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OZONATION OF SILYLKETENES

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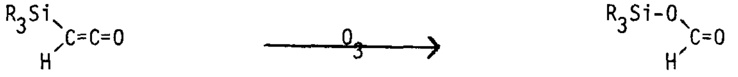
The recent reports on the oxidation of highly hindered unreactive ketenes, di-t-butyl-and dineopentylketenes,[1-3] to the elusive α-lactones prompted us to examine the ozonation of the stable and unreactive trimethylsilyl- and triethylsilylketenes.[4] This ozonation yielded trimethylsilyl- and triethylsilyl formates respectively.



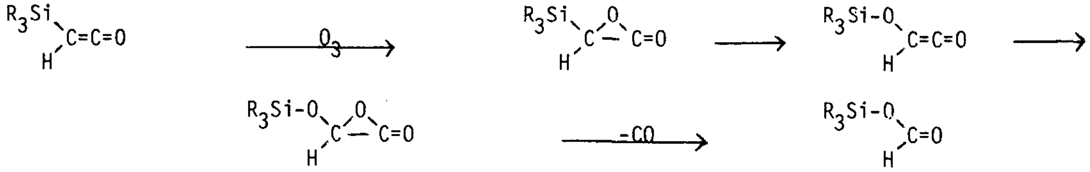
I, R = Me III, R = Me

II, R = Et IV, R = Et

Thus, a solution of 2 g. (17 mm) of trimethylsilylketene,[5] (I), in 25 ml. of dry methylene chloride was cooled to -78°[6] under a nitrogen atmosphere and ozone bubbled through the solution. A monitoring of the reaction solution by infrared revealed the disappearance of the ketene band at 2080 cm.$^{-1}$, and the appearance of a carbonyl band at 1720 cm.$^{-1}$ The solution was allowed to warm to room temperature and the solvent removed by distillation. The major component of the residue was identified as trimethylsilyl formate, (III), by comparison with an authentic sample;[7] ir, 1720 cm.$^{-1}$; nmr (CCl_4 and $CHCl_3$), δ, 0.35 (s, 9H), and 8.0 (s, 1 H). The yield was estimated by vapor phase chromatography to be about 40%.[8,9]

Triethylsilylketene,[10] (II), was ozonized in a similar manner and triethylsilyl formate, (IV), was formed in 60% yield and characterized as follows: ir, 1720 cm.$^{-1}$; nmr (CCl_4 and $CHCl_3$), δ, 1.0 (m, 15 H) and 8.0 (s, 1 H). Anal. Calcd. for $C_7H_{16}O_2Si$: C, 52.50; H, 10.00. Found, C, 52.49; H, 9.59.

We believe this oxidation proceeds via the α-lactones intermediate which undergoes a silyl migration to oxygen with the resultant formation of trimethylsilyloxyketene. Brook and coworkers have recently described the rearrangement of epoxysilanes to siloxyalkenes which is the result of the silyl substituent migrating to oxygen.[11] This silyl migration in the α-lactone of I would lead to trimethylsilyoxyketene. The oxidation of the reactive trimethylsilyloxyketene would be expected to yield the corresponding α-lactone.[12] The loss of carbon monoxide from this α-lactone would yield the trimethylsilyl formate.[13,14]



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5. L.L. Schukouskaya, R.I. Palchik and A.N. Lazarez, Dokl. Akad. Nauk USSR, 164, 357 (1965).
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8. In the early runs there was always a component present which had a base peak in the mass spect. of m/e 147. This compound has been identified as hexamethyldisiloxane and the m/e 147 peak is a result of the loss of a methyl group. This ether is formed by the reaction of atmospheric moisture with trimethylchlorosilane. The trimethylsilylketene contained 5-10% of hexamethyldisiloxane which is unreactive through the ozonolysis reaction.
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