Intramolecular Reaction of Carbonyl Oxide. Formation of a Silyl Ester in the Photosensitized Oxygenation of a Silyl Diazo Compound

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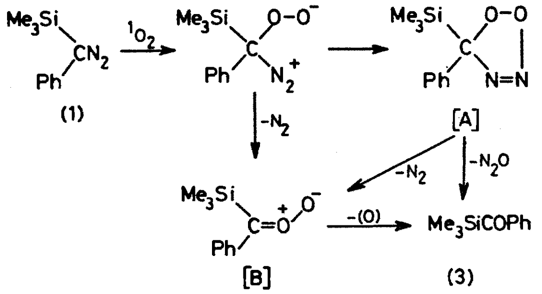
Summary Dye-sensitized photo-oxygenation of trimethylsilylphenyldiazomethane produced phenyl trimethylsilyl ketone and trimethylsilyl benzoate; the latter may be formed from the silyl substituted carbonyl oxide *via* intramolecular reaction.

INTEREST has increased over the last few years in the chemistry of carbonyl oxide. The photo-oxygenation of diazo compounds involves the formation of carbonyl oxides which are trapped by aldehydes and naphthalenes to give ozonides and naphthols, respectively.[1,2] While intermolecular reactions of carbonyl oxides from diazo compounds have been reported,[1–3] there are no reports on intramolecular reactions. Silyl substituted diazo compounds may be especially suitable subjects for the investigation of the intramolecular reaction of carbonyl oxides since silicon has a strong affinity for oxygen. We have therefore studied the photosensitized oxygenation of silyl diazo compounds. We report here the first intramolecular reaction of carbonyl oxide, which rearranges to give a silyl ester.



A mixture of trimethylsilylphenyldiazomethane (**1**) (0·7 mmol) in CCl_4 (10 ml) containing TPP (*meso*-tetraphenylporphine) as sensitizer was photolysed in a water-cooled Pyrex tube with a 300 W halogen lamp under bubbling oxygen. The strong stretching absorption of the diazo group disappeared within 10 min irradiation. Analysis of the mixture by g.l.c. showed two products. Separation by preparative g.l.c. gave trimethylsilyl benzoate (**2**) and phenyl trimethylsilyl ketone (**3**) in 38 and 60% yields, respectively. The structures of the silyl benzoate (**2**) and the silyl ketone (**3**) were confirmed by comparison of their n.m.r. and i.r. spectra with those of authentic samples. Similar results were obtained when the reaction was carried out in benzene, chloroform, and dichloromethane. However, significant effects of solvent, reaction temperature (room temperature or −78 °C), and sensitizer [TPP or Methylene Blue (MB)] on the product yields were not observed. The results are summarized in the Table.

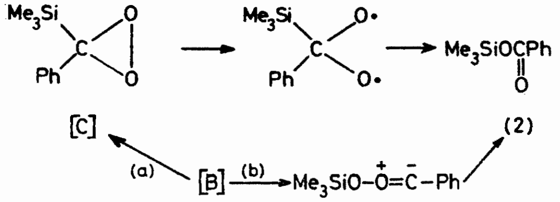
TABLE. Photosensitized oxygenation of (**1**).[a]

Solvent	% Yield[b] of (**2**)	% Yield[b] of (**3**)
CCl_4	38	60
C_6H_6	40	48
$CHCl_3$	38	57
$CHCl_3$[c]	36	55
CH_2Cl_2	41	53
CH_2Cl_2[d]	43	54

[a] Reactions were carried out for 10 min with bubbling oxygen at room temperature and with TPP as sensitizer unless otherwise stated. [b] Determined by g.l.c. using an internal standard. [c] MB sensitizer; room temp. [d] TPP sensitizer; −78 °C.

The reaction did not proceed in the absence of the sensitizer and *ca.* 86% of (**1**) was recovered after 10 min irradiation. The silyl ketone (**3**) was stable under the oxygenation conditions and did not give the silyl benzoate

(**2**). Singlet oxygen may be the reactive species as reported by Murray in the dye-sensitized photo-oxygenation of diphenyldiazomethane.[1]



The formation of the silyl ketone (**3**) may arise from the loss of nitrous oxide from the adduct [A]. G.l.c. analysis of the gas produced showed the presence of nitrous oxide and nitrogen.† We are mainly concerned here with the formation of the silyl benzoate (**2**) and it would be reasonable to propose that the carbonyl oxide [B] is formed in the photo-oxygenation of (**1**). Carbonyl oxides are known to be intercepted by aldehydes.[1,3] However, the photo-oxygenation of (**1**) with 5 mol. equiv. of benzaldehyde gave no significant difference in the yields of (**2**) and (**3**). Similarly the reaction of (**1**) in the presence of diphenyl sulphide as an oxygen accepting reagent did not give any diphenyl sulphoxide.

These results, and the small effect of solvent and reaction temperature, suggest that the silyl benzoate (**2**) may be produced intramolecularly, not intermolecularly. An alternative possibility is that the carbonyl oxide [B] may oxidize the silyl ketone (**3**) to the silyl benzoate (**2**). Indeed, the dye-sensitized photo-oxygenation of diphenyldiazomethane in the presence of the silyl ketone (**3**) produced the silyl benzoate (**2**) together with benzophenone.[4] However, the possibility that the carbonyl oxide [B] reacts with the silyl ketone (**3**) may be eliminated since the reaction of (**1**) in the presence of dimethylphenylsilyl phenyl ketone did not give dimethylphenylsilyl benzoate, and the silyl benzoate (**2**) was formed. The most probable mechanism for the formation of the silyl benzoate (**2**) involves intramolecular silyl migration *via* either path (a) or (b). Path (a) involves the dioxiran [C] which may give (**2**) *via* O–O bond scission. This is supported by calculation[5] and by the recent observation of the dioxiran CH_2O_2.[6] This mechanism also offers a rationale for recent results on the ozonation of trimethylsilyl ketene[7] and a recent suggestion of Moriarty.[8] Our results give more direct evidence for the transformation of a silyl substituted dioxiran to a silyl ester.

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† The retention times of nitrous oxide and nitrogen were identical with those of authentic samples (1 m molecular sieve column). The mass spectrum of nitrous oxide had a peak at m/e 44 (N_2O^+).

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