Photo-oxygenation of Diphenyldiazomethane in the Presence of Phenyl Trimethylsilyl Ketone. Oxygen Transfer from Carbonyl Oxide to the Silyl Ketone

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Summary Dye-sensitized photo-oxygenation of diphenyldiazomethane in the presence of phenyl trimethylsilyl ketone produced trimethylsilyl benzoate by reaction of a carbonyl oxide with the silyl ketone accompanied by 1,2-rearrangement of the trimethylsilyl group, together with benzophenone.

The suggestion of Bartlett that the photo-oxygenation of diphenyldiazomethane produces a carbonyl oxide has been supported by the isolation of benzophenone diperoxide.[1] Additional support for the intermediacy of the carbonyl oxide in the photo-oxygenation of diazo-compounds was provided by Hamilton in reactions with saturated hydrocarbons.[2] More recently, the reaction of diazo-compounds with singlet oxygen has been reported,[3,4] in which carbonyl oxides are shown to be the most important species in dye-sensitized oxygenation of diazo-compounds and they are trapped by aldehydes and naphthalene to give ozonides and naphthols, respectively, but in low yields. We have been particularly interested in the chemistry of carbonyl oxides and have reported that carbonyl oxides produced by the photo-oxygenation of sulphonium ylides can oxidize sulphides and sulphoxides to sulphoxides and sulphones, respectively.[5] We now report an entirely new type of reaction in which carbonyl oxides from diazo-compounds oxidize silyl ketones to silyl esters.

In a typical reaction, a mixture of 2·0 mmol of diphenyldiazomethane and 1·0 mmol of phenyl trimethylsilyl ketone 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 absorption due to the diazo-group disappeared with 10 min of irradiation. Analysis of the mixture by g.l.c. showed two products together with unchanged silyl ketone. Separation by preparative g.l.c. gave trimethylsilyl benzoate (42%, based on the silyl ketone), benzophenone (74%, based on diphenyldiazomethane), and the recovered silyl ketone (30%).

$$Ph_2CN_2 + Me_3SiCOPh \xrightarrow[TPP]{h\nu-O_2} Me_3SiOCOPh + Ph_2C{=}O$$

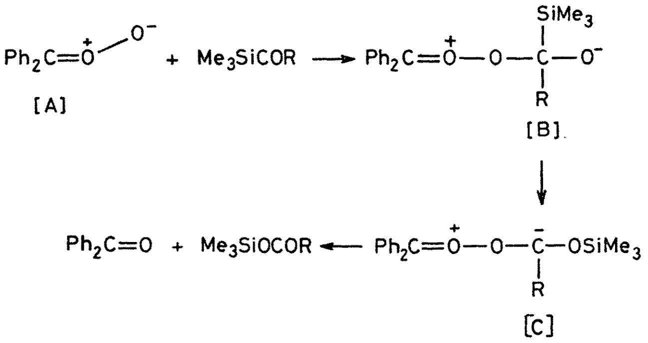
Similar results were obtained when the photo-oxygenation was carried out in other solvents such as benzene, chloroform, and dichloromethane. The formation of trimethylsilyl benzoate was confirmed by comparison of its n.m.r. and i.r. spectra with those of an authentic sample. Similar silyl benzoates were obtained with other silyl ketones (Table). The photo-oxygenation of phenyldiazomethane with TPP in benzene in the presence of phenyl trimethylsilyl ketone also produced trimethylsilyl benzoate, together with benzaldehyde.

Table. Photo-oxygenation of diphenyldiazomethane in benzene in the presence of silyl ketones.[a]

Time /min[b]	Silyl ketone	Recovered (%)	Silyl ester (%)[c]
10	$Me_3SiCOPh$	16	$Me_3SiOCOPh$ (67)
20	$Et_3SiCOPh$	33	$Et_3SiOCOPh$ (47)
10	$PhMe_2SiCOPh$	42	$PhMe_2SiOCOPh$(48)
10	$Me_3SiCOPr^i$	51	$Me_3SiOCOPr^i$ (21)

[a] O.5 Equiv. silyl ketone to diphenyldiazomethane was used. [b] The reaction was carried out until the diazo-compound was decomposed completely with TPP as sensitizer under bubbling oxygen. [c] Yields are based on silyl ketones used. Benzophenone was also produced in *ca.* 70% yield in each case.

Phenyl trimethylsilyl ketone was stable under the photosensitized oxygenation conditions and no trimethylsilyl benzoate was formed in the absence of diphenyldiazomethane. Singlet oxygen may be the reactive species in the dye-sensitized photo-oxygenation of diphenyldiazomethane as reported by Murray,[3,4] and it is reasonable to speculate that the carbonyl oxide [A] is formed in this reaction. A plausible mechanism involves addition of the carbonyl oxide [A] to the silyl ketone to give the zwitterion [B]; the oxy-anion may undergo ring closure or silyl migration. One would expect silicon migration to prevail sufficiently over ring closure, leading to the formation of the intermediate [C].



The reaction appears to be closely related to the rearrangement of silylmethanols to the isomeric silyl ethers.[6] Indeed, aryl silyl ketones formed silyl benzoates in high yields, and isopropyl trimethylsilyl ketone yielded trimethylsilyl isobutyrate in low yield. This indicates that the nature of the group R attached to the carbonyl carbon of the silyl ketone may play an important role in the reaction. Migration may occur most readily when the aryl group on carbon is able to delocalize a negative charge. Elimination of benzophenone from the intermediate [C] would result in the formation of the silyl ester.

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