Tetrahedron Letters No. 15, pp 1317 - 1320.
©Pergamon Press Ltd. 1979. Printed in Great Britain.

0040-4039/79/0408-1317$02.00/0

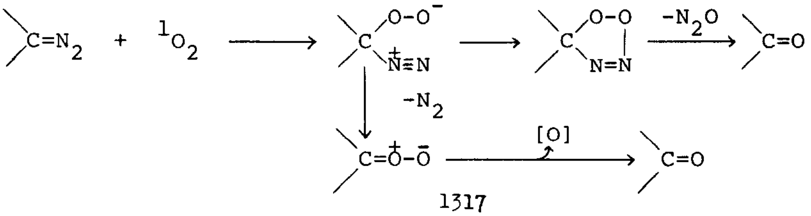
OXYGEN ATOM TRANSFER BY AN INTERMEDIATE IN THE PHOTOSENSITIZED OXYGENATION OF DIAZO COMPOUNDS

Wataru Ando*, Hajime Miyazaki and Shigeo Kohmoto
Department of Chemistry, The University of Tsukuba
Sakura-mura, Ibaraki 300-31, Japan

Summary: The photosensitized oxygenations of various diazo compounds in the presence of oxygen atom acceptors were carried out. An electrophilicity of the intermediate was investigated.

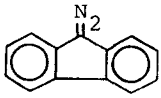
It has become fashionable to claim that the oxygen atom transfer or oxenoid mechanism is involved in many monooxygenase catalyzed reactions.1) Some chemical systems function apparently as oxenoid oxygen atom transfer agents, notably pyridine N-oxide,2) selenium oxide,3) the oxidant from ozonolysis of alkyne,4) and iodosobenzene.5) Murray et al. showed that an intermediate produced in the photosensitized oxygenation of diphenyldiazomethane was a most likely carbonyl oxide which can be trapped by aldehydes and naphthalene to give ozonides6) and naphthols7), respectively.

Recently, as a part of our studies on oxidation by singlet oxygen and oxygen atom transfer reaction,8) the oxenoid intermediate produced from the photosensitized oxygenation of α-carbonyl-stabilized sulfur or pyridinium ylids is capable of transferring oxygen atom to sulfides. We present here that the oxenoid intermediates produced in the photosensitized oxygenation of α-carbonyl-stabilized diazo compounds have different character from those in the photosensitized oxygenation of non-stabilized ones.



In a typical reaction, 0.2 mmol of benzoylphenyldiazomethane in benzene solution containing 30 mg of tetraphenylporphine(TPP) as sensitizer and 1 mmol o dimethyl sulfoxide was photolyzed using 300 W Halogen lamp. The reaction mixture was worked up by removing solvent and analyzed by GLC. The major products were benzil(86%) and dimethyl sulfone(45%). Using similar procedure the photosensitized oxygenation of benzoylphenyldiazomethane in the presence of diphenyl sulfide and phenyl(trimethylsilyl)ketone led to the formation of the sulfoxide and the trimethylsilyl benzoate, respectively, together with benzil. Similar results were also obtained when the reaction was carried out in carbon tetrachloride, diethyl ether and chloroform, and summarized in Table I.

Table I Photosensitized Oxygenation of Various Diazo Compounds in the Presence of Oxygen Atom Acceptors.*

RC(N_2)R' 0.2 mmol	Acceptor 1.0 mmol	Solvent 30 ml	RCOR'	Me_2SO_2	Ph_2SO	$Me_3SiOCOPh$
PhCOC(N_2)Ph	Me_2SO	C_6H_6	86%	45%		
		Et_2O	92	30		
		CCl_4	99	36		
		$CHCl_3$	82	29		
	Ph_2S	C_6H_6	98		24%	
		CCl_4	98		29	
		$CHCl_3$	72		26	
	$Me_3SiCOPh$	C_6H_6	83			20%
	Me_2SO	C_6H_6	78	41		
		$CHCl_3$	83	46		
	Ph_2S	C_6H_6	81		3	
		$CHCl_3$	78		14	
	$Me_3SiCOPh$	C_6H_6	79			33
PhC(N_2)Ph	Ph_2S	C_6H_6	81		1	
		$CHCl_3$	78		6	
	$Me_3SiCOPh$	C_6H_6	77			31

* The reaction was carried out under oxygen with TPP for 30 min., and the yields were determined by GLC based on the diazo compounds.

Interestingly, the yields of diphenyl sulfoxide in the photosensitized oxygenation of benzoylphenyldiazomethane find a large difference in those of diphenyldiazomethane and diazofluorenone.[9)] The photosensitized oxygenation of diphenyldiazomethane is known to form carbonyl oxide which is smoothly capable of transferring oxygen atom to phenyl(trimethylsilyl)ketone.[10)] The oxenoid species produced from diphenyldiazomethane and diazofluorenone may have different nature to its analogous oxenoid species produced from benzoylphenyldiazomethane. Control experiments indicated the sulfone and sulfoxide were not formed under the reaction conditions in the absence of either sensitizer or the diazo compound.

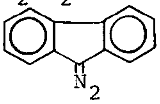
The relative rates of oxygen atom transfer in the diazoalkane and the sensitized oxygenation system toward diphenyl sulfide, dimethyl sulfoxide, and phenyl(trimethylsilyl)ketone were determined from the yield of the sulfoxide, the sulfone, and the benzoate.

$$\begin{array}{ccccccccccc} CH_2N_2 & + & Me_3SiCOPh & + & Me_2SO & \xrightarrow[\text{ether}]{\text{sens}/h\nu/O_2} & Me_3SiOCOPh & + & Me_2SO_2 & + & [CH_2O] \\ 0.2\ \text{mmol} & & 0.2\ \text{mmol} & & 0.2\ \text{mmol} & & 11\% & & 22\% & & \end{array}$$

$$\begin{array}{ccccccccccc} PhCOC(N_2)Ph & + & Me_3SiCOPh & + & Ph_2S & \xrightarrow[\text{ether}]{\text{sens}/h\nu/O_2} & Me_3SiOCOPh & + & Ph_2SO & + & PhCOCOPh \\ 0.2\ \text{mmol} & & 0.2\ \text{mmol} & & 0.2\ \text{mmol} & & 5\% & & 24\% & & 97\% \end{array}$$

The relative rates obtained from competitive experiments are summarized in Table II. The large differences in the reactivities of silylketone and diphenyl sulfide were observed in the oxygenation of diphenyldiazomethane, diazofluorenone and diazomethane.

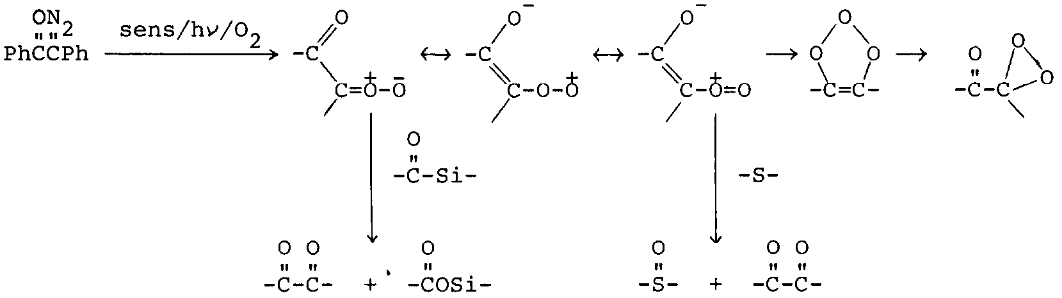
Table II. Relative Rates of Oxygen Atom Transfer by Acceptor in Various Diazo Compounds-Oxygen System.*

Diazo Compounds	Relative Rate		
	$Me_3SiCOPh$	Me_2SO	Ph_2S
$PhCOC(N_2)Ph$	(1)	6.6	4.8
CH_2N_2	(1)	2.0	0.01
Ph_2CN_2	(1)	0.2	0.01
	(1)	0.6	0.01

* Competitive experiment was carried out in benzene solution containing 0.2 mmol of diazo compound, each 2.0 mmol of two oxygen atom acceptors and 30 mg of TPP. The relative reactivities were calculated from the relative molar yields, after 30 min. irradiation.

On the other hand, the relatively higher reactivity of diphenyl sulfide and dimethyl sulfoxide was observed towards the oxenoid from benzoylphenyldiazomethane. These data suggest that the oxenoids from diphenyldiazomethane, diazofluorenone, and diazomethane possess less electrophilic character than that from benzoylphenyldiazomethane.

The present and earlier results obtained from carben-oxygen complex indicated that essentially all the oxygen atom transfer products are formed from calbonyl oxide intermediate. The following scheme shows the possible oxenoid structures for the oxygen atom transfer from benzoylphenyldiazomethane.



References

1) G. A. Hamilton in "Molecular Mechanisms of Oxygen Activation" (O. Hayaishi, Ed.), p-405, Academic Press, New York, 1974.
2) T. Tsuchiya, H. Arai, and H. Igeta, Tetrahedron Letts., 2213 (1970).
3) T. Tezuka, H. Suzuki, and H. Miyazaki, Tetrahedron Letts., 4885 (1978).
4) R. E. Keay and G. A. Hamilton, J. Am. Chem.Soc., 98, 6578 (1976); references cited therein.
5) F. Lichtenberger, W. Nastainczyk, and V. Ullrich, Biochem. Biophys. Res. Comm. 70, 939 (1976).
6) D. P. Higley and R. W. Murray, J. Am. Chem. Soc., 96, 3330 (1974).
7) S. K. Chaudhary, R. A. Hoyt, and R. W. Murray, Tetrahedron Letts., 4235 (1974)
8) W. Ando, S. Kohmoto, and K. Nishizawa, J.C.S.Chem.Comm., 894 (1978).
9) H. H. Wasserman and I. Saito, J. Am. Chem. Soc., 97, 905 (1975).
10) A. Sekiguchi, Y. Kabe, and W. Ando, J.C.S.Chem.Comm., in press.