We do not have an analytical method for S^- in our reaction mixtures that is completely reliable. We have tried to determine $[S^-]$ in runs in which $[S^-]_0$ was in excess both by ion chromatography and by a GC method in which methyl tosylate was added and S^- was determined as *N*-methylsuccinimide. The results from the two methods were not in good agreement, but both methods pointed to side reactions involving S^-. Since the succinimide polymer has both C–C and C–N linkages between succinimide groups, it must have some available N–H groups, which we might represent as PNH. The equilibrium shown in eq 12 now becomes possible. It is reasonable to expect

$$PNH + S^- \rightleftharpoons PN^- + SH \quad (12)$$

that PN^- is less effective than S^- in electron transfer. This proton transfer can, therefore, slow the SCl–S^- reaction. Another possible path for consumption of S^- is Michael addition of S^- to maleimide and the anionic polymerization that such addition might initiate.[9]

Experimental Section

Chemicals. Reagent-grade *N*-chlorosuccinimide from the Aldrich Chemical Company was recrystallized from water–acetone and dried over P_2O_5 in vacuo before use; mp 149–151 °C (lit. mp 150–151 °C[11]). The purity was assayed by an iodimetric procedure;[12] active chlorine was 26.4% corresponding to 99.6% purity. Tetra-*n*-butylammonium fluoborate was prepared as previously described.[13] Linde ultrahigh purity nitrogen was used to remove oxygen and maintain an inert atmosphere during the electrochemical experiments. The nitrogen was saturated with acetonitrile (AN) before passage into the electrochemical cell. The purification of the AN, the preparation of *N*-methylsuccinimide, and the preparation of a standardized solution of tetra-*n*-butylammonium succinimide in AN were all carried out as described previously.[1]

Apparatus and Instrumentation. Electrochemical experiments were performed using the following equipment supplied by EG&G Princeton Applied Research Corporation: a Model 175 universal programmer in conjunction with a Model 173 potentiostat/galvanostat and Model RE0089 X–Y recorder, jacketed cell bottom (K0064), cell top (K0066), purge tube (G0028), and glassy carbon electrode (G0021). Temperature control at 25 °C during electrochemical experiments was maintained with a Lauda Model C-3 circulator. For the experiments at 1 ± 1 °C an ice–water bath was used. A tube (12-mm diameter × 125-mm length) with a fritted glass tip (porosity "C") from Ace Glass (7209-06) was the anode compartment. A 50-mil Pt wire was inserted through a red rubber septum, and the septum was fitted over the end of the tube. The glass/septum boundary was wrapped with Parafilm M (American Can Company), and the air-tight seal prevented significant mixing of anolyte and catholyte solutions. A 2.3-mm diameter Pt disk sealed in soft glass and polished to a flat surface was employed for voltammetry. The working electrode for controlled-potential electrolyses was constructed from Pt gauze. Platinum electrodes were treated with chromic acid, rinsed with water, and dried before use. The Pt and glassy carbon voltammetric electrodes were manually polished between scans with γ-alumina (Gamal from Fisher Scientific Co.) on a felt polishing cloth. The reference electrode consisted of an Ag wire in contact with an AN solution containing 0.10 M $AgNO_3$ and 0.25 M TBAF, and it was terminated with a 3-mm diameter Vycor disk. For voltammetry experiments the reference electrode was placed into a salt bridge tube containing 0.25 M TBAF in AN, and it contacted the test solution through a Luggin capillary.

A Varian Model 2720, dual-column gas chromatograph equipped with a 6 ft × 0.25 in. stainless steel column packed with 10% poly(*m*-phenyl ether) (PMPE) on 80/100-mesh Chromosorb W and a 6 ft × 0.25 in. stainless steel column packed with Porapak Q was employed for product analyses. Infrared spectra were obtained with a Perkin-Elmer Model 281B infrared spectrophotometer.

Procedures. The general procedures for carrying out voltammetry and controlled-potential electrolyses of SCl were similar to those described previously.[1] Rate measurements of the SCl–S^- reaction were made at 1 ± 1 °C with the cell bottom immersed in an ice-bath. A voltammetric scan at 200 mV s^{-1} of SCl in AN containing 0.25 M TBAF was initially executed. An aliquot of the standardized TBAS solution was added to the cell, the solution was mixed by magnetic stirring and N_2 deaeration for ca. 45 s, and then ca. 15 s were allowed for the solution to become quiescent before the first voltammetric sweep was made. The working electrode was removed from the cell between sweeps, polished, and replaced. Voltammetric sweeps were performed every 2–5 min to record the SCl concentration vs. time. The second-order rate constants were obtained from the appropriate linear plots of the experimental data.

Products from the SCl electrolyses and chemical reactions were analyzed without prior workup. Succinimide and *N*-methylsuccinimide were determined by GC using the PMPE column isothermally at temperatures of 180 and 160 °C, respectively. Chloride ion was determined as *n*-butyl chloride on Poropak Q at 200 °C using an on-column derivatization procedure.[4] Determination of SH by IR was carried out differentially in 0.2-mm cells with AN as a reference. The intensity of the absorption at 3280 cm^{-1} (N–H stretch) was used as a measure of the SH concentration.

Registry No. SCl, 128-09-6; S^-, 28627-67-0.

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A New Synthesis of Bicyclo[4.1.1]octa-2,4-diene and Its Cycloaddition Reactions with Dienophiles

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Bicyclo[4.1.1]octa-2,4-diene (**4**) has been synthesized by a new, nine-step route, starting from 2-[(trimethylsilyl)oxy]-1,3-butadiene and acrolein. Diene **4** proved almost as unreactive toward Diels–Alder cycloadditions as the previously studied 7,7-dimethyl derivative **1**. However, unlike **1**, **4** did react with phenyltriazolinedione to give a 4 + 2 cycloadduct. This difference between **1** and **4** is discussed in terms of a steric effect involving the endo methyl group in **1**, an explanation that is supported by the results of molecular mechanics calculations.

Several years ago we reported the synthesis of 7,7-dimethylbicyclo[4.1.1]octa-2,4-diene (**1**).[1] As part of our exploration of the chemistry of **1**,[2,3] we investigated its Diels–Alder reactivity.[4] The diene proved quite inert

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toward such potent dienophiles as phenyltriazolinedione (PTAD) and tetracyanoethylene (TCNE). Even at elevated temperatures no cycloadducts were isolated. Moreover, although 1 did react with benzyne, the product was not the Diels–Alder adduct 2 but instead the 2 + 2 adduct 3.

1, R = Me
4, R = H

2, R = Me
5, R = H

3, R = Me
6, R = H

Molecular models clearly indicate that the endo methyl group at C-7 sterically shields one face of the diene. This methyl group might also serve to inhibit Diels–Alder reactions at the other face, since, to the extent that C-2 and C-5 have rehybridized from sp^2 toward sp^3 in the transition state, the increased steric interactions between the endo methyl group and the four-atom bridge would serve to raise the activation energy. Indeed, MM2 molecular mechanics calculations on 1 and on a model for 2, lacking the benzo group, found the increase in strain energy on going from reactant to product to be 12 kcal/mol greater than in the comparable reaction of the unsubstituted diene 4.[5] With an inhibitory role thus indicated for the methyl groups, it became of some interest to explore the cycloaddition reactions of the parent diene, in which these groups are absent.

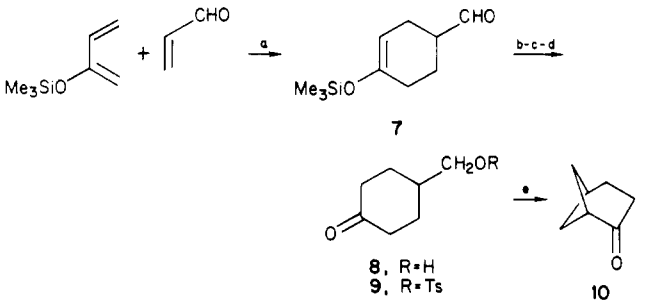
Bicyclo[4.1.1]octa-2,4-diene (4) has been previously prepared by Volz and Paquette;[6] but their synthesis is lengthy, and two of the last four steps each proceed in less than 20% yield. In this paper we report a new synthesis of 4 and the results of our investigations of the cycloaddition reactions of 4 with PTAD, TCNE, and benzyne.

Results and Discussion

In designing a new synthesis of 4, we took cognizance of the ready availability of bicyclo[3.1.1]heptanone (10) from the base-catalyzed cyclization of tosylate 9 of 4-(hydroxymethyl)cyclohexanone (8), a reaction developed by Musso and by Nicolaou.[7] Ketones can be ring expanded by addition of carbenes to their enol ethers,[8] a fact that has been recently exploited by Paquette et al. in their syntheses of deuterated derivatives of 1 from nopinone.[9] Therefore, we investigated the ring expansion of the parent bicyclo[3.1.1]heptanone (10) by this method.

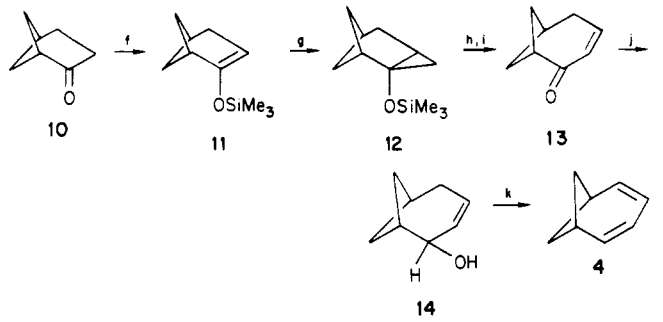
Unlike both Musso and Nicolaou, we prepared the keto alcohol precursor (8) of bicyclic ketone 10 by a cycloaddition route. As shown in Scheme I, 2-[(trimethylsilyl)oxy]butadiene[10] was allowed to react with acrolein to afford the Diels–Alder adduct 7 in 81% yield. Reduction with $LiAlH_4$, followed by base-catalyzed removal of the trimethylsilyl group, gave an 81% yield of hydroxy ketone 8, which was converted to tosylate 9. The cyclization of 9 to 10 was carried out with potassium hydride

Scheme I[a]



[a] (a) Hydroquinone, toluene, reflux, 81%; (b) $LiAlH_4$, ether; (c) NaOH, CH_3OH, 81% for two steps; (d) TsCl, pyridine, 0 °C, 93%; (e) KH, THF, 50 °C, 32%.

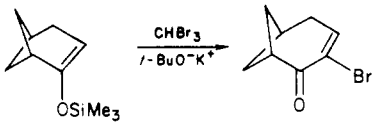
Scheme II[a]



[a] (f) Me_3SiCl, Et_3N, DMF, 80 °C, 76%; (g) Zn-Cu, CH_2I_2, ether, 81%; (h) $FeCl_3$, DMF; (i) NaOAc, methanol, reflux, 74% for two steps; (j) $LiAlH_4$, ether, -20 °C; 86%; (k) 2,4-dinitrobenzenesulfenyl chloride, Et_3N, 1,2-dichloroethane, reflux, 51%.

in THF instead of in Me_2SO, the solvent employed by Nicolaou and co-workers. Although the yields of 10 were lower than those reported by Nicolaou with Me_2SO as the reaction solvent, for large-scale runs the convenience of isolating the product from THF more than compensated for the reduced yields.

Ring expansion of 10 could be effected by addition of dibromocarbene to trimethylsilyl enol ether 11. However,



attempts to remove the bromine from the α,β-unsaturated bromo ketone product 15 led to competitive reduction of the conjugated double bond. In their synthesis of deuterated derivatives of 1 by the same type of route, Paquette and co-workers overcame this problem by reducing the carbonyl group prior to removing the bromine reductively.[9] We solved the problem differently.

As shown in Scheme II, the enol ether 11 was cyclopropanated to 12 by the Simmons–Smith procedure reported by Murai and co-workers.[11] Oxidative ring opening was effected with $FeCl_3$, as described by Saegusa et al.;[12] and the crude β-chloro ketone formed was transformed

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(5) The Allinger MM2 force field was used: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. The calculations found that the unsubstituted one-carbon bridge (C-8) shields the diene moiety more in 1 than in 4, because in 1 the diene moiety is predicted to be bent slightly toward C-8 in order to avoid the endo methyl group at C-7. However, the computed distance between C-3 and C-8 in the two molecules differs by only 0.05 A. We thank Dr. George Renzoni for performing the MM2 calculations for us.
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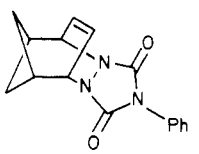
into the α,β-unsaturated ketone **13** with sodium acetate in methanol. Pure **13** was isolated in 63% yield after purification by preparative GLC.

We had intended to convert **13** to **4** by the same type of modified Shapiro reaction that we used to prepare **1**.[1] However, base-catalyzed decomposition of the tosylhydrazone formed from **13** gave only small amounts of **4**. Thus, another route from **13** to **4** was explored.

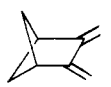
Reich and Wollowitz have reported the conversion of allylic alcohols to dienes by treatment with 2,4-dinitrobenzenesulfenyl chloride.[13] The reaction is unsatisfactory for the preparation of **1** from the corresponding allylic alcohol, apparently because the endo methyl group sterically inhibits the elimination step.[4] However, it seemed likely that the reaction would proceed better in molecules lacking the offending endo methyl group. Therefore, **13** was reduced with $LiAlH_4$ to the allylic alcohol **14**, which was then treated with 2,4-dinitrobenzenesulfenyl chloride in 1,2-dichloroethane at reflux. From the latter reaction the parent bicyclo[4.1.1]octa-2,4-diene (**4**) was isolated in 45% yield after purification by preparative GLC.

The parent diene **4** also proved to be extremely unreactive toward dienophiles. Like **1** it failed to react with TCNE, either at room temperature or on heating for several hours at 50 °C. Also like **1**, **4** reacted with benzyne to afford the 2 + 2 cycloadduct **6**, instead of the 2 + 4 Diels–Alder adduct **5**.

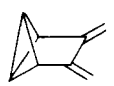
However, in contrast to **1**, the unsubstituted diene did undergo Diels–Alder reaction with PTAD. After being stirred in chloroform for 15 h at room temperature, **16** was



16



17



18

isolated in 68% yield, following purification by sublimation. The simplicity of the ^1H NMR spectrum and the number of peaks in the decoupled ^{13}C NMR spectrum were both indicative of the existence of the symmetry plane present in **16** but absent in the 2 + 2 cycloadduct.

Thus, although **4** is a rather unreactive Diels–Alder diene, **4** does give evidence of being more reactive toward 2 + 4 cycloadditions than its 7,7-dimethyl derivative **1**. It should be noted that methyl substitution on the four-membered ring also reduces the Diels–Alder reactivity of 2,3-bis(methylene)bicyclo[2.1.1]hexane (**17**)[14] but increases the reactivity of 3,4-bis(methylene)tricyclo[3.1.0.0^{2,6}]hexane (**18**).[15] The latter result suggests that in molecules containing unsaturatively bridged small rings methyl substitution on the ring affects diene reactivity electronically[16] as well as sterically. However, we feel that the simplest interpretation of the greater Diels–Alder reactivity of **4** compared to **1** is in terms of the steric effects discussed above.

Experimental Section

^1H NMR spectra were obtained with either a Varian EM-360 L (60 MHz) or a Bruker WM-500 (500 MHz) spectrometer, ^{13}C NMR spectra were obtained on a Bruker CXP-200 (50 MHz) spectrometer. The NMR specta were recorded as chloroform-*d* solutions with chemical shifts reported in ppm downfield from internal reference tetramethylsilane. IR spectra were obtained with a Beckmann Acculab 4 spectrometer on chloroform solutions, and UV spectra were obtained with a Hewlett-Packard HP8450A instrument on hexane solutions. Mass spectra were measured with a Hewlett-Packard 5985A GC/MS system, equipped with a fused silica capillary column and operating in the electron impact mode with ionizing energy of 70 eV. Exact masses were determined with a VG 7070 GC/MS and associated VG 2035 F/B data system operating in the electron impact mode. Gas chromatographic analyses were performed on a Hewlett-Packard 5790A chromatograph, equipped with a 25-m ultraperformance capillary column of crosslinked 5% phenylmethyl silicone and a flame ionization detector. Preparative gas chromatography was performed on a Varian Aerograph Model 920 thermal conductivity gas chromatograph with an He flow rate of 50 mL/min. The following $^3/_8$ in. preparative columns were used: (1) QF-1 12 ft and (2) Carbowax 20M 12 ft, both 20% on Chromasorb W. Solvents were stirred over and distilled from appropriate drying agents.

1-[(Trimethylsilyl)oxy]cyclohexene-4-carboxaldehyde (7). 2-Trimethylsilyloxy-1,3-butadiene(64 g, 0.44 mol) was mixed with 50 g (0.88 mol) of pre-dried and freshly distilled acrolein, 1 g of hydroquinone, and 80 mL of toluene. The solution was heated at reflux for 24 h, and the solvent and unreacted starting material were then removed on a rotary evaporator. The residue was distilled at 67–70 °C (1.2 mm) to give 75.8 g (87.0%) of **7**, which was 93% pure by GLC: ^1H NMR δ 0.2 (s, 9 H), 1.8-2.5 (m, 7 H), 4.9 (m, 1 H), and 9.78 (s, 1 H); IR 1730, 1680 cm^{-1}; MS; *m/e* (relative intensity) 73, 127, 155 (100), 170, 198; exact mass calcd for $C_{10}H_{18}O_2Si$ 198.1076, found 198.1062.

4-(Hydromethyl)cyclohexanone (8). To a solution of 4.2 g (0.11 mol) of $LiAlH_4$ in 400 mL of anhydrous ether was added 39.6 g (0.20 mol) of **7** dropwise at −78 °C. After the addition was complete, the reaction mixture was warmed to room temperature over a period of 2 h and stirred for another 30 min at room temperature. Then 6 mL of water, 6 mL of 15% NaOH, and 18 mL of water were added successively at 0 °C. The clear solution was filtered and dried over anhydrous $MgSO_4$. After removal of solvent by rotary evaporator, 34.4 g of crude 4-(hydroxymethyl)-1-[(trimethylsilyl)oxy]cyclohexene was obtained, which was then stirred with 200 mL of methanol and 5 mL of 15% NaOH at room temperature for 30 min. After removal of most of the methanol under reduced pressure, the residue was taken up in 300 mL of ether and dried over anhydrous $MgSO_4$. Removal of the ether gave 22.6 g (81.2%) of **8**, which was 93% pure by GLC and was used without further purification: ^1H NMR δ 1.1–2.7 (m, 10 H) and 3.60 (d, J = 5 Hz, 2 H); IR 3640, 3500, 1730 cm^{-1}; MS, *m/e* (relative intensity) 55 (100), 72, 81, 97, 110, 128, exact mass calcd for $C_7H_{12}O_2$ 128.0837, found 128.0837.

4-[[(*p*-Tolylsulfonyl)oxy]methyl]cyclohexanone (9). Alcohol **8** (20.4 g, 0.16 mol) was dissolved in 160 mL of freshly distilled pyridine, and tosyl chloride (38 g, 0.18 mole) was added slowly at 0 °C. The mixture was kept in a refrigerator at 0 °C for 2 days and then poured into 400 mL of water and 400 mL of ether. After separation, the aqueous layer was extracted twice with 50 mL of ether. The combined organic layers were washed with aqueous $CuSO_4$ until the washings remained light blue and then washed with water, saturated NaCl, and dried over anhydrous $MgSO_4$. After removal of solvent, 41.8 g (92.6%) of **9** was obtained as a solid. Recrystallization from ether–hexane gave a sample with mp 57–58 °C (lit.[7] mp 63–64 °C). The melting point was not altered by subsequent recrystallizations; however, the ^1H NMR spectrum matched that reported in the literature.

Bicyclo[3.1.1]heptan-2-one (10). Potassium hydride (25% in mineral oil, 31.1 g) was washed 3 times with 100-mL portions of dry pentane under argon atmosphere. After most of the pentane was removed through a double-tip needle, the remaining pentane was evaporated by flushing with argon and gentle warming. Then 730 mL of dry THF was added. Keto tosylate **9** (28.2 g, 0.10 mol) in 120 mL of dry THF was added over a period of 15 min. Hydrogen evolution began immediately, and the reaction mixture was stirred overnight at 50 °C. Approximately 500 mL of THF was removed under vacuum, and the mixture was poured into ether–ice water. After separation, the aqueous layer was extracted

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(16) Evidence exists for strong interactions between the orbitals of small rings and unsaturated bridging groups; see Borden et al. (Borden, W. T.; Young, S. D.; Frost, D. C.; Westwood, N. P. C.; Jorgensen, W. L. *J. Org. Chem.* **1979**, *44*, 737) for a brief summary and leading references.

3 times with 50-mL portion of ether and the combined organic layers were washed with three 100-mL portions of water, saturated NaCl, and dried over anhydrous $MgSO_4$. Most of solvent was removed by rotary evaporator, and the residue was vacuum distilled, bp 80–85 °C (15 mm), to give 4.1 g (37%) of crude product, 85% pure by GLC. The major component **10** was purified by preparative GLC (column 1, 150 °C, 32 min) for spectroscopic characteriation. The ^1H NMR and IR spectra matched those reported in the literature.[7]

2-[(Trimethylsilyl)oxy]bicyclo[3.1.1]hept-2-ene (11). In a 50-mL, three-necked flask, equipped with reflux condenser and magnetic stirrer, was placed 4.2 g (41.3 mmol) of triethylamine and 6 mL of DMF. Chlorotrimethylsilane (3.8 g, 35 mmol) was added by syringe, followed by 3.0 g (27 mmol) of crude ketone **10**. The resulting mixture was warmed to 80 °C and stirred for 2 days. After being cooled to room temperature, the reaction mixture was filtered into a separatory funnel containing 50 mL of pentane. The residue was washed thoroughly with 50 mL of pentane. To the combined pentane solutions was added 30 mL of cold 5% $NaHCO_3$. After separation of the phases, the aqueous layer was quickly extracted twice with 25-mL portions of pentane. The combined organic layers were washed with cold water (30 mL) and dried over anhydrous $MgSO_4$. Vacuum distillation, bp 75–78 °C (10 mm), yielded 4.2 g (75.6%). The major component (85% by GLC) was separated and purified by preparative GLC (column 1, 140 °C, 15 min) for spectroscopic characterization: ^1H NMR δ 0.20 (s, 9 H), 1.3–1.6 (m, 2 H), 2–2.5 (m, 4 H), 2.5–2.9 (m, 2 H), and 4.6 (m, 1 H); IR 1675 cm^{-1}; MS, *m/e* (relative intensity) 73 (100), 151, 167, 182; exact mass calcd for $C_{10}H_{18}OSi$ 182.1127, found 182.1106.

2-[(Trimethylsilyl)oxy]tricyclo[4.1.1.0^{2,4}]octane (12). A mixture of zinc (1.94 g, 29.6 mmol) and cuprous chloride (2.92 g, 29.6 mmol) in 36 mL of anhydrous ether was stirred and heated to reflux in a nitrogen atmosphere for 30 min. Crude silyl enol ether **11** (3.0 g, 16.4 mmol) and methylene diiodide (7.1 g, 26.1 mmol) were added successively. The resulting mixture was maintained at reflux for 30 h. After being cooled to room temperature, the reaction mixture was diluted by adding ether and filtered. The filtrate was washed successively with cold saturated NH_4Cl, saturated $NaHCO_3$, water, and saturated NaCl, and dried over anhydrous $MgSO_4$. Removal of solvent yielded 6.0 g (81% yield) of crude product. The major component (85% by GLC) was purifed by preparative GLC (column 1, 140 °C, 22 min) for spectroscopic characterization: ^1H NMR δ 0.15 (s, 9 H), 0.8–1.2 (m, 4 H), 1.3–1.7 (m, 2 H), 1.8–2.3 (m, 4 H), and 2.3–2.6 (m, 1 H); IR 2970 cm^{-1}; *me* (relative intensity) 73 (100), 155, 167, 181, 196; exact mass calcd for $C_{11}H_{20}OSi$ 196.1283,und 196.1275.

Bicyclo[4.1.1]oct-3-en-2-one (13). Anhydrous ferric chloride (4.0 g, 24.6 mmol) was placed in a 100-mL three-necked flask, and 17 mL of dry DMF was added slowly at 0 °C and stirred until the ferric chloride was dissolved. A solution of 2.2 g (11.2 mmol) of crude silyl ether **12** in 5 mL of DMF was added dropwise over a period of 1 h. The internal temperature was maintained at 0–5 °C. Then the reaction mixture was allowed to warm to room temperature and stirred for another 3 h. The mixture was poured into 50 mL of cold 1 N HCl and extracted 3 times with 50-mL portion of chloroform. The organic layers were washed with 20-mL portions of cold 1 N HCl, saturated $NaHCO_3$, H_2O, and saturated NaCl and dried over anhydrous $MgSO_4$. After removal of solvent, the crude β-chloro ketone product was mixed with 25 mL of methanol saturated with sodium acetate and heated at reflux for 2 h. Half of the methanol was removed by rotary evaporator, 25 mL of water was added, and the mixture was taken up in 60 mL of ether. The ethereal layer was then washed with water and saturated NaCl and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by preparative GLC (column 1, 150 °C, 60 min) to give 0.86 g (74%) of pure **13**: ^1H NMR δ 1.90 (m, 2 H), 2.63 (m, 2 H), 2.70 (m, 2 H), 2.82 (m, 1 H), 3.08 (m, 1 H), 6.00 (d of q, J = 12.7 and 2.4 Hz, 1 H), and 6.48 (d of t, J = 12.7 and 4.0 Hz, 1 H); IR 1675, 1650 cm^{-1}; UV λ_{max} 229 nm (log ϵ = 3.8); exact mass calcd for $C_8H_{10}O$ 122.0732, found 122.0735.

Bicyclo[4.1.1]oct-3-en-2-ol (14). Ketone **13** (0.73 g, 6.0 mmol) in 10 mL of anhydrous ether was added dropwise to a solution of 0.30 g (7.9 mmol) of $LiAlH_4$ in 45 mL of ether at −20 °C. After being stirred at −20 °C for 1 h, the reaction mixture was warmed to 0 °C. then 0.36 mL of water, 0.36 mL of 15% NaOH, and 1.3 mL of water were added successively. The clear solution was filtered and dried over anhydrous $MgSO_4$. After removal of solvent, 0.73 g (98%) of crude product was obtained. The major component (88% by GLC) was separted by preparative GLC (column 1, 160 °C, 48 min) for spectroscopic characterization. ^1H NMR δ 1.2–2.0 (m, 3 H), 2.1–2.9 (m, 6 H), 4.2–4.4 (m, 1 H), and 5.6 (b, s, 2 H); IR 3590, 3500, 1660 cm^{-1}; exact mass calcd for $C_8H_{12}O$ 124.0888, found 124.0900.

Bicyclo[4.1.1]octa-2,4-diene (4). To crude alcohol **14** (0.1 g, 0.8 mmol) and 0.25 g (2.5 mmol) of triethylamine in 7 mL of 1,2-dichloroethane was added 0.56 g (2.4 mmol) of 2,4-dinitrobenzenesulfenyl chloride at 0 °C. The mixture was stirred and heated at reflux for 15 h. After being cooled to room temperature, the mixture was poured into 25 mL of pentane and filtered, and the residue was washed thoroughly with 25 mL of pentane. The mixture was then passed through a short pad of silica gel. After most of solvent was carefully distilled off, the mixture was separated and purified by preparative GLC (column 2, 85 °C, 64 min) to give 0.038 g (51%) of pure **4**. The ^1H NMR spectrum of **4** was identical with that reported in the literature.[6]

Attempted Diels–Alder Reactions of 4. (a) With Tetracyanoethylene. Under a nitrogen atmosphere, diene **4** (5 mg, 0.047 mmol) and 9 mg (0.07 mmol) of tetracyanoethylene in 2 mL of 1,2-dichloroethane were stirred at room temperature for 3 h. The starting materials were recovered unchanged. On heating the mixture at 50 °C for 2 h, there was also no reaction, nor was any observed after 2 days in refluxing benzene.

(b) With Benzyne. A solution of 0.137 g (0.1 mmol) of anthranilic acid and 3 mg (0.019 mmol) of diene **4** in 2 mL of 1,2-dichloroethane was brought to reflux, and 0.13 mL (0.1 mmol) of isoamyl nitrite was added dropwise over a period of 5 min. The resulting mixture was allowed to reflux for 1 h. After cooling to room temperature, the solvent was removed, and the residue was separated by TLC, using hexane as eluting solvent, to give 1.5 mg (43%) of adduct **6**: ^1H NMR δ 1.17 (m, 1 H), 1.63 (m, 1 H), 2.28 (m, 1 H), 2.60 (m, 1 H), 2.73 (m, 1 H), 3.02 (m, 1 H), 4.00 (t, 1 H), 4.43 (m, 1 H), 5.93 (m, 1 H), 6.11 (m, 1 H), and 6.97–7.17 (m, 4 H); exact mass calcd for $C_{14}H_{14}$ 182.1095, found 182.1079.

(c) With 4-Phenyl-1,2,4-triazoline-3,5-dione. Diene **4** (10 mg, 0.094 mmol) and 16.5 mg (0.094 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione in 2 mL of chloroform was stirred at room temperature for 15 h. After removal of solvent, the residue was carefully sublimed under reduced pressure to give 18 mg (68%) of the 2 + 4 adduct **16**: mp 213–215 °C; ^1H NMR δ 1.57 (m, 1 H), 2.08 (m, 1 H), 2.42 (m, 1 H), 2.46 (m, 1 H), 2.83 (m, 2 H), 5.28 (m, 2 H), 6.34 (d of d, J = 3.7 and 4.4 Hz, 2 H), and 7.37–7.50 (m, 5 H); ^{13}C NMR 33.2, 37.1, 40.3, 56.4, 106 .4, 125.5, 128.1, 128.9, 131.2, and 154.5 ppm; exact mass calcd for $C_{16}H_{15}N_3O_2$ 281.1164, found 281.1160.

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