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Generation of Singlet Diatomic Sulfur from 9,10-Epidithio-9,10-dihydroanthracene

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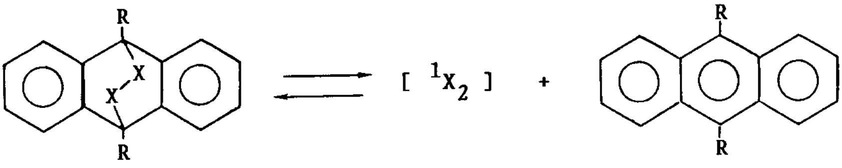
Summary: The novel 9,10-epidithio-9,10-dihydroanthracene (2a) was formed as an intermediate in the reaction of 9,10-dihydro-9,10-(1,3-epidithio-2-methano-2-p-methoxyphenyl-1-oxide)propanoanthracene (3) with perchloric acid. Singlet diatomic sulfur was generated from endodisulfide 2a and trapped with conjugated dienes.

The explosive development of research on singlet molecular oxygen1) has reflected the exploration of the new chemistry of an analogous sulfur species, singlet diatomic sulfur.2,3) Although singlet diatomic sulfur has been known to exist in molten sulfur and vaporized sulfur,2) relatively few studies on its chemistry have been reported because of no convenient generation method under mild conditions in liquid phase.3a,b) Anthracene endoperoxide 1 obtained from the reaction of singlet molecular oxygen and anthracene regenerates reversibly singlet molecular oxygen efficiently.4) This result is suggestive for analogous sulfur compound, anthracene endodisulfide 2, to be a good precursor of singlet diatomic sulfur.

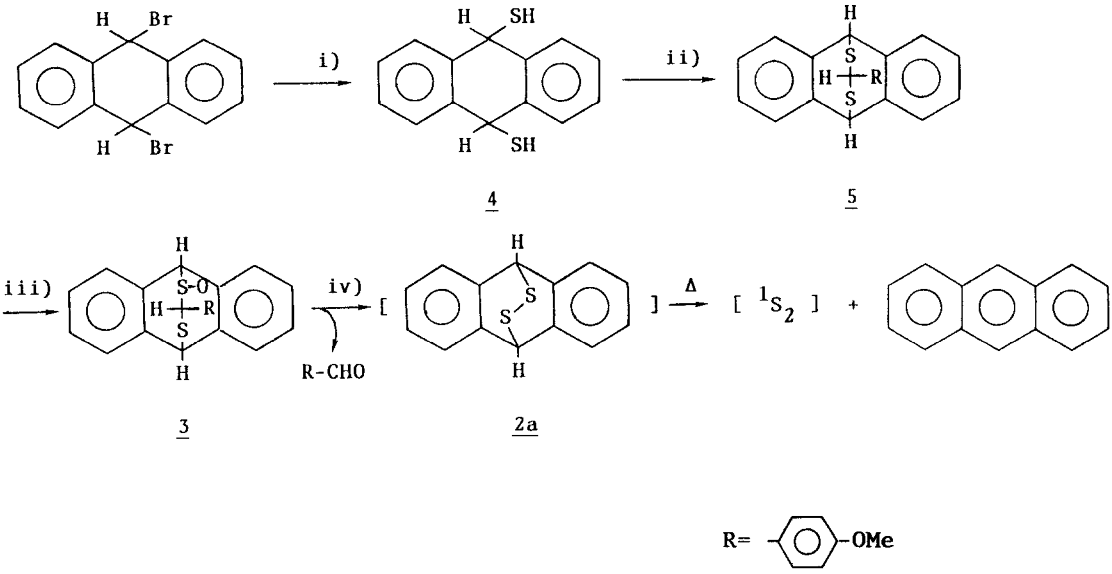


1: X=O

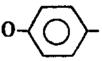
2: X=S

We decide to take advantage of formation of 9,10-epidithio-9,10-dihydroanthracene (2a; R=H) as an intermediate in the reaction of 9,10-dihydro-9,10-(1,3-epidithio-2-methano-2-p-methoxyphenyl-1-oxide)-propanoanthracene (3) with perchloric acid. Singlet diatomic sulfur can be trapped with conjugated dienes.3b)

Treatment of 9,10-dibromo-9,10-dihydroanthracene5) with thiourea in ethanol followed by hydrolysis afforded 9,10-dihydro-9,10-dimercaptoanthracene (4).6) The dithiol 4 was transformed into the p-anisaldehyde adduct 57) in



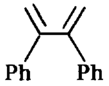
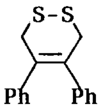
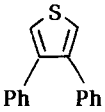
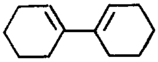
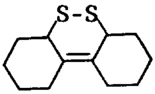
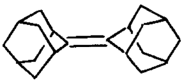
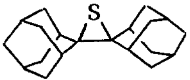
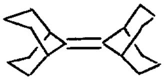
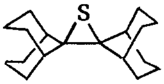
i) 1) S=C(NH_2)$_2$/EtOH/0°C 2) KOH 3) H_2SO_4

ii) MeO-**-CHO/BF_3·Et_2O/CH_2Cl_2/0°C iii) m-CPBA/CH_2Cl_2/0°C**

iv) $HClO_4$/CH_2Cl_2/55°C

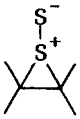
methylene chloride containing boron trifluoride etherate, and then oxidized to the sulfoxide 3[8)] with m-chloroperbenzoic acid (m-CPBA).[9)] Unfortunately on treatment of 3 with perchloric acid,[9)] anthracene endodisulfide 2a was not isolated after separation of the reaction mixture by preparative HPLC. Instead anthracene, p-anisaldehyde and elemental sulfur were obtained in 60 %, 98 % and 56 % yields, respectively, accompanied with polymeric materials. 3 was slowly consumed at 0 C and also when boron trifluoride etherate was used as acid. The reaction did not occur in the absence of acid. Since 2a might be formed as an intermediate, the reaction was carried out in the presence of 2,3-diphenyl-1,3-butadiene and 1,1'-bicyclohexenyl. The Diels-Alder type adducts,[3b)] i.e., 1,2-dithiins ((6)[3,10)] and (7)[11)]) were obtained in addition to anthracene , p-anisaldehyde and small amounts of elemental sulfur (Entries 1 and 2). The dithiins 6 and 7 are not so stable under the reaction conditions; 6 decomposes to 3,4-diphenylthiophene[12)] by elimination of hydrogen sulfide under the reaction conditions. These sulfurization reactions did not take place at all in the presence of elemental sulfur and perchloric acid. These results are similar to the case of addition reaction of singlet oxygen to diene.[13)] Based on the above results the formation of singlet diatomic sulfur in our systems might be evident.

Table. Reaction of Singlet Diatomic Sulfur with Olefins.

Entry	Olefin	Products and Yields(%)					
1		 6	25[a]		40[a]	Anthracene 47[b]	p-Anisaldehyde 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]
5		No adduct.				" 54[b]	" 75[b]

a) Yields were determined based on the anthracene obtained.

b) Yields were determined based on the sulfoxide 5 used.



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The addition reaction of sulfur occurred with electron rich olefins. Biadamantylidene and bis(bicyclo-[3.3.1]non-9-ylidene) formed the corresponding episulfides, 8[14] and 9,[15] respectively, (Entries 3 and 4), instead of 1,2-dithietane[18]. The formation of the episulfides can be understood if singlet diatomic sulfur reacts with olefin to form thiosulfoxide intermediate 10 followed by desulfurization.[16] Norbornylene failed to react with singlet diatomic sulfur[3b] (Entry 5).

For further studies on singlet diatomic sulfur chemistry substituted anthracene endodisulfide systems are currently being pursued in our laboratory.

References and Notes

1) a) "Singlet Oxygen"; Wasserman, H. H.; Murray, R. W., Eds.; Academic Press: New York, 1979.; b) "Singlet O_2"; Frimer, A. A., Ed.; CRC Press: Florida, 1985.; c) Ando, W.; Akasaka, T.; Takata, T., J. Syn. Org. Chem., Japan., 1986, 44, 974 and references cited therein.
2) a) Meyer, B.; Oommen, T. V.; Jensen, D., J. Phys. Chem., 1971, 75, 912.; b) Meyer, B., Chem. Rev., 1976, 76, 367 and references cited therein.
3) a) Steliou, K.; Gareau, Y.; Harpp, D. N., J. Am. Chem. Soc., 1984, 106, 799.; b) Steliou, K.; Salama, P.; Brodeur, D.; Gareau, Y., ibid., 1987, 109, 926.; c) Strausz, O. P.; Donovan, R. J.; de Sorgo, M., Ber. Bunsenges. Phys. Chem., 1968, 72, 253.
4) a) Wasserman, H. H.; Scheffer, J. R.; Cooper, J. L., J. Am. Chem. Soc., 1972, 94, 4991.; b) Corey, E. J.; Mehrotra, M. M.; Khan, A. U., ibid., 1986, 108, 2472.
5) Barnett, E. D. B.; Cook, J. W., J. Chem. Soc., 1924, 125.
6) 3: IR($CDCl_3$) 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).
7) 4: ^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).
8) 5: 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=8.8Hz), 6.74(d,2H,J=8.8Hz), 5.26(s,1H), 5.09(s,1H), 3.71(s,3H), 3.30(s,1H). Anal Calcd for $C_{22}H_{18}O_2S_2$: C,69.81; H,4.79. Found C,69.63; H,4.79.
9) a) Kishi, Y.; Fukuyama, T.; Nakatsuka, S., J. Am. Chem. Soc., 1973, 95, 6490, 6492.; b) Kishi, Y.; Nakatsuka, S.; Fukuyama, T.; Havel, M., ibid., 1973, 95, 6493.
10) 6: ^1H-NMR($CDCl_3$) δ 7.30-7.10(m,10H), 3.66(s,4H). Exact Mass Calcd for $C_{16}H_{14}S_2$: 270.0537. Found: 270.0550.
11) 7: ^1H-NMR($CDCl_3$) δ 3.72-3.88(m,2H), 1.38-2,32(m,16). Exact Mass Calcd for $C_{12}H_{18}S_2$: 226.0850. Found: 226.0849.
12) Grunwell, J. R.; Foerst, D. L.; Sanders, M. J., J. Org. Chem., 1977, 42, 1142.
13) So far no trace of [2+4]-type adducts of 9,10-dimethylanthracene and 9,10-diphenylanthracene with singlet diatomic sulfur, which have the bridged disulfide structure, was obtained.
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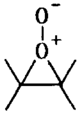
15) 9: mp 166.5-167.5 °C; ^1H-NMR($CDCl_3$) δ 1.40-2.27(m,28H). Anal Calcd for $C_{18}H_{28}S_1$: C,78.19; H,10.20. Found C,78.31; H,10.40.
16) Thiosulfoxide intermediate 10 may be considered as the sulfur analogue of a perepoxide intermediate 11 initially formed in the reaction of singlet molecular oxygen with biadamantylidene.17) For the intermediacy of a thiosulfoxide intermediate, see; Harpp, D. N., In "Perspectives in the Organic Chemistry of Sulfur"; Zwanenburg, B.; Klunder, A. J. H., Eds.; Elsevier Science Publishers B. V.: Amsterdam, 1987. p1.



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17) Schaap, A. P.; Recher, S. G.; Faler, G. R.; Villasenor, S. R., J. Am. Chem. Soc., 1983, 105, 1691.
18) Recently the first stable 1,2-dithietane was isolated.; Nicolaou, K. C.; Hwang, C. -K.; Duggan, M. E.; Carroll, P. J., J. Am. Chem. Soc., 1987, 109, 3801.

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