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NEW EPOXIDATION OF OLEFINS WITH SUPEROXIDE ANION IN THE PRESENCE OF ORGANIC SULFUR COMPOUNDS(1)

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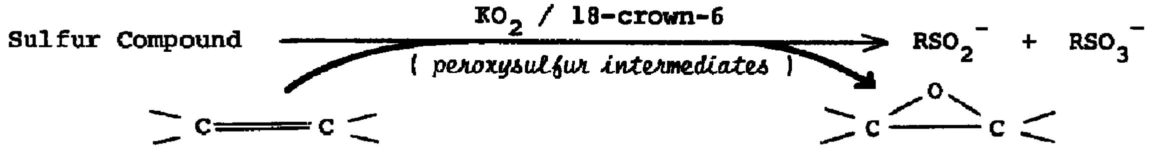
Summary: Epoxidation of olefins such as stilbene and chalcone with superoxide anion in the presence of several sulfur compounds was investigated.

Earlier peroxysulfenate and peroxysulfinate was postulated by Berger to be the key intermediates in alkaline air-oxidation of thiol to sulfinate, part of which is further oxidized to sulfonate by these peroxysulur intermediates.(2) Recently we have revealed that several organic sulfur compounds bearing mainly sulfur-sulfur linkages can readily be oxidized with superoxide anion, $O_2^{\overline{\cdot}}$, to afford both sulfinate and sulfonate, presumably involving the analogous peroxysulfur intermediates as in the alkaline air-oxidation of thiol and disulfide.(3a,b) However, none of these peroxysulfur intermediates has been detected or isolated, despite their potential oxidizing abilities. Among several attempts to bring forth the oxidizing abilities of these unstable peroxysulfur intermediates, we have found that phosphines and sulfoxides, both of which are inert in the reaction of disulfidic compounds with $O_2^{\overline{\cdot}}$ and in the alkaline autoxidation, are oxidized to the corresponding phosphine oxides and sulfones in the reactions of these sulfur compounds with $O_2^{\overline{\cdot}}$ and in the alkaline autoxidations of thiols and disulfides.(3c)



We now wish to report another example of the oxidation with a system consisting with organosulfur compounds and $O_2^{\overline{\cdot}}$, namely epoxidation of electrophilic olefins. When a few olefins such as stilbene and chalcone were placed in the reaction systems of the sulfur compounds with $O_2^{\overline{\cdot}}$, they were found to be oxidized effectively to the corresponding epoxides.(4)

In a typical run, a solution of TsCl(2.7 mmole) and 4-bromochalcone

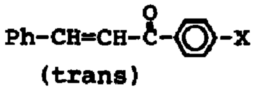
(1.3 mmole) in dry CH_3CN(10 ml) was added with syringe into a heterogeneous solution of KO_2(8.0 mmole, finely powdered) and dry 18-crown-6-ether(0.27 mmole) in the same solvent(10 ml), and the resulting heterogeneous mixture was stirred for 12.5h at ca. 20° under dry argon atmosphere. The mixture was stirred for a few hours additionally after the disappearance of TsCl was confirmed by HPLC. Yield of the epoxide estimated by HPLC was ca. 85% based on the added olefin. The reaction mixture was filtrated and the residual solid was washed with CH_2Cl_2. Conbined organic layer was concentrated and the residue was subjected to the column chromatography(eluent: benzene, on silica gel). Yield of the pure epoxide isolated was 66%. The epoxide was identified by the chemical shifts of the methine protons of 3-membered ring at high field in NMR spectrum of it(δ , $CDCl_3$, TMS, 4.03 & 4.25, J= 1.6 Hz).[5)]

Results obtained are listed in Table I and II, though the yields are not optimized.

Table I Epoxidation of Olefins(at 20°)[a]

No.	Substrate	Olefin	Solvent	Time[h]	Yield[%][b] Epoxide	Yield[%][b] Recovery
1	TsCl	1, X= Br	CH_3CN	15.5	85(66)[c]	trace(5)[c]
2	"	1, X= H	"	15	85	8
3	"	1, X= OMe	"	3	60(45)[d]	trace
4	p-TolSOCl	1, X= H	benzene	22.5	60	35
5	4	1, X= H	CH_3CN	20.5	26	58
6	PhCOCl	1, X= H	"	9	41	49
7	TsCl	2	benzene	24	40(39)[c]	55
8	PhCOCl	2[e]	"	10	30(20)[c]	20(15)[c]
9	TsCl	3	CH_3CN	10	-(30)[d]	-(70)[d]

a) Molar ratio; sub:olefin:KO_2:crown ether= 10 : 5 : 30 : 1. b) Yield by HPLC. c) Isolated yield. d) Yield by NMR. e) Amount of olefin= 2/5.

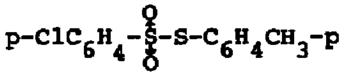


1 X= H, Br, OMe

Ph-CH=CH-Ph
(trans)

2

3



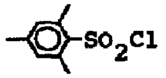
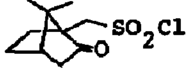
$p\text{-}ClC_6H_4\text{-}\overset{O}{\underset{O}{S}}\text{-}S\text{-}C_6H_4CH_3\text{-}p$

4

Although in the reactions of sulfonyl chloride, sulfinyl chloride and thiolsulfonate with $O_2^{\overline{\cdot}}$ not only chalcone and its derivatives but also stilbene and acenaphthylene were oxidized to the epoxides in relatively high yields, the epoxidation proceeded very little when disulfide, thiolsulfinate and sodium thiolate were used as substrates. Presumably because thiyl radical and thiolate anion which can be formed incipiently in the reaction and also the starting material remained, would react faster with oxidizing species formed *in situ* than olefins.6) Cinnamonitrile and cyclohexene, however, were not oxidized under the conditions. Meanwhile, we also confirmed the epoxidations of these olefins(1 & 2) with acyl chloride and $O_2^{\overline{\cdot}}$(No. 6 & 8)7), though the yields were somewhat lower than those with the sulfonyl and sulfinyl chlorides with $O_2^{\overline{\cdot}}$.

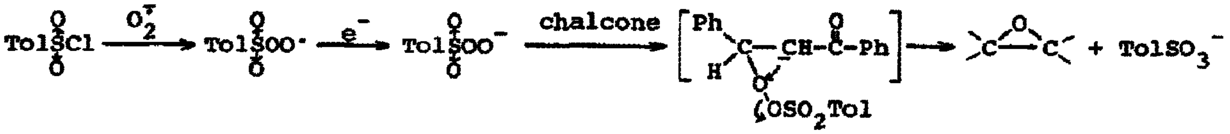
Inspection of the data in Table II, reveals that such a polar solvent as CH_3CN is better than benzene in the epoxidation of chalcone, though it was not a good solvent in the epoxidation of stilbene which gave other polar products including benzaldehyde, formed by the cleavage of C-C bond. Without crown ether, the yield of the epoxide was rather little in benzene but in CH_3CN the yield of the epoxide remained nearly the same as shown in Table II(No. 8 & 9). A few other sulfonyl chlorides were tested and even the sterically hidered mesithylenesulfonyl and d-camphorsulfonyl chlorides were also found to be effective in the epoxidation of olefins, though both yields of the epoxides and the rates were lower than those with TsCl.

Table II Effects of Solvent, Crown Ether and Substrate(at 20°)^{a}

No.	Substrate	Olefin	Crown ether	Solvent	Time	Yield[%]^{b} Epoxide	Recovery
1	TsCl	1, X= H	(1)	CH_3CN	15h	85	8
2	"	"	"	CH_2Cl_2	20^{f}	65	25
3	"	"	"	benzene	17	39	52
4	"	2	"	benzene	24	40(39)^{c}	55
5	"	2^{g}	"	CH_3CN	3	complex mixture	
6	PhCOCl	2	"	benzene	10	30(20)^{c}	20(15)^{c}
7	"	2	"	CH_3CN	1	10	20
8	TsCl	1, X= H	(0)	CH_3CN	22	75	10
9	"	I, X= OMe	(0)	benzene	13	trace	95
10		"	(1)	CH_3CN	11^{f}	-(75)^{d}	-(25)^{d}
11	Cl_3CSO_2Cl	1, X= H	"	CH_3CN	15.5^{f}	40	55
12		"	"	CH_3CN	104	50(41)^{c,e}	35

a) Molar ratio; sub:olefin:KO_2:crown ether= 10 : 5 : 30 : 1. b) Yield by HPLC. c) Isolated yield. d) Yield by NMR. e) Optically active d-camphor-10-sulfonylchloride: $[\alpha]_D$ + 20.9°.8) But chalcone oxide obtained did not have any optical activity. f) Reaction at 18°. g) Amount of olefin= 2/5.

Since the reaction of the sulfonyl chloride with $O_2^{\overline{\cdot}}$ is considerably faster than that of chalcone with $O_2^{\overline{\cdot}}$9), the reaction is considered to proceed via the initial nucleophilic substitution of TsCl with $O_2^{\overline{\cdot}}$ and one electron transfer12) to afford peroxy intermediate which then oxidizes olefin to the epoxide, as shown in the following equation. The epoxidation of chalcone, a typical electrophilic olefin, is well known to be an oxidation involving an initial nucleophilic attack of oxidant such as hydroperoxy anion10), and stilbene is also known to undergo the Michael addition by the attack of strong nucleophile.11)



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1) Support of this work by Toray Science and Technology Prize and Grants for 1980 is gratefully acknowledged.
2) Berger, H., Rec. Trav. Chim., 82, 773(1963).
3)a) Takata, T., Kim, Y.H., and Oae, S., Tetrahedron Letters, 821(1979). b) Oae, S., Takata, T., and Kim, Y.H., Tetrahedron, in press. c) Oae, S., Takata, T., and Kim, Y.H., unpublished result.
4) Both stilbene and chalcone have not been reported to be oxidized to the epoxides only with $O_2^{\overline{\cdot}}$, but chalcone was oxidized with $O_2^{\overline{\cdot}}$ only to the carboxyli acid, as reported previously: Rohsenthal, I., and Frimer, A.A., Tetrahedron Letters, 2805(1976).
5) Turner, A.B., Lutz, R.E., McFarlane, N.S., and Boykin, Jr., D.W., J. Org. Chem., 36, 1107(1971). For other epoxide; chalcone: Mitsui, S., Senda, Y., Shimodaira, T., and Ichikawa, H., Bull. Chem. Soc. Japan, 38, 1897(1965). stilbene oxide: The Aldlich Library of NMR Spectra, vol. 4, pp 103, 1974. acenaphthylene oxide: Hunter, D.H., and Shearing, D.J., J. Am. Chem. Soc., 95, 8333(1973).
6) However, phosphines and sulfoxides can compete with a few sulfur species formed *in situ* in the reactions with peroxysulfur species, thus being oxidized to their oxides in the system.
7) Epoxidation of stilbene in the reaction of benzoyl chloride with $O_2^{\overline{\cdot}}$ has been observed: Nagano, T., Aragane, K., and Hirobe, M., 6th Symposium on Progress of Reaction and Synthesis, Abstract pp 114, 1979.
8) Eliel, E.L., and Frazee, W.J., J. Org. Chem., 44, 3598(1979).
9) Chalcone was found to be consumed in a shorter period in the absence of substrate than in the presence of substrate.4)
10) Patai, S., and Rappoport, Z.," The Chemistry of Alkenes", ed. by Patai, S, Chapter 8, pp 469, Wiley, 1964.
11)a) Oae, S.," Chemistry of Organic Sulfur Compounds(Japanease)", Chapter 6, Kagakudojin, Kyoto, 1969. b) Baker, R., and Spielet, M.J., Chem. Commun., 757(1966).
12) One electron transfer from $O_2^{\overline{\cdot}}$ is well known as a nature of $O_2^{\overline{\cdot}}$. See review; L-Luff, E., Chem. Soc. Rev., 6, 165(1977).

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