MONOOXYGEN TRANSFER POTENTIAL OF THE TRANSANNULAR OZONIDE OF

9-TERT-BUTYL-10-METHYLANTHRACENE

Yoshikatsu Ito, Akira Matsuura, and Teruo Matsuura*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

Summary: The efficiency of oxygen transfer from the transannular ozonide 1 to

several organic substrates was investigated. The efficiency was

estimated to be as high as 90% in the case of Ph_3P as the substrate.

A number of examples for oxygen transfer reactions between peroxides and organic

substrates have so far been reported.[1] Little study, however, was done concerning the

oxidative ability of the transannular ozonides of anthracenes.[2] For example, Murray studied

only briefly a decomposition of the unstable trioxide 1a in the presence of tetracyclone and

1,3-diphenylisobenzofuran.[2b] Now we have found for the first time that monooxygen transfer

ability of the transannular ozonide of 9-tert-butyl-10-methylanthracene 1, an unusually stable

1,2,3-trioxide recently communicated by us,[3] is high.

The decomposition under a nitrogen atmosphere of the trioxide 1 in the presence of

various substrates S (triphenylphosphine, diphenyl sulfide, norbornene, mesitylene, and trans-

and cis-stilbenes) gave 10-methyl-10-(tert-butyldioxy)-9-anthrone (2), 10-methyloxanthrone (3)

and the corresponding substrate oxidation products SO (Table, entries 1 - 6). Except the case

of Ph_3P, the yields of the oxidation products SO are low probably because of the competitive

decomposition of the trioxide 1 to the peroxide 2 and unknown products. The thermal

rearrangement of 1 into 2 at elevated temperatures was already reported.[3] The epoxidation of

cis- and trans-stilbene proceeded stereoselectively to produce trans-stilbene oxide from

either isomer. The same stereoselectivity was observed in the α-diketone- or α-acyloin-

sensitized photoepoxidation.[4]

The peroxide 2 was found to be stable in the presence of each substrate under the

reaction conditions shown in Table. Thus the observed values for the SO/3 ratio (0.6 - 0.9;

Table, entries 1 - 6) may be considered to indicate high efficiency for monooxygen transfer

from $\underset{\sim}{1}$ to S. Note, however, that the total yield of $\underset{\sim}{2}$ and $\underset{\sim}{3}$ is not good for entries 3 - 6.

In these cases the SO/$\underset{\sim}{3}$ ratio should be taken as a maximum oxygen transfer efficiency.

Since the trioxide $\underset{\sim}{1}$ is stable at room temperature,[3] its decomposition is greatly

promoted by the presence of Ph$_3$P, as seen from Table (entry 1). It appears that the main

mechanism for oxygen trasnfer from Ph$_3$P involves the direct reaction with $\underset{\sim}{1}$ to produce an

ionic intermediate such as $\underset{\sim}{4}$.[5] The X-ray structural analysis of $\underset{\sim}{1}$[3] revealed that the lengths

of two O-O bonds (a and b) are different: 1.428 Å and 1.361 Å, respectively. As a result,

the sequence $\underset{\sim}{1} \to \underset{\sim}{4} \to \underset{\sim}{3}$ involves an initial cleavage of the longer(weaker) O-O bond, i.e.,

bond a. On the other hand, as is already reported,[3] the thermal decomposition of $\underset{\sim}{1}$ into $\underset{\sim}{2}$ can

be most reasonably rationalized by an initial cleavage of the shorter(stronger) O-O bond in

a sequence $\underset{\sim}{1} \to \underset{\sim}{5} \to \underset{\sim}{2}$. We are yet unable to explain this difference.

It is confirmed by independent experiments that Ph$_2$S, when used as a solvent, almost

doubles the decomposition rate of $\underset{\sim}{1}$ as compared with that in CDCl$_3$, while trans-stilbene does

not affect the rate. Thus, the predominant mechanism for oxygen transfer to trans-stilbene

appears to involve the radical intermediate $\underset{\sim}{5}$, while that to Ph$_2$S both $\underset{\sim}{4}$ and $\underset{\sim}{5}$. As seen from

comparison of the SO/$\underset{\sim}{3}$ values listed in Table (entries 1, 2, 5 and 7 - 9), the effect of an
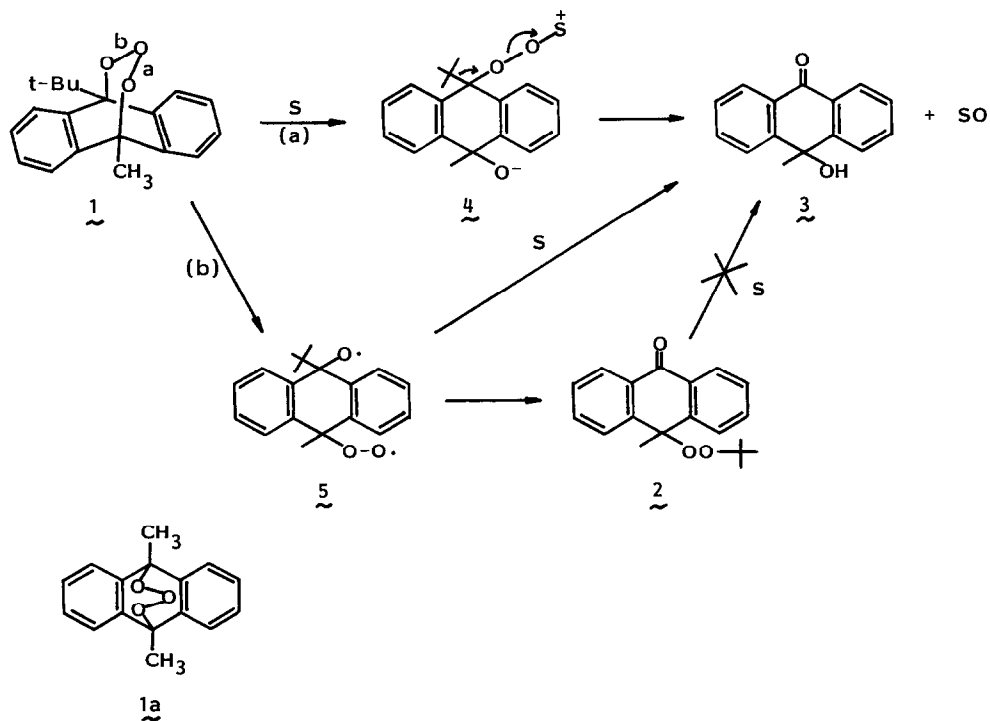
Table. Reaction of the transannular ozonide 1̰ with organic substrates S.[a]

entry	substrate S (M)	reaction conditions			conversion of 1̰, %	isolated yields of products, %[b]			SO/3̰
		solvent	temp, °C	time, h		2̰	3̰	SO	
1	Ph_3P (0.34)	CH_2Cl_2	room temperature	38	59	19	78	70[c]	0.90
2	Ph_2S (6.00)	Ph_2S	60	12	100	37	41	26[d]	0.63
3	norbornene (0.30)	$CDCl_3$	45	20	63	45	23	15[e]	0.65
4	mesitylene (0.72)	CH_2Cl_2	40	15	52	41	19	12[f]	0.63
5	trans-stilbene (0.25)	CH_2Cl_2	40	38	75	39	29	20[g]	0.69
6	cis-stilbene (0.44)	CH_2Cl_2	40	40	81	40	21	16[g]	0.76
7	Ph_3P[h] (0.34)	CH_2Cl_2	room temperature	40	69	13	70	58[c]	0.83
8	Ph_2S[h] (0.44)	CH_2Cl_2	40	44	82	35	17	7[d]	0.41
9	trans-stilbene[h] (0.22)	CH_2Cl_2	40	38	60	16	14	4[g]	0.29

[a]Under nitrogen, ∿5 x 10^{-2} M of 1̰ was allowed to react with the substrate. The products were separated by preparative TLC on silica gel. [b]Calculated on the basis of 1̰ consumed. [c]Triphenylphosphine oxide. [d]Diphenyl sulfoxide. [e]Exo-2,3-epoxy-norbornane. [f]2,4,6-Trimethylphenol. [g]Trans-stilbene oxide. [h]∿3 x 10^{-2} M of 2,6-di-tert-butyl-4-methylphenol is present as an additive.

radical inhibitor, 2,6-di-tert-butyl-4-methylphenol, on the oxygen transfer reactions increased in the order Ph_3P < Ph_2S < trans-stilbene. This trend supports the aforementioned oxygen transfer mechanism for Ph_3P, Ph_2S and trans-stilbene.

References and Notes

(1) H. Mimoun, Angew. Chem. Int. Ed. Engl. 21, 734 (1982).

(2) (a) P. S. Bailey, "Ozonation in Organic Chemistry", Academic Press, New York; Vol. 2, p. 86 (1982). (b) R. W. Murray in "Singlet Oxygen", H. H. Wasserman and R. W. Murray (Eds), Academic Press, New York; p. 106 (1979).

(3) Y. Ito, A. Matsuura, R. Otani, T. Matsuura, K. Fukuyama, and Y. Katsube, J. Am. Chem. Soc., 105, 5699 (1983).

(4) (a) N. Shimizu and P. D. Bartlett, J. Am. Chem. Soc., 98, 4193 (1976). (b) Y. Sawaki and Y. Ogata, ibid., 103, 2049 (1981).

(5) Since the endoperoxide, prepared from the reaction of 9-tert-butyl-10-methylanthracene with singlet oxygen, was found to be entirely inert toward Ph_3P at room temperature, its presence in the course of the reaction 1 → 3 is unlikely.