

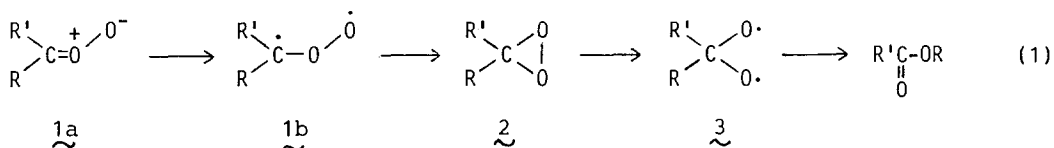
¹⁸O-TRACER STUDY ON THE REARRANGEMENT OF CARBONYL OXIDE
 INTERMEDIATES TO ESTERS

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Summary: A tracer study for the rearrangement of carbonyl oxides to esters using doubly-labeled oxygen lead to a conclusion that carbonyl oxides do not isomerize directly to dioxiranes and the rearrangement to esters proceeds via a cyclic tetroxide.

Carbonyl oxides are important reactive intermediates in the ozonolysis of olefins¹⁾ and of interest as a model for monooxygenase enzymes.²⁾ The oxides are conveniently produced by the photooxidation of diazo compounds³⁾ and transfer oxygen atom to various types of organic compounds.⁴⁾ One of the most characteristic reactions is a nucleophilic O-transfer as shown in the oxidation of sulfoxides^{5,6)} and electron-deficient olefins.⁷⁾

Structure and stability of carbonyl oxides (1) and related intermediates are also interested theoretically. Dioxirane (2) is calculated to be more stable than 1 by 30-40 kcal/mol,⁸⁾ and its structure was identified at low temperature.⁹⁾ Recently, carbonyl oxides have been detected in low temperature matrices,¹⁰⁾ or transiently by laser flash photolysis.¹¹⁾ Thus it is interesting to see if carbonyl oxides and dioxiranes could be interconvertible in solutions. A diagnostic test for such interconversions would be the previously reported rearrangement of phenyl alkyl carbonyl oxides (1, R' = Ph, R = alkyl) to the corresponding esters (eq. 1).^{12,13)}

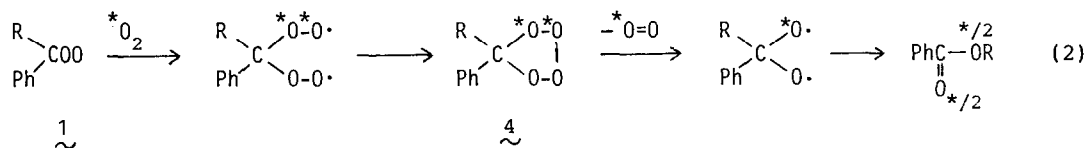


In order to ascertain the intermediacy of carbonyl oxides in the rearrangement to esters, trapping experiments were undertaken with sulfoxides which are known as an efficient scavenger for carbonyl oxides.⁵⁾ Figure 1 illustrates that the ester formation in the photooxidation of phenyl ethyl diazomethane in the presence of meso-tetraphenylporphine (TPP) is signifi-

cantly reduced as phenyl methyl sulfoxide traps carbonyl oxide intermediates; the intercept corresponds to the 56% yield production of carbonyl oxide. Dimethyl sulfoxide afforded similar results. Solvent methanol, which is also an efficient trapping agent,⁵⁾ inhibited completely the rearrangement to ester. These results clearly suggested the involvement of carbonyl oxide in the rearrangement.

We then undertook an ¹⁸O-tracer experiment using ³⁶O₂ to ascertain the rearrangement mechanism. According to eq. 1, doubly-labeled ³⁶O₂ should be retained in the ester since the rearrangement is intramolecular. To our surprise, the data in Table I are not consistent with the scheme of eq. 1, indicating almost complete scrambling of oxygen atom in ester. Similar results were obtained with phenyl methyl diazomethane. The complete scrambling suggests that the two oxygen atoms in the ester are originated from two different O₂ molecules. The scheme of eq. 1 as often proposed in the ozonolysis of olefins is thus ruled out.

Other plausible pathways to esters are a decomposition of carbonyl oxide dimer (*i.e.*, ketone diperoxide)¹⁴⁾ or a Baeyer-Villiger type reaction between 1 and ketones.¹⁵⁾ But, several control experiments indicated that these pathways were not operative under our conditions. We therefore propose that the rearrangement to esters proceeds via a cyclic tetroxide (4) and dioxy diradical (eq. 2).



The addition of O₂ to 1 is not unreasonable since carbonyl oxides are a resonance hybrid mixture of 1a and 1b^{5,8c)} and the addition of triplet oxygen to carbon radicals is well-known to be very facile. Acyclic tetroxides are known to be stable at low temperature and decompose to two alkoxy radicals and oxygen gas.¹⁶⁾ Eq. 2 requires a scrambling in the remaining oxygen gas as well. In fact, we could detect such a scrambling; for the case of R = Et, for example, ca. 3% scrambling based on the nitrogen gas evolved was observed. The value of % scrambling is reasonably high in view of the ester yields of 5-10%. These tracer experiments clearly substantiate the mechanism of eq. 2.

Above results and discussion lead to an interesting suggestion that carbonyl oxides do not isomerize to dioxirane 2 or diradical 3. The inconvertibility of 1 to more stable 2 is probably due to the high energy barrier for the isomerization of 1 as calculated by MINDO/3 method.¹⁷⁾ Finally, it is interesting to note that present study demonstrates the radical addition of oxygen to carbonyl oxides and that the resulting peroxidic species such as

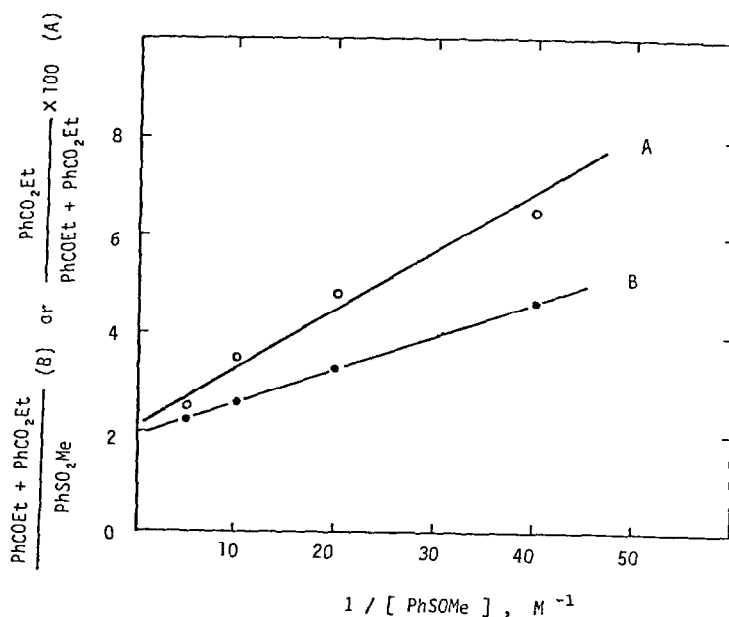


Figure 1. Reciprocal plots for the effect of phenyl methyl sulfoxide (0.025-0.2 M) in the photooxidation of phenyl ethyl diazomethane (6.4 mM). TPP (0.2 mM) was irradiated at 400 nm in MeCN-PhH (4:1) under oxygen.

Table I. Mass Spectral Data for ^{18}O -tracer Study in the Photooxidation of $\text{PhC}(=\text{N}_2)\text{Et}$ ^{a)}

	PhCOEt			PhC=O ⁺	
	M	M + 2	M + 4	M	M + 2
Calculation:					
Retention	100	1.2	27.9	100	28.3
Scrambling	100	56.4	7.9	100	28.3
Observed:					
$\text{O}_2/\text{TPP}/h\nu/30 \text{ min}$	100	55.5	9.1	100	24.6
O_2 (spontaneous, 3 days) ^{b)}	100	52.8	7.4	100	25.5

a) Starting gas: $^{32}\text{O}_2 : ^{34}\text{O}_2 : ^{36}\text{O}_2 = 100 : 1.17 : 27.9$. See Figure 1 for the photooxidation conditions. b) Spontaneous means the autoxidation of the diazomethane at room temperature in the dark.

4 may explain the chemiluminescence observed in the reaction of carbenes with oxygen.¹⁸⁾

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