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SELECTIVE SULFURIZATION OF OLEFINS BY 9,10-EPIDITHIO-9,10-DIHYDROANTHRACENE: INTERMEDIACY OF DIATOMIC SULFUR

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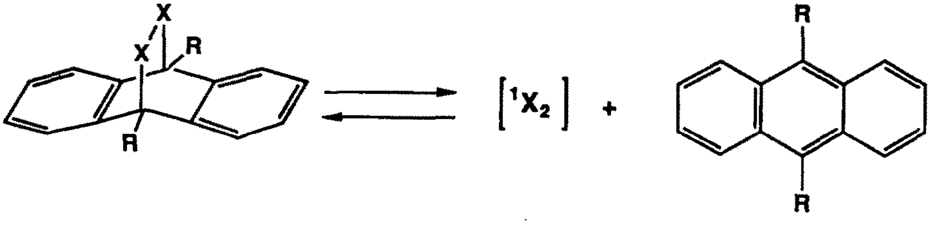
Abstract: The reaction of 9,10-dihydro-9,10-(1,3-epidithio-2-methano-2-p-methoxyphenyl-1-oxide)propanoanthracene (3) with perchloric acid in the presence of 1,3-butadienes and electron-rich olefins gave 1,2-dithiins and episulfides, respectively. The reaction is explained in terms of an intermediate anthracene endodisulfide with transfer of singlet diatomic sulfur to the dienes and olefins.

Introduction

The explosive development of research on singlet molecular oxygen1) has stimulated studies on the chemistry of the analogous sulfur species, i.e., singlet diatomic sulfur.2-4) Although diatomic sulfur is known to exist in molten and vaporized sulfur,2) little is known of its chemistry in solution owing to the lack of convenient preparative methods. In 1984, the chemical generation of diatomic sulfur was reported from the reaction of triphenylphosphine dibromide with digermyl trisulfides.3a) Recently diatomic sulfur has been produced by the decomposition of organic sulfur heterocycles3b-d) and organometallic sulfur compounds.3e) The fact that anthracene endoperoxide **1** readily liberates anthracene and singlet molecular oxygen5) led us to believe that the analogous sulfur compound, anthracene endodisulfide **2**, would be a suitable source of singlet diatomic sulfur

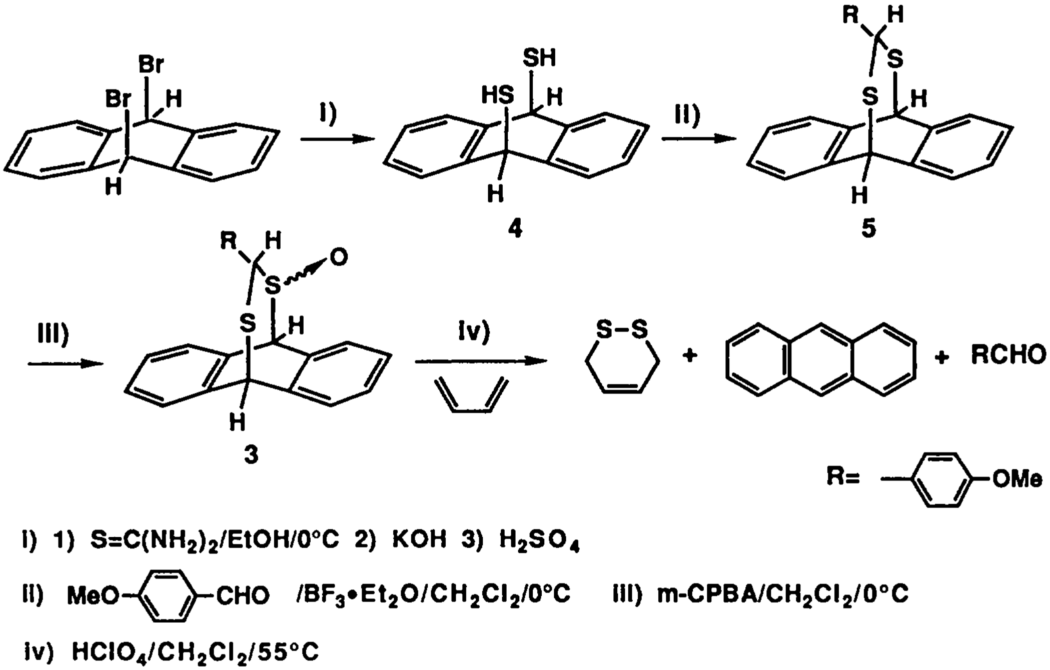
Our point of departure is the understanding that an intermediary 9,10-epidithio-9,10-dihydroanthracene (**2a**, R=H) might be obtained by the treatment of 9,10-dihydro-9,10-(1,3-epidithio-2-methano-2-p-methoxyphenyl-1-oxide)-propanoanthracene (3) with perchloric acid.4) Consequently **2a** would be expected to thermally extrude producing singlet diatomic sulfur which could be captured by conjugated dienes3) and electron-rich olefins to afford 1,2-dithiins and episulfides, respectively. We now describe such experiments which have enabled us to obtain new insights on the behavior of singlet diatomic sulfur.

1: X=O
2: X=S



Results and Discussion

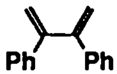
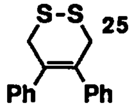
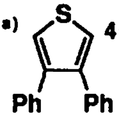
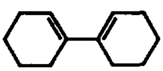
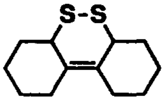
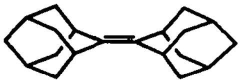
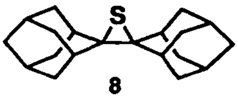
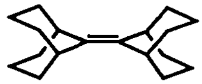
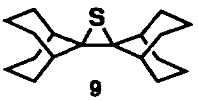
Treatment of 9,10-dibromo-9,10-dihydroanthracene[6] with thiourea in ethanol followed by hydrolysis afforded 9,10-dihydro-9,10-dimercaptoanthracene (4). The dithiol 4 and anisaldehyde were dissolved in methylene chloride containing boron trifluoride etherate. The adduct 5 so obtained was oxidized to the sulfoxide 3 with m-chloroperbenzoic acid (mCPBA).[7] Subsequent treatment of 3 with perchloric acid[7] failed to give the desired anthracene endodisulfide 2a. Separation of the reaction mixture by preparative HPLC revealed only the formation of anthracene, p-anisaldehyde, and elemental sulfur in yields of 60%, 98% and 56%, respectively, and polymeric material.



Despite these unpromising efforts to produce the parent disulfide 2a itself, its intermediacy was evident by trapping experiments. In a typical experiment, a solution of perchloric acid (0.26 mmol) in tetrahydrofuran (1 ml) was added to a solution of the trapping agent, 2,3-diphenyl-1,3-butadiene or 1,1'-bicyclohexenyl (2 eq.), and 3 (0.26 mmol) in methylene chloride. The resulting solution was stirred at 55°C for 100 min under an atmosphere of nitrogen. The Diels-Alder type adducts,[3] i.e., 1,2-dithiins (6 and 7) were isolated as well as anthracene, p-anisaldehyde, small amount of elemental sulfur, and polymeric material (Entries 1 and 2). The 1,2-dithiin 6 gradually decomposed to 3,4-diphenylthiophene[8] by elimination of hydrogen sulfide under the reaction conditions.

In a control experiment, no sulfurization occurred when elemental sulfur was used instead of 3. The formation of dithiins is analogous to the reaction of singlet molecular oxygen with dienes.[9] Clearly, the above results provide intermediacy for the formation of singlet diatomic sulfur from anthracene endodisulfide 2a.

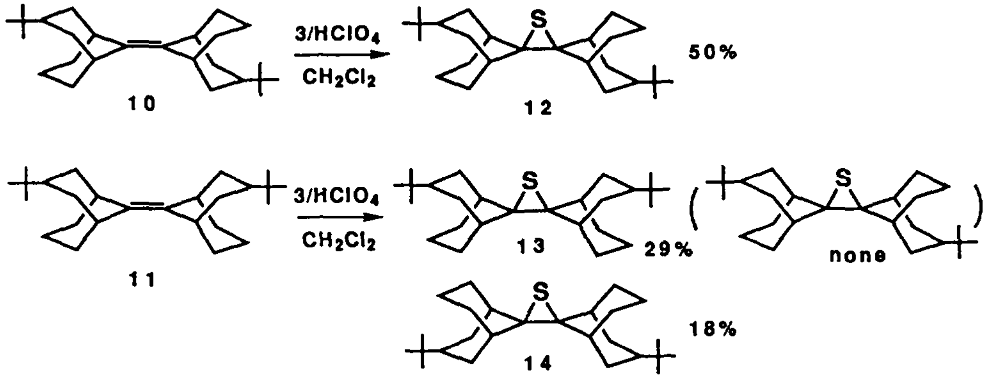
Table. Reaction of Singlet Diatomic Sulfur with Olefins.

Entry	Olefin	Products and Yields(%)					
						Anthracene	p-Anisaldehyde
1		 6	25%[a]		40%[a]	47%[b]	70%[b]
2		 7	48%[a]			〃 67%[b]	〃 72%[b]
3		 8	52%[a]			〃 52%[b]	〃 84%[b]
4		 9	49%[a]			〃 48%[b]	〃 70%[b]

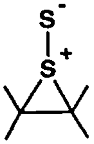
a) Yields were determined based on the anthracene obtained.
b) Yields were determined based on the sulfoxide 3 used.

We also carried out several experiments to trap singlet diatomic sulfur generated in situ using electron-rich substrates. Diatomic sulfur-transfer from 2a to 9,10-dimethylanthracene and 9,10-diphenylanthracene was not observed. Cyclic dienes, such as 1,3-cyclohexadiene, 1,3-cycloheptadiene and 2,5-dimethylfuran, only gave polymeric material, no sulfurization products were obtained. Although singlet molecular oxygen readily undergoes [2+2]-cycloaddition or ene reaction, similar behavior was not observed in the case for 3. Olefins, such as 2,3-dimethyl-2-butene, norbornylene, 2-(methoxymethylene)adamantane,[10] 3-adamantylidenetricyclo[3.2.1.0^{2,4}]-octane[11] and dimethyl acetylenedicarboxylate which all react normally with singlet molecular oxygen, proved unreactive toward 3 in the presence of perchloric acid affording no isolable sulfurization products. Sterically hindered electron-rich olefins, such as biadamantylidene and bis(bicyclo[3.3.1]non-9-ylidene), all react readily with singlet molecular oxygen to afford 1,2-dioxetane[12] via [2+2]-cycloaddition. However, they behaved differently with **3** and perchloric acid, gave the corresponding episulfides, **8** and **9**, respectively (Entries 3 and 4). No trace of 1,2-dithietanes[13] were detected.

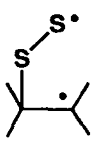
These results prompted us to examine the stereochemistry of the reaction of singlet diatomic sulfur with sterically hindered electron-rich olefins in order to elucidate the reaction mechanism. The obvious candidates are the two stereoisomeric di-t-butylbis(bicyclo[3.3.0]non-9-ylidenes) (**10** and **11**).[12] Both **10** and **11** on treatment with **3** afforded the corresponding episulfides in which the configurational integrity was conserved; i.e., **12** from **10**, both **13** and **14** from **11**. The yield of **13** was superior to that of **14**, and the ratio of **13/14** is similar to that observed for the corresponding 1,2-dioxetanes, formed from singlet molecular oxygen and **11**,[12] and for the epoxides[14] produced from sulfoxide[15] or sulfur dioxide.[16]



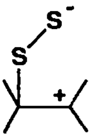
In the case of the reaction of singlet diatomic sulfur, we surmise that a primary thiosulfoxide intermediate **15**[17] may suffer desulfurization to the corresponding episulfide rather than cyclize to the sterically unstable 1,2-dithietane.[13] The results also rule out alternatives, such as the biradical (**16**) and the zwitterionic intermediate (**17**).



15



16



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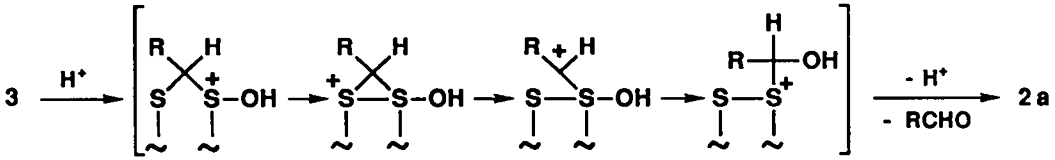
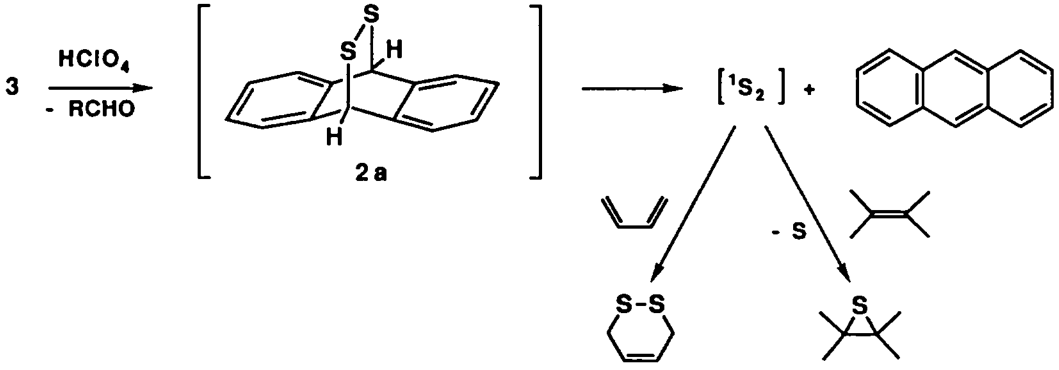
It has been known that dimethyl mercaptal S-oxide is readily converted in the presence of a catalytic amount of acid to the corresponding aldehyde and dimethyl disulfide.18) Possible reaction mechanism for formation of **2a** would be protonation on the oxygen of sulfoxide group, followed by migration of hydroxyl group and elimination of aldehyde to afford **2a**.



The present study demonstrates a new method of generating singlet diatomic sulfur and further suggests that anthracene endodisulfide intermediate **2a** is implicated, thereby accounting for the formation of cyclic disulfides and episulfides.



Experimental

All melting points are uncorrected. IR spectra were recorded with a Hitachi 260-50 infrared spectrometer, ^{1}H-NMR spectra recorded with a JEOL JNM-PMX60SI spectrometer, ^{13}C-NMR spectra recorded with a JEOL JNM-FX100 spectrometer (solvent, deuteriochloroform; tetramethylsilane as an internal standard). Mass spectra were obtained on a Hitachi RMU-6M mass spectrometer and exact mass data on a JEOL LMS-D300 mass spectrometer. Gel permeation chromatography (preparative HPLC) was performed on a series of JAIGEL 1H and 2H columns with a flow of chloroform on a LC-08 liquid chromatograph of Japan Analytical Industry Co. Ltd.

Reagent grade tetrahydrofuran and ethanol were distilled in the presence of appropriate drying reagents before use. Methylene chloride was washed with water, dried over calcium chloride and then distilled in the presence of calcium hydride. 2,3-Diphenyl-1,3-butadiene,[19] 1,1'-bicyclohexenyl,[20] biadamantylidene,[12] bis(bicyclo-[3.3.1]non-9-ylidene)[12] and di-t-butylbis(bicyclo[3.3.1]non-9-ylidene)s (**10** and **11**)[12] were prepared according to the literature method.

9,10-Dihydro-9,10-dimercaptoanthracene (4)

A mixture of 9,10-dibromo-9,10-dihydroanthracene[6] (17.6 mmol) and thiourea (35.2 mmol) in ethanol (35 ml) was stirred at 0°C over night. After concentration of the mixture under vacuo, the residue was stirred with potassium hydroxide (2.2 mol) in water (30 ml) at 0°C for 5h, and then acidified with sulfuric acid. The reaction mixture was extracted with methylene chloride, and the extract dried over anhydrous $MgSO_4$. After removal of solvent, the residue was separated by preparative HPLC. 9,10-Dihydro-9,10-dimercaptoanthracene (4)was obtained as white precipitates in 56% yield. 4: IR(CDCl3) 2530 cm^{-1}; ^1H-NMR($CDCl_3$) δ 7.10-8.45(m,8H), 5.28(d,2H,J=7.0Hz), 3.00(d,2H,J=7.0Hz) ppm; m/e 244(M^+).

9,10-Dihydro-9,10-(1,3-epidithio-2-methano-2-p-methoxyphenyl)propanoanthracene (5)

To a mixture of **4** (10 mmol) and p-anisaldehyde (20 mmol) in methylene chloride (35 ml) was added dropwise 1.5 mmol of boron trifluoride etherate at 0°C under nitrogen. After standing for over night, the mixture was extracted with methylene chloride. The extract was washed with water and dried over anhydrous $MgSO_4$. Separation of the products by preparative HPLC afforded **5** in 26% yield. 5: mp 224.5-225.5°C; ^1H-NMR($CDCl_3$) δ 7.13-7.60(m,8H), 7.11(d,2H,J=8.8Hz), 6.70(d,2H,J=8.8Hz), 5.20(s,2H), 4.42(s,1H), 3.70 (s,3H) ppm; ^{13}C-NMR($CDCl_3$) δ 159.7(s), 141.0(s), 137.0(s), 130.3(d), 129.4(s), 127.9(d), 127.3(d), 126.7 (d), 125.6(d), 113.7(d), 55.2(q), 51.9(d), 49.4(d) ppm; m/e 352(M^+); Anal. Calcd for $C_{22}H_{18}O_1S_2$: C, 72.89; H, 5.00. Found: C, 72.95; H, 5.22.

9,10-Dihydro-9,10-(1,3-epidithio-2-methano-2-*p*-methoxyphenyl-1-oxide)propanoanthracene (3).

To a methylene chloride (20 ml) solution of **5** (0.55 mmol) at 0°C under nitrogen was added dropwise 0.55 mmol of mCPBA in methylene chloride (5 ml). After 1 h with stirring, the reaction mixture was washed with aq. $NaHCO_3$ and dried over anhydrous Na_2SO_4. Separation of the products by preparative HPLC afforded **3** in 90% yield. 3: mp 175.0-177.0°C; IR($CDCl_3$) 1035 cm^{-1}; ^1H-NMR($CDCl_3$) δ 7.26-7.70(m,8H), 7.10(d,2H,J=8.8 Hz), 6.74(d,2H,J= 8.8Hz), 5.26(s,1H), 5.09(s,1H), 3.71(s,3H), 3.30(s,1H) ppm; ^{13}C-NMR($CDCl_3$) δ 160.5 (s), 144.2(s), 134.7(s), 131.7(s), 131.5(d), 129.3(d), 128.8(d), 128.5(s), 128.2(d), 127.7(d), 126.8(d), 125.4 (d), 124.7(s), 114.2(d), 71.9 (d), 68.0(d), 55.2(q), 48.4(d) ppm; m/e 378(M^+); Anal. Calcd for $C_{22}H_{18}O_2S_2$: C,69.81; H, 4.79. Found: C, 69.63; H, 4.79.

Reaction of 3 with Perchloric Acid[7]

To a methylene chloride (5 ml) solution of 3 (0.26 mmol) at 55°C under nitrogen was added dropwise perchloric acid (0.26 mmol) in tetrahydrofuran (1 ml). After 100 min with stirring, the reaction mixture was extracted with methylene chloride. The extract was washed with water and dried over anhydrous Na_2SO_4. Separation of the products by preparative HPLC afforded anthracene, p-anisaldehyde and elemental sulfur in 60%, 98% and 56% yields, respectively, accompanied with polymeric material.

Reaction of 3 with Perchloric Acid in the Presence of Trapping Reagents

A typical trapping experiment in the presence of two equimolar amount of dienes or olefins was carried out as the same manner mentioned above. 6 (25%): ^1H-NMR($CDCl_3$) δ 7.30-7.10(m,10H), 3.66(s,4H) ppm; m/e

270(M$^+$); Exact Mass Calcd for $C_{16}H_{14}S_2$: 270.0537. Found: 270.0550. **7** (48%): ^{1}H-NMR(CDCl$_3$) δ 3.72-3.88(m,2H), 1.38-2.32(m,16H) ppm; m/e 226(M$^+$); Exact Mass Calcd for $C_{12}H_{18}S_2$: 226.0850. Found: 226.0849. **9** (49%): mp 166.5-167.5°C; ^{1}H-NMR(CDCl$_3$) δ 1.40-2.27(m,28H) ppm; ^{13}C-NMR(CDCl$_3$) δ 70.3(s), 34.8(d), 33.7(t), 31.9(t), 21.2(t), 20.8(t) ppm; m/e 278(M$^+$); Anal. Calcd for $C_{18}H_{28}S_1$: C, 78.19; H, 10.20. Found: C, 78.31; H, 10.40.

Three stereoisomeric episulfides (**12**, **13** and **14**) afforded in the reaction of **3** with **10** and **11** in the presence of perchloric acid were identified by means of the chemical shifts of three-membered ring carbon in ^{13}C-NMR spectra in a similar manner as in the case of the corresponding epoxides.$^{14,15)}$ **12** (50%): mp 179.0-181.0°C; ^{1}H-NMR(CDCl$_3$) δ 1.48-2.10(m,26H), 0.86(s,18H) ppm; ^{13}C-NMR(CDCl$_3$) δ 70.2(s), 70.1(s), 41.9(d), 41.4(d), 35.6(d), 35.2(d), 34.8(t), 33.6(t), 33.5(t), 33.2(s), 32.7(t), 31.9(s), 27.2(q), 27.2(q), 21.9(t), 31.1(t) ppm; m/e 388(M$^+$); Anal. Calcd for $C_{26}H_{44}S_1$: C, 80.34; H, 11.41. Found: C, 80.46; H, 11.33. **13** (29%) and **14** (18%): ^{1}H-NMR(CDCl$_3$) δ 1.30-2.30(m,26H), 0.86(s,18H) ppm; ^{13}C-NMR(CDCl$_3$) δ 70.9(s), 70.1(s), 41.8(d), 41.5(d), 35.7(d), 35.2(d), 34.8(t), 34.8(t), 33.4(s), 33.1(t), 32.6(s), 32.3(t), 27.8(q), 27.2(q), 21.5(t), 20.7(t) ppm; m/e 388(M$^+$); Anal. Calcd for $C_{26}H_{44}S_1$: C, 80.34; H, 11.41. Found: C, 80.46; H, 11.54. The isomeric mixtures (**13** and **14**) were not separated but showed a 62:38 (for **13**:**14**) ratio.

Acknowledgment

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