (3.91 g, 24 mmol) in a Trapp solvent mixture (THF, 70 mL; ether, 17 mL; pentane, 17 mL) was cooled under dry nitrogen to −68 °C in a dry ice acetone bath. *Tert*-Butyllithium in pentane (24 mL of 2 M, 48 mmol) was added slowly from a syringe. After 3 h, trimethylsilyl chloride (2.8 mL, 24 mmol) was added. After 10 min the reaction was slowly warmed to room temperature. The reaction was allowed to proceed overnight. A deep yellow color formed that disappeared upon washing with brine. The brine extraction was repeated and the solution was dried over $MgSO_4$. Solvent was removed by columm distillation. The compound was distilled to give 1.60 g (45%) at 49–52 °C, 15 torr. ^1H NMR ($CDCl_3$): 5.7 (m, 1 H, $CH{=}$), 5.45 (m, 2 H, $=CH_2$), 5.03 (m, 2 H, $=CH_2$), 2.20 (m, 4H, CH_2), 0.10 (s, 9 H, $SiCH_3$). ^{13}C NMR: δ 151.61 ($=CSi$), 136.66 ($=CH$), 123.69 ($=CH_2$), 114.38 ($=CH_2$), 35.22 (CH_2), 33.19 (CH_2), −1.52 ($SiCH_3$). Anal. Calcd for $C_9H_{18}Si$: C, 63.47; H, 10.65. Found: C, 61.63; H, 10.73.

Epoxidation of 40 mg, 0.26 mmol, of **5** was carried to approximately 80% of completion by a procedure similar to that for epoxidation of **3**. Cappillary gas chromatography showed some **4**, identical in retention time with that whose preparation is described above, and a major product having a slightly different retention time, presumed to be **6**, in a ratio of 1:7.7. Since we needed a preparation of **4**, no further characterization was done.

5-Hexen-1-ynyltrimethylsilane (9). A solution of 2-chloro-1,5-hexadiene (2.46 g, 0.021 mol) in THF (69 mL), ether (17 mL), and pentane (17 mL) was cooled in a dry ice–acetone bath to −68 °C under dry nitrogen. *tert*-Butyllithium (2 M, 21 mL) was added slowly by syringe. Four hours later trimethylsilyl chloride was added. The mixture turned deep red while reacting overnight. An insoluble salt formed. The color and salt disappeared when the solution was extracted with brine. The organic layer was dried overnight over $MgSO_4$ and the solvent was removed by columm distillation. The product was distilled to give 1.1 g (38%), bp 58–61 °C, 15 torr. ^{13}C NMR ($CDCl_3$): δ 136.73 ($=CH$), 115.54 ($=CH_2$), 106.60 ($\equiv CSi$), 84.79 ($\equiv C$), 32.89 (CH_2), 19.70 (CH_2), 0.10 (CH_3Si). The IR and ^1H NMR spectra closely matched those given in ref 11.

Registry No. 1, 513-31-5; 2, 101933-87-3; 3, 101933-89-5; 4, 101933-90-8; 5, 101933-91-9; 6, 101933-92-0; 7, 78-88-6; 8, 101933-88-4; 9, 1578-50-3; allyl bromide, 106-95-6; chlorotrimethylsilane, 75-77-4.

Baeyer–Villiger Oxidation of Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione

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Recent interest in Baeyer–Villiger oxidation of polycyclic ketones[1-5] prompts us to report on recent results obtained

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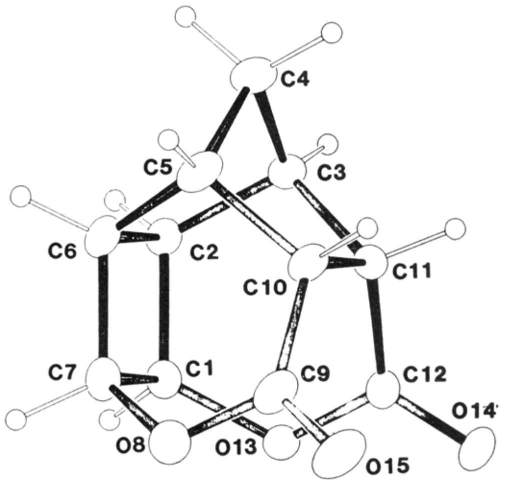


Figure 1. Diagram of **6a** as determined by X-ray diffraction.

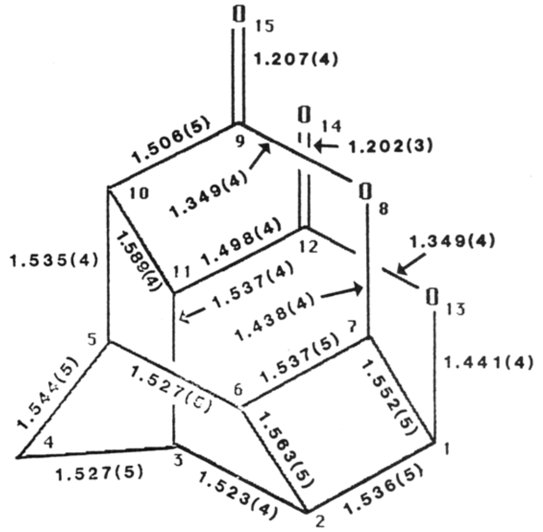
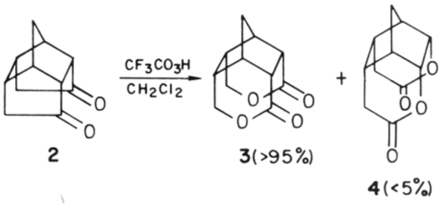


Figure 2. Bond lengths (Å) in **6a**.

in the pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione system (**1**). Butler and Munshaw[4] reported that a related

1, X=O
5, X=NOH

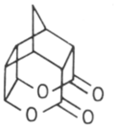
tetracyclic diketone, **2**, reacted with trifluoroperacetic acid to afford two symmetrical dilactones, **3** and **4**, the former being obtained as the principal reaction product:



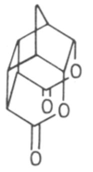
2 **3**(>95%) **4**(<5%)

The structure of **3** was established from spectroscopic evidence. Butler and Munshaw[4] have also reported obtaining a mixture of dilactones, with one symmetrical isomer (mp 250–255 °C) being formed as the major product in a similar oxidation reaction with the cage diketone, **1**. Mehta et al.[1] reported that reaction of **1** with *m*-chloroperbenzoic acid led to the isolation of a dilactone with mp >300 °C. However, the authors in the above two reports did not clearly establish the structure of the dilactones.

We now report that Baeyer–Villiger oxidation of **1** is promoted by a variety of oxidizing agents, viz., (i) 30% H_2O_2–*t*-BuOH in the presence of selenium dioxide;[6] (ii) *m*-chloroperbenzoic acid and *p*-toluenesulfonic acid in either benzene or methylene chloride as a solvent;[1,5] and (iii) 90% H_2O_2–trifluoroacetic anhydride in methylene chloride solvent.[4] Additionally, dioxime **5**, when treated with 90% HNO_3–30% H_2O_2 in methylene chloride solvent, afforded a mixture of mono- and dilactones. It seemed likely that **5** under these reaction conditions would yield the cage diketone **1** as an intermediate and the latter would then undergo oxidation to yield the mixture of lactones. The fact that **1** is formed as an intermediate in the reaction of **5** was confirmed by the isolation of **1** when **5** was treated with 90% HNO_3 in methylene chloride solvent in the absence of 30% H_2O_2. Methods i–iii, above, all produced a single dilactone (**6**) as the predominant oxidation product. The proton noise-decoupled ^{13}C NMR spectrum of **6** displayed only six absorptions. This observation suggests that dilactone **6** contains an element of symmetry, and hence, it must possess one of the two (symmetrical) structures **6a** or **6b**.



6a



6b

The fact that this dilactone possesses structure **6a** rather than **6b** was confirmed unambiguously via single-crystal X-ray structural analysis (Figures 1 and 2).

Compound **6a**, 8,13-dioxapentacyclo[6.5.0.0^{2,6}.0^{5,10}.0^{3,11}]tridecane-9,12-dione ($C_{11}H_{10}O_4$), shown in Figure 1, crystallizes in space group $P2_1/c$ with unit cell dimensions a = 6.558 (1), b = 10.603 (2), and c = 13.395 (2) Å, β = 108.43 (1)°, and Z = 4. The volume of the cell in 883.6 (2) Å^3, the formula weight is 206.20, and the calculated crystal density is 1.550 mg mm^{-3}.

The structural results are depicted in Figure 2. All of the bond distances are typical lactone or hydrocarbon bond lengths except the three carbon–carbon bonds directly linking the two lactone rings, which are 1.552 (5) for C(1)–C(7), 1.563 (5) for C(2)–C(6), and 1.589 (4) Å for C(10)–C(11). These bonds are longer than a typical unstrained Csp^3–Csp^3 bond (1.53–1.54 Å) due to internal cage strains, primarily eclipsed torsion angles. The lactone rings bend away from one another in the carbonyl vicinity, where they are not constrained by cross-cage bonds. The nonbonded intramolecular C9···C12 contact is only 2.743 (4) Å, which is much less than the usual nonbonded distance range of 3.2–3.4 Å, seen in graphite and numerous aromatic crystal structures.

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Experimental Section[7]

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (1) was prepared according to the literature procedures.[8,9]

Baeyer–Villiger Oxidations of Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (1). i. With 30% Hydrogen Peroxide and Selenium Dioxide in *tert*-Butyl Alcohol. 8,11-Dione 1 (1.04 g, 6.0 mmol) was added to a stirred suspension of *tert*-butyl alcohol (24 mL), 30% hydrogen peroxide solution (12 mL), and selenium dioxide (0.11 g, 1.0 mmol) kept at room temperature. The mixture was then heated at 85 °C for 3 days. The reaction mixture was cooled to room temperature, poured into a saturated solution of brine (50 mL), and extracted with dichloromethane (6 × 25 mL). The organic extracts were washed with water (10 mL) and dried over anhydrous $MgSO_4$. Removal of solvent gave 1.11 g of crude product (90%). Crystallization from ethanol afforded **6a** as colorless long needles (0.99 g, 80%): mp 348–352 °C dec; IR (KBr) 3440 (w), 2980 (w), 2880 (w), 1750 (s), 1730 (s), 1385 (s), 1330 (m), 1275 (m), 1265 (m), 1190 (s), 1130 (s), 1090 (m), 950 (m), 860 (m), 700 (m), 600 (m), 530 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.8 (s, 2 H), 2.9 (br d, 4 H), 3.3 (s, 2 H) and 5.0–5.4 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 36.6 (d, J = 150 Hz), 39.8 (d, J = 150 Hz), 40.4 (t, J = 135 Hz), 45.3 (d, J = 145 Hz), 73.9 (d, J = 165 Hz) and 168.3 (s); mass spectrum (70 eV), m/e (relative intensity) 206 (6) M$^+$, 178 (19), 177 (13), 150 (28), 149 (41), 136 (19), 135 (16), 134 (85), 122 (12), 121 (47), 110 (27), 109 (31), 108 (32), 107 (16), 100 (80), 97 (37), 93 (17), 92 (15), 91 (32), 82 (100), 81 (40), 80 (11), 79 (60), 78 (41), 77 (39), 68 (20), 67 (12), 66 (95), 65 (24), 63 (10), 55 (39), 54 (22), 53 (37), 52 (12), 51 (22). Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.08; H, 4.89.

ii. With *m*-Chloroperbenzoic Acid. (a) To a solution of diketone 1 (1.04 g, 6 mmol) in dry benzene (60 mL) were added *m*-chloroperbenzoic acid (3.23 g, 15 mmol, technical grade, 80–85%, Aldrich) and a catalytic amount of *p*-toluenesulfonic acid (0.1 g). The mixture was stirred at room temperature for 4 h, poured into water (60 mL), and extracted with ether (6 × 50 mL). The combined organic extracts were washed with aqueous sodium bicarbonate (3 × 30 mL) and brine (15 mL) and dried over anhydrous magnesium sulfate. Removal of solvent yielded 1.05 g of a white solid (85%). The solid was crystallized from ethanol as colorless long needles (0.93 g, 75%) and was identified as dilactone **6a**.

(b) A mixture of diketone 1 (1.04 g, 6 mmol), *p*-toluenesulfonic acid (0.1 g), and *m*-chloroperbenzoic acid (6.46 g, 30 mmol, technical grade, 80–85%, Aldrich) in dichloromethane (60 mL) was refluxed for 2 days. Workup as described above yielded a product (1.00 g, 81%) which was identical with the dilactone **6a**.

iii. With 90% Hydrogen Peroxide. To a solution of 8,11-dione 1 (1.04 g, 6 mmol) in dichloromethane (20 mL) was added trifluoroperacetic acid prepared by the addition of trifluoroacetic anhydride (2.0 mL) to a solution of 90% hydrogen peroxide (0.4 mL) in dichloromethane (10 mL). The reaction mixture was stirred under gentle reflux for 36 h. The yellow solution was concentrated under vacuum to a volume of 2 mL. The resulting oil was dissolved in carbon tetrachloride (20 mL), then absolute ethanol (5 mL) was added, and the solution was cooled in an ice bath. The tan precipitate was collected by filtration. The crude product (0.93 g, 75%) was crystallized from ethanol to afford as the major product the pure dilactone **6a** (0.80 g, 65%) in the form of long colorless needles.

Baeyer–Villiger Oxidation of Pentcyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione Dioxime (5). Dioxime 5 was prepared by the reaction of 1 with hydroxylamine hydrochloride according to the procedure described by Sasaki and co-workers.[10] To a stirred suspension of dioxime **5** (2.04 g, 10 mmol) in dichloromethane (80 mL) was added a solution of 90% fuming HNO_3 (10 mL) in dichloromethane (80 mL) dropwise over a period of 15 min. During this period, the reaction became slightly exothermic, and the dioxime dissolved completely, resulting in a bluish green solution. Hydrogen peroxide (30%, 7 mL) was added dropwise, and the solution was stirred at room temperature for 0.5 h, then refluxed for 4 h. The colorless solution was transferred to a separatory funnel and the organic layer was collected and washed successively with water (20 mL), aqueous sodium bicarbonate (2 × 20 mL), and brine (20 mL). The organic extracts were dried over anhydrous magnesium sulfate and filtered, and the filtrate was then concentrated in vacuo to afford a pale yellow paste. Trituration with diethyl ether yielded a yellow solid. The solid was collected by filtration and was washed with fresh ether to leave the crude product (0.95 g) as a pale yellow solid. This was dissolved in a minimum amount of chloroform, and the solution was chromatographed on a silica gel column (2.5 cm × 30 cm). Elution with ether removed yellow byproducts. The column was then washed with methanol and this solution was evaporated to yield a tan solid. Several recrystallizations from ethanol afforded the dilactone **6a** (0.40 g, 20%).

Conversion of Dioxime 5 to Dione 1. The dioxime **5** (2.04 g, 10 mmol) was suspended in dichloromethane (80 mL) and was brought to reflux. Fuming HNO_3 (90%; 10 mL) in dichloromethane (80 mL) was added dropwise and the resulting bluish green homogeneous reaction mixture was refluxed for 4 h. The pale yellow solution was cooled and poured into water (30 mL), and the organic layer was separated, washed with aqueous sodium bicarbonate (3 × 20 mL) and with brine (20 mL), and then dried over anhydrous magnesium sulfate. Evaporation of solvent left a pale yellow solid which was crystallized from toluene to afford the dione 1 (0.78 g; 45%) mp 245–246 °C.

X-ray Crystallography. Cell dimensions were obtained by a least-squares fitting of the diffraction coordinates of 25 centered peaks with 2θ values between 12.5° and 23° using Mo Kα X-rays (λ = 0.71069 Å). The 1158 independent reflections were collected out to 2θ = 45° on a Nicolet R3m diffractometer using Mo Kα radiation and an incident beam graphite monochromator. The structure was solved by direct methods[11] using the program[12] MULTAN80. Atomic positions for all atoms and anisotropic thermal parameters for the C and O atoms were refined by using the full matrix least-squares program[13] ORXFLS3. The hydrogen atoms, which were all found in Fourier difference maps, were assigned isotropic thermal factors equal to the equivalent isotropic thermal factors of their bonded neighbors. The function minimized the refinement was $\sum w(F_o - F_c)^2$ where the reflection weights, $w_{hkl} = [1/\sigma(F_o)]^2$ were estimated by combining counting statistics errors with an overall 2% random intensity error.[14] The final R factors were 0.066 (unweighted) and 0.050 (weighted) using all 1158 reflections (none were considered "unobserved"). In the final Fourier difference map, the ripple density ranged from −0.25 to + 0.28 e Å^{-3}.

Acknowledgment. C. R. Surapaneni expresses his appreciation to Dr. S. Bulusu for obtaining the mass spectrum and the ^{13}C NMR spectrum of **6a** and to Dr. A. P. Marchand and Dr. E. E. Gilbert for stimulating discussions.

Registry No. 1, 2958-72-7; **2**, 80661-90-1; **5**, 54142-92-6; **6a**, 80707-70-6.

Supplementary Material Available: (a) Table I listing bond distances (in angstroms) and bond angles (in degrees); (b) Table

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(7) Melting points were determined with a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 467 grating infrared spectrophotometer. Proton NMR spectra (60 MHz) were recorded on a Varian T-60 NMR spectrometer. ^{13}C NMR spectra were recorded on a Varian Model XL-200 NMR spectrometer. The chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Mass spectra were obtained with a DuPont Model 21-492B mass spectrometer using a solids probe. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NJ.

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II listing fractional atomic coordinates and equivalent isotropic thermal parameters; (c) Table III listing anisotropic thermal parameters; (d) ^{13}C NMR spectrum of the dilactone **6a** (4 pages). Ordering information is given on any current masthead page.

Synthesis and Diels-Alder Reactivity of 2,3,6,7-Tetrakis(methylene)bicyclo[3.2.1]octane

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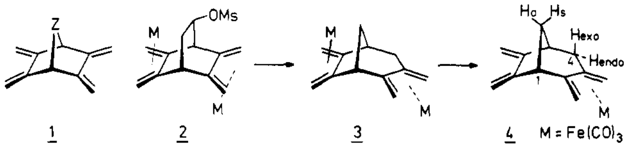
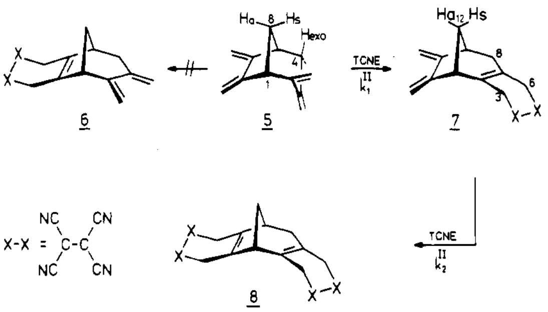
The tetraenes **1** (Z = O, CH_2, CH=CH, $(CH_3)_2C{=}C$) react with a dienophile (k_1) more rapidly than the corresponding monoadducts (k_2).[1] This principle (tandem Diels–Alder reactions) has been applied to the convergent synthesis of anthracyclinones.[2] We report here the synthesis of 2,3,6,7-tetrakis(methylene)bicyclo[3.2.1]octane (**5**), a new type of exocyclic double diene. We have found that the diene moiety at C(2),C(3) reacts more rapidly toward tetracyanoethylene (TCNE) than the diene moiety at C(6),C(7).



The mesylate **2**, prepared from the corresponding alcohol (MsCl, pyridine, 20 °C, 30 min)[3] was reduced and rearranged[4] into **3** (73%) with $NaBH_4$ in $CF_3CH(OH)CF_3$ (20 °C, 8 min). On treatment of **3** with a 15-fold excess of trimethylamine oxide (acetone, 20 °C, 3 h) selective oxidation of the *exo*-$Fe(CO)_3$ moiety at C(6),C(7) was achieved, yielding **4** (88%, isolated).[5] On treating **3** with a 20-fold excess of $Fe(NO_3)_3$ in 1:1 CH_2Cl_2/EtOH (20 °C, 1.5 h), the tetraene **5** was obtained (72%). The relative configuration of the $Fe(CO)_3$ groups in **3** and **4** was given by X-ray crystallography on a derivative of **3**.[6] The structure of **3**–**5** and TCNE adducts **7** and **8** were deduced from their elemental analyses and spectral data. Unambiguous 360-MHz ^1H NMR signal assignments were based on NOE measurements. As expected, the H–H coupling constants suggested a chair conformation[7] for the C(1–5),C(8) ring in **5**, with a twisted diene moiety at C(2),C(3). A W ^4J coupling constant of 2.4 Hz was measured between H–C(4-endo) and H–C(8-anti). The latter coupling constant was only 1 Hz in the ^1H NMR spectrum of **4**. It was not visible in the case of **3**, in agreement with half-chair or envelope conformations for the C(1–5),C(8) rings in **3** and **4**. This is due to the rigidity of the diene–$Fe(CO)_3$ moieties that makes the C(1–4) centers to be coplanar or nearly coplanar.[6] The chair conformation of the C(1–5),C(8) ring in **5** was also indicated by the 2.5 Hz ^4J coupling constant observed for both the olefinic protons of the $H_2C{=}C(3)$ group with H–C(4-exo) (copolanarity of these atoms). The 1,4-distance between the terminal carbon atoms of the diene at C(2),C(3) in **5** must be larger than that in the diene moiety at C(6),C(7). Accordingly,[8] the latter diene was predicted to react faster than the former in a Diels–Alder addition. Our kinetic data with TCNE (see Table I) contradict this prediction.



In the presence of 1 molar equiv of TCNE, **5** gave the monoadduct **7** (93%); no trace of the isomeric product **6** or bisadduct **8** could be detected in the mother liquor of crystallization of **7**. The addition of a second equivalent of TCNE to **7** was a much slower reaction, giving **8** (93%, isolated). The second-order rate constants of reaction **5** + TCNE → **7** (k_1^{II}) and **7** + TCNE → **8** (k_2^{II}) measured at various temperatures allowed the evaluation of the activation parameters reported in the table. A rate ratio k_1/k_2 = 300 was obtained at 25 °C and appears to be mostly due to a difference in the activation entropy term. Further data with other dienophiles and/or solvents are required to substantiate this result. Tetraene **5** was about 100 times more reactive than **1** (Z = CH_2) toward TCNE.[1] Among the several possible interpretations for our kinetic results, we can invoke a possible larger steric hindrance to the approach of the dienophile to the diene moiety at C(6),C(7) than for the diene moiety at C(2),C(3) and a higher flexibility (fast chair/twist interconversion of the six-membered ring) of the latter than of the former diene moiety in **5**. In any event, our preliminary results show the new tetraene **5** to be a valuable synthetic intermediate for tandem Diels-Alder reactions. Monoadducts with the diene moiety at C(6),C(7) are available by using the semiprotected tetraene **4**. Substituted derivatives of **4** and **5** can be envisioned as starting material for the synthesis of naphthocyclinones.[10]

Experimental Section

General Remarks, see ref 2.

***trans*-μ-[(1*RS*,2*RS*,4*SR*,5*SR*,6*RS*,7*RS*,8*SR*)-*C*,5,6,*C*-η:*C*,7,8,*C*-η-(5,6,7,8-Tetrakis(methylene)-2-bicyclo[2.2.2]octyl methanesulfonate)]bis(tricarbonyliron) (2).** Hydroboration of **1** (Z = CH=CH) followed by oxidative workup gave the corresponding alcohol **1** [Z = $CH_2CH(OH)$].[3] The latter (227 mg, 0.5 mmol) was dissolved in anhydrous pyridine (1 mL) and then cooled to 0 °C. After addition of methanesulfonyl chloride (74 mg, 0.6 mmol) the mixture was stirred at 20 °C for 30 min under N_2 atmosphere. CH_2Cl_2 (15 mL) was added and the mixture was

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[4] For related Wagner–Meerwein rearrangement, see e.g.: Walborsky, H. M.; Baum, M. E.; Youssef, A. A. *J. Am. Chem. Soc.* **1961**, *83*, 988. Goering, H. L.; Sloan, M. F. *Ibid.* **1961**, *83*, 1397.

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[9] Kinetic measurements, see: Pilet, O.; Chollet, A.; Vogel, P. *Helv. Chim. Acta* **1979**, *62*, 2341.

[10] Krone, B.; Zeeck, A. *Liebigs Ann. Chem.* **1983**, 471. Egert, E.; Noltemeyer, M.; Sheldrick, G. M.; Saenger, W.; Brand, H.; Zeeck, A. *Ibid.* **1983**, 503.

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