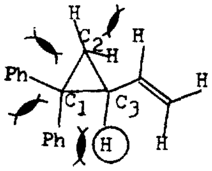
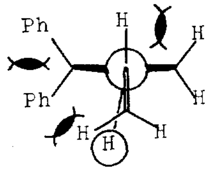
an orientation does not only provide for a closest approach between the allylic hydrogen and the oxygen atom which is not involved in C–O bonding, but also for a maximum overlap of the *p*–orbitals of the developing new $\pi_{c=c}$ bond.

With regard to VCP–DPh, the conformation of 'axially positioned' allylic hydrogen atom is hindered by the two phenyl groups attached to C_1 atom of cyclopropane ring and the π–electron density of the vinyl group is not enough to produce photoene–product because of the absence of electron–donating groups attached to the vinyl group.





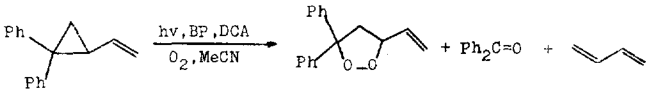
Newman projection of VCP-DPh at C_3 atom.

In most cases, 1,2–cycloaddition of singlet oxygen to olefins requires the presence of electron–donating groups in the alkene, such as $-NR_2$, $-OR$, and $-SR$. photooxygenation of alkyl–substituted olefins generally results in the formation of allylic hydroperoxides. However, if the ene reaction is precluded by the substitution pattern or for steric reasons, 1,2–dioxetanes or their cleavage products may be formed.

The enhanced reactivity of π–electron–rich olefins in 1,2–cycloaddition with singlet oxygen is in accord with the formulation of this species as an electrophilic reagent–a conclusion in harmony with its electronic structure. Bond formation thus requires transfer of electron density from the highest occupied molecular orbital (HOMO) of the olefin to the lowest unoccupied molecular orbital (LUMO) of singlet oxygen.

In the case of VCP–DPh, if the vinyl group is conjugated with the two phenyl groups *via* π–character of the cyclopropane ring, the vinyl group is activated and undergoes 1,2–cycloaddition with singlet oxygen to yield 1,2–dioxetane. However, two phenyl groups attached to cyclopropane ring are not conjugated with the vinyl group and cyclopropane ring does not transmit the conjugation. Therefore, the vinyl group of VCP–DPh is not π–electron–rich and does not undergo 1,2–cycloaddition with singlet oxygen to produce 1,2–dioxetanes.

Cosensitized photooxygenation of VCP–DPh ($1\times10^{-2}\,M$) in oxygen–saturated acetonitrile solution with bipheny ($1\times10^{-2}\,M$) and 9,10–dicyanoanthracene ($1\times10^{-4}\,M$) yielded 3,3–diphenyl–5–vinyl–1,2–dioxolane (64.8 % yield), benzophenone (35.2 % yield), and 1,3–butadiene.[7]



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(7) The reaction was carried out at 10°C under oxygen with a Hanovia 450 W medium–pressure mercury arc lamp by using a $CuSO_4$–filter solution. 1,3–Butadiene was detected in brominated form, 1,2,3,4–tetrabromobutane.

Novel Dechlorination of Arylsulfenyl Chlorides with Superoxide Anion ($O_2^{\cdot-}$)

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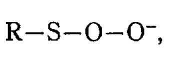
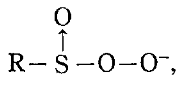
The discovery of superoxide dismutase (SOD) by Fridovich and McCord in 1969[1] has considerably stimulated the investigation of superoxide anion radical ($O_2^{\cdot-}$), not only in biochemistry but also in organic chemistry recently. Although commercially available potassium superoxide (KO_2), sodium superoxide (NaO_2), and ammonium superoxide (NH_4O_2), as sources of superoxide had been prepared, both its instability in protic solvents and its limited solubility in organic solvents such as dimethylsulfoxide (DMSO) and acetonitrile had prevented studies of the chemistry of superoxide ion. However, the observation of Valentine and Curtis in which KO_2 can be appreciably dissolved in aprotic solvents by complexation with crown ethers[2] has quickly promoted the use of this reagent for many reactions with simple organic substrates. Numerous reports dealing with reactions of various organic substrates with "naked" superoxide anion have appeared within only past five years. However, only a few sporadic works on the reaction of organic sulfur compounds with $O_2^{\cdot-}$ appeared until oxidations of organic sulfur compounds with $O_2^{\cdot-}$ in the presence of 18–crown–6–ether were initiated.[3–6]

The substrates of organic sulfur compounds are either those which have sulfur-sulfur linkage such as disulfide, thiolsulfinic-S-ester, thiolsulfonic-S-ester, or thiolate and sulfinate, all of which are expected to give peroxy-sulfur compounds such as peroxy-sulfenate (**1**), -sufinate (**2**), and -sulfonate (**3**) as initial initermediates in the reactions with $O_2^{\cdot -}$.



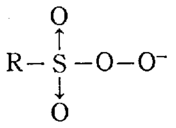
$R-S-O-O^-$,

1



$R-\overset{\overset{O}{\uparrow}}{S}-O-O^-$,

2



$R-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-O-O^-$

3

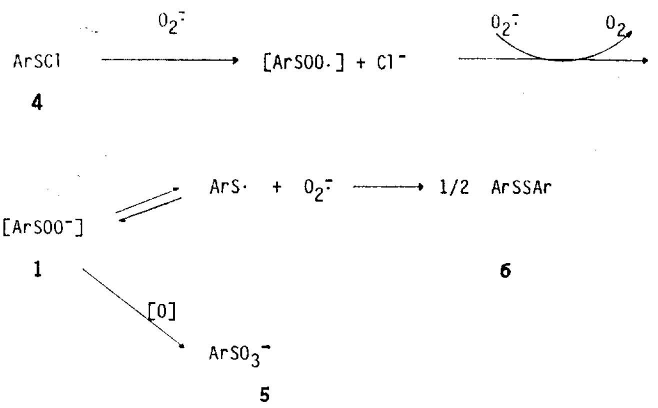
Earlier, Berger[7] postulated the first intermediary peroxy-sulfenate (**1**) and peroxy-sulfinate (**2**) in the autoxidation of thiols to the sulfinic and sulfonic acids in strong alkaline media without any evidence for the formation of peroxy-sulfur intermediates. Though the two reactions are presumed to involve common intermediates of peroxysulfur species, these peroxy-sulfur intermediates which may have potential oxidizing abilities have neither been isolated nor detected.

In our previous communication[8] on the epoxidations of olefins with a peroxy-sulfur intermediate generated from superoxide anion ($O_2^{\cdot -}$) and nitrobenzenesulfonyl chlorides, the formation of the peroxy-sulfonate intermediate was postulated to be 3, which is stable enough at low temperature. During the study of the peroxy-sulfenate intermediate, we have found that arylsulfenyl chlorides reacted with $O_2^{\cdot -}$ in tetrahydrofuran or acetonitrile at low temperature to give the corresponding diaryldisulfides or arylsulfonates depend upon the substrates used. All the reactions were carried out without using crown ether.[11] The products were identified by the comparison of their IR, ^1H NMR spectra, and mp. with those of the authentic samples. The results are summarized in Table 1.

In a typical experiment, KO_2 (74 mg, 1.0 mmol) in dry THF (1.0 m*l*) was crushed with a glass rod. 2,4-Dinitrobenzenesulfenyl chloride (117 mg, 0.5 mmol) was dissolved in dry THF (2.0 m*l*). A solution of sulfenyl chloride was added into a heterogeneous solution of KO_2, and then stirred vigorously at *ca.* 0°C under argon atmosphere. After 1.0 h, the reaction mixture was centrifused for three times to separate the clean solution, which was concentrated to recover the starting material. Solid part was washed with H_20 and ethyl ether three times respectively and dried in vacuo to give di-*p*-nitrobenzene disulfide (99.5 mg, 85 %, mp, 278-280°C, decomp., ref.[9] mp. 280°C, dec.).

2,4-Dinitrobenezenesulfenyl chloride, which has two strong electron withdrawing nitro groups, reacted with $O_2^{\cdot -}$ to form the corresponding disulfide (85 %) as the main product together with trace amount of the corresponding sulfonate. While, less electron withdrawing benzenesulfenyl chloride yielded the benzenesulfonate potassium salt (91 %) as the main products.

The formation of peroxy-sulfenate (**1**) is indicated by the epoxidation of chalcone to the epoxide (10 %) when the former is used as a trapping agent for the activated oxygen of **1** which is expected to have an oxidizing ability.[12]



Scheme 1

TABLE 1: Reaction of Arylsulfenyl Chlorides with KO_2

$$\underset{\mathbf{4}}{ArSCl} \xrightarrow[0°C]{O_2^{\cdot -}} \underset{\mathbf{5}}{ArSO_3^-} + \underset{\mathbf{6}}{ArSSAr}$$

Run	**4**, Ar	Solvent	KO_2/**4**[b]	Reactn. Time(h)	Yield(%)[a] **5**	**6**
1	C_6H_5[9a]	THF	2	6.0	91	trace
2	C_6H_5[9a]	THF	1.3	1.0	90	-[c]
3	p-Me-C_6H_4[9b]	THF	2	6.0	85	10
4	p-Br-C_6H_4[9c]	THF	2	6.5	71	21
5	β-Naphthyl[9c]	THF	2	5.5	50	45
6	*o*-NO_2-C_6H_4[d]	THF	2	1.5	29	62
7	*o,p-di*-NO_2-C_6H_3[d]	THF	2	1.0	trace	85
8	*o,p-di*-NO_2-C_6H_3[d]	CH_3CN	2	1.5	-[c]	84

[a] isolated yields, [b] molar ratio; KO_2: substrate, [c] not checked [d] purchased from Aldrich Chemical Co.

The reactions appear to be initiated *via* a nucleophilic attack of $O_2^{\cdot -}$ on the sulfenyl sulfur atom to form a peroxy-sulfenate radical, which may be readily converted to **1** by one electron transfer from $O_2^{\cdot -}$. The intermediate **1** may be further oxidized to **5**. In the case of dinitrobenzene peroxy-sulfenate, the thiyl radical formed by the cleavage of sulfur-oxygen bonds of **1** are stabilized by the two nitro groups and readily couple to **6**.

There have been a few reductive synthesis of disulfides from aryl sulfenyl chlorides using carbonyl complexes of metals[13] and potassium iodide[14] in protic solvents. The methods for the preparation of arylsulfonic or arylsulfinic acids by the oxidations of thiols[14-19] or sulfenyl_[20] and sulfonyl chlorides[21] need strong oxidation conditions such as boiling nitric acid[15], potassium permanganate[16], Caro's acid[17], alkaline autoxidation[18] or basic hydrogen peroxide[19]. Our new reactions, however, can be carried out in aprotic solvents such as tetrahydrofuran and acetonitrile at lower temperature than 0°C.

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(11) Most of known reactions with superoxide ion require to use crown ether[2] to promote the solubility of KO_2. However, surprisingly, our reactions underwent smoothly without using crown ether within 6 h at 0 °C.

(12) Since an intermediate, **1** is unstable, the epoxidation was carried out at –20 °C in the reaction system of o, *p*–dinitrobenzenesulfenyl chloride, potassium superoxide and chalcone.

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