obtained as a neat liquid by this method. A solution of 1 can be obtained by distillation of CS_2 into the cold trap after the pyrolysis is complete. Presumably, other inert solvents such as $CHCl_3$, CH_2Cl_2, and hexane would also work. The acetic acid is removed by passing the solution of 1 through the frit covered with Na_2CO_3. Freshly prepared 1 is stored under nitrogen in a dry ice/isopropyl alcohol bath.[12] Slow decomposition is observed for samples stored at room temperature.

2,3-Dihydrothiophene obtained by this preparation was characterized by its mass and ^1H and ^{13}C NMR spectra. In the mass spectrum, the molecular ion peak is observed at m/e 86, and the base peak is at m/e 85, in agreement with a previously reported spectrum.[6c] The ^1H NMR spectrum of this compound was reported earlier.[13] The chemical shifts we observed closely match those reported earlier as do the coupling constants seen for the olefinic resonances. However, for the H_4 protons only an average of the two coupling constants to H_2 and H_3 was observed. No apparent second-order splitting of the methylene protons was seen as reported by Korver et al.[13b] The ^{13}C NMR spectrum of 1 has not been reported. The resonances which were observed are very close to those reported for the olefinic carbons in thiophene, 126 and 124 ppm (neat), and for the methylene carbons in tetrahydrothiophene, 31.7 and 31.2 ppm.[14]

Experimental Section

The experimental procedure and apparatus for the gas-phase pyrolysis have been previously described.[15] NMR spectra were obtained on a Nicolet 300-MHz or Bruker WM 300-MHz spectrometer. Chemical shifts are reported in ppm from the internal standard, tetramethylsilane. Electron ionization mass spectra (EIMS) were obtained on a Finnigan 4000 spectrometer. Reagent grade solvents and chemicals were used without further purification.

Tetramethylene sulfoxide was prepared as described previously[16] in 90% yield (bp 105–107 °C (15 torr)). 2-(Acetoxy)-tetrahydrothiophene (2) was prepared by the method of Horner and Kaiser[17] in 84% yield (bp 96 °C (12 torr)): mass spectrum (70 eV), m/e (relative intensity) 146.1 (6.2, M^+), 103.1 (8.5), 86.1 (31.1), 85.1 (10.0), 60.1 (9.6), 58.1 (10.0), 45.1 (16.6), 43.1 (100.0).

2,3-Dihydrothiophene (1) was prepared by pyrolysis of 2. Freshly distilled 2-(acetoxy)tetrahydrothiophene (5.00 g, 34.0 mmol) was placed in the sample compartment of the pyrolysis unit which was covered by a jacketed heating mantle to keep the sample at approximately 60 °C during the pyrolysis. The oven temperature was maintained at 400 °C, and the pressure was lowered to ca. 10^{-4} torr.[11] Products were collected in a U-shaped trap immersed in liquid nitrogen. After 2 h the pyrolysis was complete, and 20 mL of CS_2 was distilled into the trap if desired. Nitrogen was let into the system, and the trap was disconnected and capped under nitrogen flow. The trap was removed from the liquid nitrogen bath, and the product melted. The resulting liquid was transferred by syringe to a medium schlenk frit covered with 2.7 g (26 mmol, 1.5 equiv) of Na_2CO_3 under nitrogen. The solution was allowed to sit on the frit until no further evolution of CO_2 gas was observed (ca. 5 min) and then was filtered into a storage flask. If CS_2 was added earlier, then the frit was washed 3 times with 5-mL portions of CS_2, and the solution and washings were stored in a dry ice/isopropyl alcohol bath. The yield of the neat liquid product was 2.53 g (86%): ^1H NMR ($CDCl_3$) δ 6.14 (dt, 1 H, J_{2-3} = 5.93 Hz, J_{2-4} = 2.18 Hz, H_2), 5.59 (dt, 1 H, J_{2-3} = 5.93 Hz, J_{3-4} = 2.75 Hz, H_3), 3.21 (t, 2 H's, J_{4-5} = 8.72 Hz, H_5), and 2.74 (tt, 2 H's, J_{4-5} = 8.72 Hz, J = 2.46 Hz, H_4); ^{13}C(H) NMR ($CDCl_3$) δ 126.1 (C_2), 122.0 (C_3), 32.3 (C_5), and 35.1 (C_4); EIMS (70 eV), m/e (relative intensity) 86.1 (62.0, M^+), 85.1 (100), 71.7 (7.0), 60.1 (4.0), 59.1 (5.3), 58.0 (11.0), 57.0 (6.1), 50.1 (7.3), 46.0 (4.6), 45.0 (41.5), 43.1 (22.9), 41.1 (6.2), 39 (15.6).

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-ENG-82.

(12) Solutions stored in this manner were found to be quite stable for periods of 2–3 weeks.

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Diels–Alder Reactions of Quinone Sulfoxides

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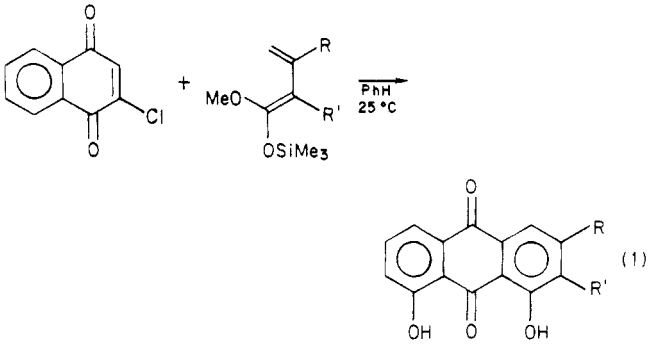
Received June 14, 1985

The Diels–Alder reaction has often been used to construct polycyclic quinones from either benzoquinones or naphthoquinones.[1] This strategy has led to elegant syntheses of certain anthracyclines and also many other acetate-derived compounds. Several researchers, most notably Gesson and Brassard, have determined that the presence of a chlorine or bromine atom on the starting quinone framework permits the ready assemblage of the polycyclic quinone[2] (eq 1). The regeneration of the



(1)

quinone moiety is facilitated by the elimination of the HCl or HBr. Recently, Rapoport has reported improved yields of certain anthraquinones by the simple expedient of delaying the dehydrohalogenation step.[3] A limitation of the haloquinone strategy is that the requisite haloquinone may not be easily synthesized, especially if the halogen group must be introduced late in the synthetic sequence. This is particularly difficult if an alkene or amine is present. We report herein that sulfinyl quinones represent convenient alternatives to haloquinones. With appropriate selection of reaction conditions, sulfoxide elimination regenerates the quinone unit during the Diels–Alder reaction. Moreover, with quinones such as juglone, either the 2- or 3-sulfinyl quinones can be obtained.[4]

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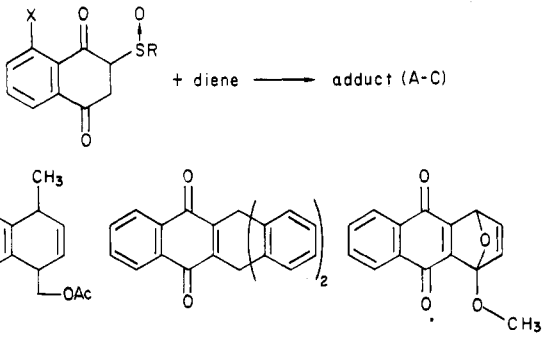
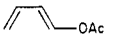
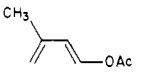
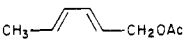
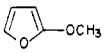
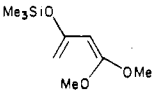
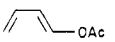
0022-3263/86/1951-0114$01.50/0

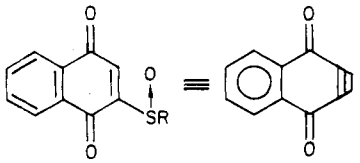
Table I. Quinone Sulfoxide Diels-Alder Reactions



A B C

entry	X	R	diene	% yield	product
1	H	CH_3		74	anthraquinone
2	H	CH_3		85	2-methylanthraquinone
3	H	CH_3		74	A
4	H	CH_3	anthracene	65	B
5	H	CH_3		65	C
6	H	CH_3		90	1-methoxy-3-hydroxy-anthraquinone
7	OH	Ph		75	1-hydroxyanthraquinone
8	OH	Ph		80	1,4-dihydro-5-hydroxy-anthraquinone

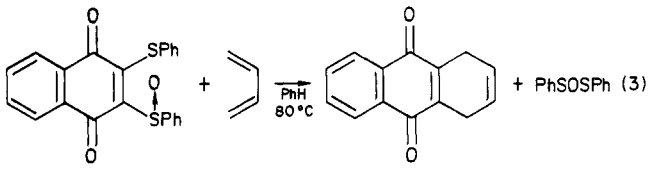
Despite the well-known electron-withdrawing effect of the sulfoxide group and the use of vinyl sulfoxides as dienophiles, the use of sulfinyl quinones in Diels–Alder reactions has only once been reported.[5] These compounds are readily prepared by oxidation of the corresponding sulfides with MCPBA in methylene chloride at 0 °C.[6] Reactions of various dienes with sulfinyl quinones are listed in Table I. These reactions are operationally convenient and have been conducted on scales ranging from 0.5 to 40 mmol. The mild reaction conditions required to effect both Diels–Alder reaction and elimination represent a useful feature of this reaction. The sulfoxide is eliminated regiospecifically to regenerate the quinone. This aspect was expected in light of rate studies on sulfoxide eliminations.[7] The aromatization to form an anthraquinone also is well precedented. The results in entry 5 are noteworthy in that furans often afford abnormal results in Diels–Alder reactions with quinones bearing electron-withdrawing groups.[8] In our case, sulfoxide elimination makes the process irreversible. The quinone sulfoxide represents a synthetic equivalent of the unknown compound naphthynoquinone (eq 2).



(2)

While selenoxides undergo elimination much faster than sulfoxides, the analogous (phenylselenyl)quinones proved difficult to prepare. Oxidation to afford the selenoxide produced several products.

Interestingly, when the quinone sulfoxide contains a phenylthio substituent at C-3,[9] which prevents reformation of the quinone subunit by the elimination of phenylsulfenic acid, the apparent expulsion of PhSOSPh is observed! This process is illustrated in eq 3. The product, which



was formed in 60% yield, was readily identified by mass spectroscopy combined with carbon and proton NMR. To the best of our knowledge, this novel reaction has not previously been observed.

In summary, the use of quinone sulfoxides represents a viable alternative to existing methodology. The ease of preparation combined with the facile elimination of phenylsulfenic acid makes this a versatile synthetic method.

Experimental Section

Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. Dichloromethane was distilled from phosphorus pentoxide. Infrared spectra were determined on a Beckman IR-4250 spectrometer. NMR spectra were determined on a Varian EM 360 60-MHz instruments and on a Nicolet 300-MHz instrument. Carbon-13 NMR spectra were determined on a JEOL FX-90Q Fourier

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transform instrument. High-resolution mass spectra (HRMS) were determined on a Kratos mass spectrometer.

General Procedure for the Diels-Alder Reaction. A solution of the diene (1-2 equiv) and quinone sulfoxide (1 equiv) was dissolved in the solvent (1 M with regard to the sulfoxide) and stirred at the temperature specified below until TLC indicated that the sulfoxide was gone. The solvent was removed in vacuo and the crude product was chromatographed on silica gel to afford pure product.

Entries 1-3, 7, and 8: refluxing carbon tetrachloride. Entries 4 and 5: refluxing toluene. Entry 6: carbon tetrachloride at room temperature.

1-Acetoxy-4-methyl-1,4-dihydro-9,10-anthraquinone: NMR ($CDCl_3$) δ 1.28 (d, J = 7 Hz, 3 H), 1.98 (s, 3 H), 3.40-4.04 (m, 2 H), 4.24 (d, J = 4 Hz, 2 H), 5.70-5.92 (m, 2 H), 7.52-7.80 (m, 2 H), 7.84-8.12 (m, 2 H); IR ($CDCl_3$) 1740, 1668, 1231, 1205, 915 cm^{-1}; mass spectrum, m/e 208, 224, 235, 266 ($M^+ - CH_2O$; HRMS for $C_{17}H_{14}O_3$ requires 266.09429, found 266.09398.

Anthracene adduct: NMR ($CDCl_3$) δ 6.03 (s, 2 H), 7.00-7.30 (m, 4 H), 7.35-7.82 (m, 4 H), 7.90-8.30 (m, 4 H); mass spectrum, m/e 334.

Methoxyfuran adduct: 300-MHz NMR ($CDCl_3$) δ 3.96 (s, 3 H), 5.48 (d, J = 2 Hz, 1 H), 7.06 (s, 1 H), 7.62 (d, J = 2 Hz, 1 H), 7.68-7.78 (m, 2 H), 8.03-8.15 (m, 2 H); mass spectrum, m/e 189, 204, 239, 254; HRMS for $C_{15}H_{10}O_4$ requires 254.0579, found 254.0573.

3-Hydroxy-1-methoxy-9,10-anthraquinone: 300-MHz NMR ($CDCl_3$) δ 3.92 (s, 3 H), 6.78 (s, 1 H), 7.25 (s, 1 H), 7.66-7.82 (m, 2 H), 8.03-8.18 (m, 2 H), 10.75 (br s, 1 H); mass spectrum, m/e 139, 152, 168, 197, 208, 225, 237, 254. The ^{13}C NMR spectrum was identical with that reported in ref 10 for the known compound.

Acknowledgment. We thank the National Institutes of Health (GM 34342) for generous support of this work.

Registry No. **A**, 99397-95-2; **B**, 6932-37-2; **C**, 99416-46-3; (*E*)-H_2C=CHCH=CHOAc, 35694-20-3; (*E*)-H_2C=C(CH_3)CH=CHOAc, 52062-24-5; (*E*,*E*)-MeCH=CHCH=$CHCH_2OAc$, 57006-69-6; H_2C=C($OSiMe_3$)CH=C($OMe)_2$, 61539-61-5; H_2C=CHCH=CH_2, 106-99-0; 2-(methylsulfinyl)naphthoquinone, 91136-55-9; 2-(methylsulfinyl)-8-hydroxynaphthoquinone, 99397-94-1; anthracene, 120-12-7; 2-methoxyfuran, 25414-22-6; anthraquinone, 84-65-1; 2-methylanthraquinone, 84-54-8; 3-hydroxy-1-methoxyanthraquinone, 28504-24-7; 1-hydroxyanthraquinone, 129-43-1; 1,4-dihydro-5-hydroxyanthraquinone, 99397-96-3.

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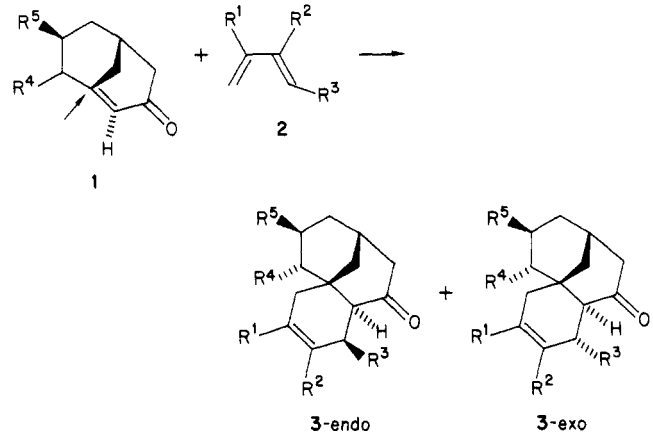
Communications

Diels-Alder Reactions of Bridgehead Enones

Summary: Diels-Alder reactions of bridgehead enone 1 with activated dienes proceed in excellent yields.

Sir: The Diels-Alder reaction and the Michael addition reaction represent two of the most versatile tools of the modern organic chemist. Both reactions employ unsaturated carbonyl compounds.[1] While both cyclic and acyclic unsaturated ketones have been extensively used, the subclass wherein either the α or β carbon of the enone is at a bridgehead has been little explored. House and coworkers, in their classic studies on bridgehead enones of various ring sizes, have identified several significant points.[2] Of interest in synthetic planning is that an enone such as 1 is too reactive to be isolated. Even substitution at the α carbon atom with a methyl group does not permit isolation. Using Allinger's MMP1 molecular mechanics program for conjugated systems, House has calculated probable geometries for 1. He has reported an average twisting deformation of the enone double bond of approximately 25° and an inherent strain energy of approximately 21 kcal/mol: House and co-workers have also investigated some characteristic reactions of the in situ derived bridgehead enones. In the presence of nucleophiles such as malonate anions or alkoxides, Michael addition reactions occur readily. However, in order to obtain good yields in Diels-Alder reactions with furan, it was necessary to use furan as the solvent. Recently Bestmann has generated enones such as 1 in ethanol and examined their chemistry.[3] Magnus has utilized a bridgehead enone in

Scheme I



an elegant synthesis of kopsanone.[4] To the best of our knowledge, this represents the first use of bridgehead enones in natural products synthesis. Our research group has recently employed an in situ derived bridgehead enone in two direct syntheses of racemic lycopodine.[5]

Information regarding regio- and stereospecificity of Diels-Alder reactions of 1 with various dienes is essential, since both House and Magnus have examined only symmetrical dienes. Additionally, reaction conditions must be identified such that only a slight excess of diene is required for a successful reaction. Molecular models indicate that the Diels-Alder reaction will occur only from the outer face of the twisted enone system. Since the enone would be expected to be polarized such that the β

(1) Michael addition: House, H. O. "Modern Synthetic Reactions"; Benjamin: Menlo Park, CA; 1972; pp 595-623. Diels-Alder reaction: Desimoni, G. "Natural Products Synthesis"; American Chemical Society: Washington, DC, 1983; ACS Monograph Series.

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