Tetrahedron Letters,Vol.25,No.14,pp 1487-1490,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

ON THE REARRANGEMENT IN CARBONYL OXIDE INTERMEDIATES

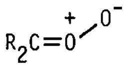
Yasuhiko Sawaki* and Katsuya Ishiguro

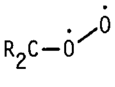
Department of Applied Chemsitry, Faculty of Engineering, Nagoya University,
Chikusa-ku, Nagoya 464, Japan

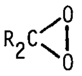
Sensitized photooxidation of alkylphenyldiazomethanes under oxygen afforded, in addition to alkyl phenyl ketones, alkyl benzoates, which are probably formed by a rearrangement via dioxirane diradical.

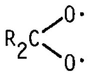
Much attention has been focused on oxygen atom transfer from carbonyl oxides as a model for monooxygenase enzymes.[1)] Carbonyl oxides are produced in the ozonolysis of olefins[2)] or the photooxidation of diazo compounds,[3)] and transfer oxygen atom to alkanes,[4)] olefins,[5)] sulfides,[6)] and aromatic rings.[7)] Characteristic reaction of carbonyl oxides is a nucleophilic O-transfer as exemplified in the oxidation of sulfoxides[8)] and electron-deficient olefins.[9)]

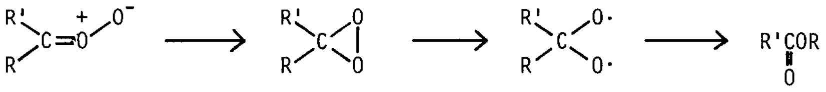
Structures and energies of carbonyl oxides (**1**) or its analogues (**2** and **3**) are also interested theoretically. Dioxirane **2** is calculated to be more stable than **1a** or **1b** by 30-40 kcal/mol[10)] and its structure has been identified at low temperature.[11)] Quite interesting is the rearrangement of carbonyl oxides to esters or acids (eq. 1), which is often written or assumed in the gas-phase ozonolysis of olefins[12)] and the reaction of carbenes with oxygen.[13)]


1a


1b


2


3


(1)

Ando et al.[14)] have reported such a rearrangement via the migration of trimethylsilyl group; but the silyl group seems not to be a diagnostic one because of well known oxygen affinity of silicon atom. Herein, we wish to report that carbonyl oxides rearrange in solution probably via dioxirane radical **3**.

Table 1. Photooxidation of Ethylphenyldiazomethane (4a)

Run no.	Conditions	Products (%)$^{b)}$			
	Sens/Solvent/Time	PhCOEt	$PhCO_2Et$	PhCH=CHMe	Others
1	TPP/PhH/30 min	90	6.9	0.5	PhOH (1%)
2	TPP/PhH/Me_2SO(1M)/5 min	96	2.6	0.5	PhOH (0.2%); Me_2SO_2 (43%)
3	None/PhH/ 6 h$^{c)}$	41	3.3	46 (3)$^{d)}$	PhOH (1%)
4	TPP/PhH-MeOH/30 min	54	0.8	0.5	$PhCO_2Me$ (41%)
5	RB/MeOH/15 min (0°C)	35	0.4	5	5 (30%); $PhCO_2Me$ (4%)

a) Irradiation of 0.01 M 4a and 0.1 mM TPP at >400 nm under oxygen at ca. 20°C if not noted otherwise. RB is Rose Bengal. b) Determined by GLC or NMR. c) Direct irradiation at >400 nm. d) Value in parenthesis is a ratio of trans/cis.

Irradiation of 0.01 M ethylphenyldiazomethane (4a) and 0.01 mM meso-tetraphenylporphine (TPP) in benzene at >400 nm under oxygen afforded propiophenone (90%) and ethyl benzoate (7%) together with small amounts of β-methylstyrene and phenol (Table 1). The yield of ethyl benzoate decreased significantly by adding Me_2SO or MeOH. For Example, the yields of $PhCO_2Et$ are 4.7, 2.6, and 2.1% with 0.1, 1, and 2 M Me_2SO, respectively. In MeOH (run 5), 4a afforded PhEtC(OMe)OOH (5), which was converted to methyl benzoate, but not to ethyl benzoate, by prolonged irradiation. These fasts seem to indicate that the ester is formed via carbonyl oxide intermediates since thay are efficiently trapped by Me_2SO or MeOH.[8)]

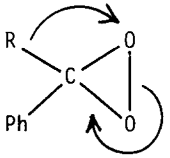
The TPP-sensitized photooxidation of other phenyldiazomethanes $PhC(=N_2)R$ (4) proceeded significantly when R = alkyl (Table 2). Interestingly, resulting ratios of $PhCO_2R$: PhCOR were rather constant in the range of 0.07-0.10 with R = Me, Et, CH_2Ph, and CH(Me)Ph. Diazomethane 4f (R = Ph) never afforded phenyl benzoate; the same was true for 4 with R = p-$MeOC_6H_4$. Thus, aryl groups do not migrate, the migratory aptitude being Me $\sim$ Et $\sim$ CH_2Ph $\gg$ Ph. Trapping experiments by Me_2SO suggest that at least ca. 40% of carbonyl oxide is produced from 4a or 4f.[15)] A small amount of benzoic acid was obtained in the photooxidation of 4f (R = H). But, it is not certain whether the acid was formed via H migration or by autoxidation of PhCHO.

There appear two mechanisms conceivable for the rearrangement to ester, either via dioxirane 2' or diradical 3'. If the ester formation proceeds by a nucleophilic 1,2-rearrangement like 2', the migratory aptitude should be Ph $\gg$ Me as often observed in the rearrangements of various peroxides[16)] (e.g., hydroperoxides and peresters). The present aptitude of

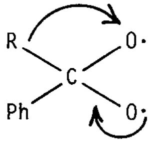
Table 2. Photooxidation fo Substituted Phenyldiazomethanes $PhC(=N_2)R$ (4)

	R	Conditions[a]	Products (%)[b]			$\frac{PhCO_2R}{PhCOR}$ X 100
			PhCOR	$PhCO_2R$	PhCH=CHR'[c]	
4a	Et	TPP/PhH	90	6.9	0.5	7.7
4b	Me	TPP/PhH	84	5.7	0.4	6.8
4c	CH_2Ph	TPP/PhH	34	3.1	44 (9.1)[c]	9.1
4d	CH(Me)Ph	TPP/C_6H_{12}	65	7.0	13 (1.7)	10.7
4e	H	TPP/C_6H_{12}	84	(3)[d]		(<3)[d]
4f	Ph	TPP/C_6H_{12}	95	0		0

a) Irradiated at >400 nm under oxygen for 10-60 min (~0.01 M 4 and 0.1 mM TPP); C_6H_{12} = cyclohexane. b) Determined by GLC and GC-MS. c) Olefins by 1,2-hydrogen shift from carbenes. The value in parenthesis is trans:cis ratio. d) Benzoic acid may also be produced by the autoxidation of PhCHO formed.



2'



3'

Me ≫ Ph clearly denies such a rearrangement. The alternative diradical mechanism via 3' may explain the aptitude, since a similar order has been known for the homolytic rearrangement of diradicals from ß-peroxyesters.[17] The reactivity of Me ≫ Ph is also known for the ß-scission of alkoxy radicals, where the order is $PhCH_2$ ≫ Et > Me reflecting the relative stabilities of departing radicals.[18] In contrast, the present rearrangemnet is not dependent on the structures of alkyls. Presumably, this reflects very facile 1,2-migration due to the high energy content of diradicals 3.[19]

In summary, carbonyl oxides in solution rearrange to esters probably via diradical intermediates 3. As for the mobility between 1, 2, and 3, any conclusion is impossible before more detailed studies including tracer experiments.

References and Notes

1) G. A. Hamilton in "Molecular Mechanism of Oxygen Activation", O. Hayaishi Ed., Academic Press, New York, 1974, p 405.

2) P. S. Bailey, "Ozonation in Organic Chemistry", Academic Press, New York, 1982, Vol. 2, p 371.
3) D. P. Higley and R. W. Murray, J. Am. Chem. Soc., 96, 3330 (1974).
4) G. A. Hamilton and J. R. Giacin, J. Am. Chem. Soc., 88, 1584 (1966).
5) T. A. Hinricks, V. Ramachindran, and R. W. Murray, J. Am. Chem. Soc., 101, 1282 (1979).
6) a) W. Ando, S. Kohmoto, and K. Nishizawa, J. Chem. Soc., Chem. Commun., 894 (1978); b) W. Ando, H. Miyazaki, and S. Kohmoto, Tetrahedron Lett., 4235 (1976); c) W. Ando, Y. Kabe, and H. Miyazaki, Photochem. Photobiol., 31, 191 (1980).
7) J. W. Jerina, D. M. Jerina, and B. Witkop, Experimentia, 28, 1129 (1972).
8) Y. Sawaki, H. Kato, and Y. Ogata, J. Am. Chem. Soc., 103, 3832 (1981).
9) W. A. Pryor and C. K. Govindan, J. Am. Chem. Soc., 103, 7681 (1981).
10) a) L. B. Harding and W. A. Goddard III, J. Am. Chem. Soc., 100, 7180 (1978); b) D. Cremer, ibid., 101, 7199 (1979).
11) R. D. Suenram and F. J. Lovas, J. Am. Chem. Soc., 100, 5117 (1978).
12) J. N. Pitts, Jr., and B. J. Finlyson, Angew, Chem. Int. Ed., Engl., 14, 1 (1975); R. I. Martinez, J. T. Herron, and R. E. Huie, J. Am. Chem. Soc., 103, 3807.
13) R. I. Martinez, R. E. Huie, and J. T. Herron, J. Chem. Phys., 75, 5975 (1981).
14) A. Sekiguchi, Y. Kabe, and W. Ando, J. Chem. Soc., Chem. Commun., 343 (1979); J. Org. Chem., 47, 2900 (1982).
15) The reaction of **4f** with singlet oxygen is reported to afford 21% yield of N_2O according to a reaction ($R_2CN_2 + {}^1O_2 \longrightarrow R_2C{=}O + N_2O$).[3] For the case of **4a** or **4b**, the N_2O formation was below 10% in our preliminary experiments.
16) a) P. A. S. Smith in "Molecular Rearrangements", P. de Mayo Ed., Interscience, New York, 1963, Vol. 1, p 563; b) R. Hiatt in "Organic Peroxides", D. Swern Ed., Wiley, New York, 1971, Vol. 2, p 65; c) L. A. Singer, ibid., 1970, Vol. 1, p 296.
17) W. Adam, Acc. Chem. Res., 12, 390 (1979).
18) a) J. D. Bacha and J. K. Kochi, J. Org. Chem., 30, 3272 (1965); b) R. R. Hiatt and W. H. J. Strachan, ibid., 28, 1893 (1963); c) Y. Sawaki and Y. Ogata, ibid., 41, 2340 (1975).
19) In fact, **3** (R = H) was calculated to be less stable than **2** by 15 kcal/mol.[10a]

(Received in Japan 10 December 1983)