Ozonolysis of Silyl Diazo Compounds and Silyl Ketones

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Summary Ozonolysis of silyl diazo compounds gives silyl ketones, which react further to give silyl esters.

SILYL KETONES are of interest because of their chemical properties and their unique spectral behaviour.[1] They must be prepared under relatively mild and neutral conditions to avoid cleavage of the silicon–carbonyl carbon bond.[1] Recently, we demonstrated a new method for the synthesis of silyl ketones possessing a functional group by the photosensitized oxygenation of silyl diazo compounds.[2] Ozonolysis is one of the most efficient methods of cleaving carbon–carbon double bonds leading to carbonyl compounds. However, ozonolysis of both vinylsilanes[3,4] and silylketens[5] did not produce the expected silyl ketones. We now report on the ozonolysis of silyl diazo compounds and silyl ketones.

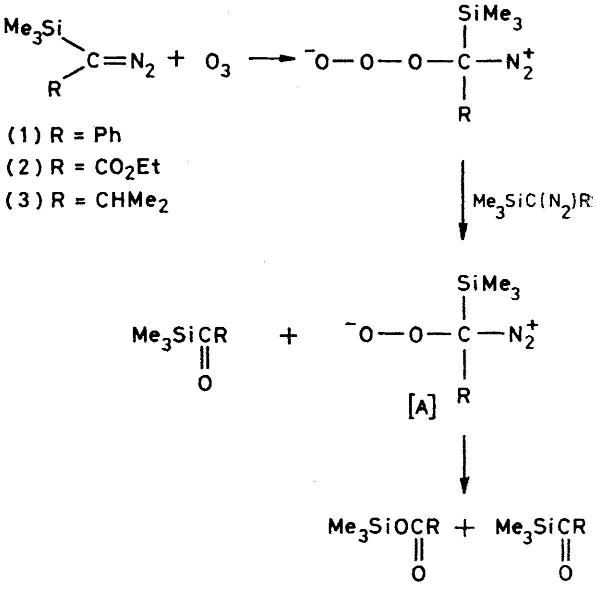
The ozonolysis of phenyltrimethylsilyldiazomethane (**1**) was carried out in dichloromethane solution at room temperature.† The progress of the reaction could be seen by a colour change from orange to intense yellow. The i.r. spectrum of the mixture showed two carbonyl absorptions at 1700 and 1615 cm^{-1}, but did not show a strong absorption due to the diazo-group, indicating essentially quantitative conversion of (**1**) into products. G.l.c. analysis showed the presence of two products which were collected by preparative g.l.c. and identified as phenyl trimethylsilyl ketone and trimethylsilyl benzoate by comparison of their n.m.r. and i.r. spectra with those of authentic samples. The silyl diazo compounds (**2**) and (**3**) were found to give similar products on reaction with ozone, but considerable amounts of (**2**) were recovered after ozonolysis for 12 min. The results are summarized in Table 1. This is the first case in which silyl ketones have been found in the ozonolysis of silicon-containing compounds.

TABLE 1. Ozonolysis of silyl diazo compounds[a]

Silyl diazo compd.	Recovered diazo compd. (%)	Silyl ketone (%)		Silyl ester (%)	
(**1**)	0	$Me_3SiCOPh$	58 (45)[b]	$Me_3SiOCOPh$	21
(**2**)	54	$Me_3SiCOCO_2Et$	30	$Me_3SiOCOCO_2Et$	16
,,	13[c]	,,	22[c]	,,	55[c]
(**3**)	0	$Me_3SiCOCHMe_2$	43	$Me_3SiOCOCHMe_2$	38

[a] The ozonolysis was carried out in dichloromethane (10 ml) for 12 min using 1 mmol of silyl diazo compounds. Yields were determined by g.l.c. [b] Isolated yield (separation by silica gel chromatography) is given in parentheses. [c] The ozonolysis was carried out for 20 min.

The ozonolysis required 1 mol of ozone for *ca.* 2 mol of the silyl diazo compound, indicating that at least two oxygen atoms of the ozone molecule were used in the conversion of the silyl diazo compounds. Similar observations were reported by Bailey in the ozonolysis of diphenyldiazomethane.[6] The reaction probably follows the path shown in the Scheme. We previously reported that the intermediate [A] (R = Ph) could produce phenyl trimethylsilyl ketone and trimethylsilyl benzoate in the photosensitized oxygenation of (**1**).[7]



SCHEME

When the ozonolysis of (**2**) was continued for 20 min, the yield of the silyl ketone decreased while that of the silyl ester increased. This indicates that silyl ketones can be oxidized by ozone to silyl esters. Indeed, the ozonolysis of silyl ketones in dichloromethane afforded the corresponding silyl esters with the absorption of an approximately equivalent amount of ozone. Only cleavage of the silicon–carbonyl bond of the silyl ketones was observed, with no cleavage of the silicon–methyl bonds. The results of the reactions of the silyl ketones with ozone are summarised in Table 2.

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† The amount of ozone (*ca.* 0·045 mmol ozone/min) was estimated by titration of the iodine produced in the reaction of potassium iodide with ozone.

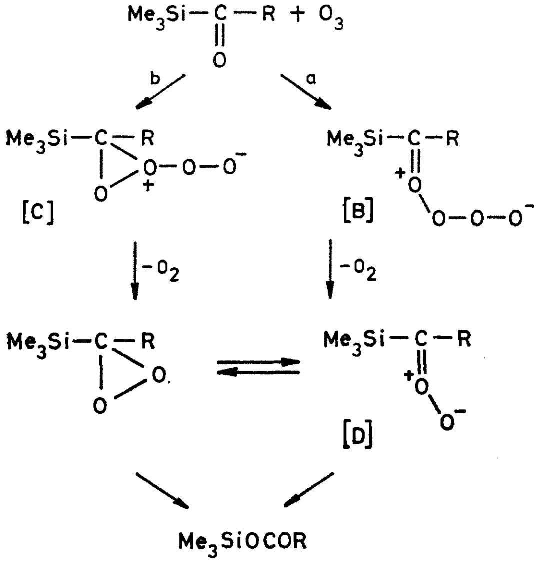

Table 2. Ozonolysis of silyl ketones[a]

Silyl ketone	Recovered silyl ketone (%)	Silyl ester (%)
$Me_3SiCOPh$	56	$Me_3SiOCOPh$ 29
$Me_3SiCOCO_2Et$	45	$Me_3SiOCOCO_2Et$ 35
$Me_3SiCOCHMe_2$	47	$Me_3SiOCOCHMe_2$ 38

[a] The ozonolysis was carried out in dichloromethane (10 ml) for 12 min using 1 mmol of silyl ketones. Yields were determined by g.l.c.

Silyl esters may be formed *via* either path (a) or path (b).‡ Ozone attacks the carbonyl oxygen or the π-bond of the carbonyl group to give a zwitterion such as [B] or [C] which gives the carbonyl oxide [D] with loss of oxygen. The carbonyl oxide [D] (R = Ph) arising from the photosensitized oxygenation of (**1**) then forms the silyl ester.[7] An alternative possibility is the direct insertion of ozone into the silicon–carbonyl carbon bond *via* a three membered transition state. At present, there is no definite evidence for the mechanism.

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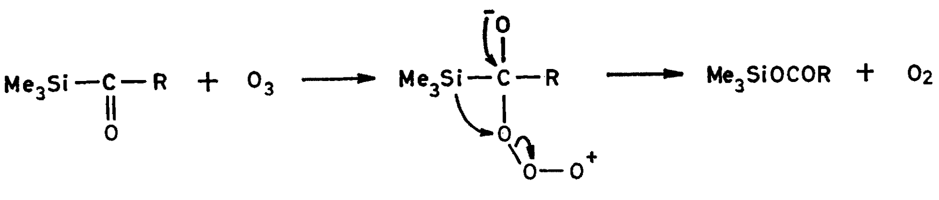
‡ One of the referees suggested an alternative reaction mechanism in which nucleophilic attack by ozone occurs at the carbonyl carbon followed by rearrangement of the silyl group. However, this is unlikely because ozone is a strongly electrophilic species.



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