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SILA PUMMERER REARRANGEMENT IN HIGHLY STERICALLY HINDERED ORGANOSILICON COMPOUNDS: A NEW ROUTE TO BIS(TRIMETHYLSILYL)KETONE

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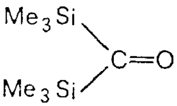
Summary: The oxidation of the tris(trimethylsilyl)methylthio-methane with m-chloroperoxybenzoic acid, leads through a sila-Pummerer rearrangement occurring in unusually mild conditions, to bis(trimethylsilyl)ketone.

It has already been reported[1] that 1-(phenylthio)-1-trimethylsilyl alkanes are latent aldehydes and ketones which can be exposed "via" sila-Pummerer rearrangement of the corresponding sulphoxides to O-trimethylsilyl hemithioacetals (or ketals); these have a unique advantage in respect to 1,3-dithianes since their hydrolysis to carbonyl derivatives, occurs in very mild conditions in which usually dithianes are stable.

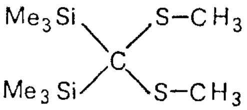
As part of our program in the study of organosilicon compounds chemistry and particularly in connection with our recent[2,3] development of synthetic strategies directed to the synthesis of previously unreported $(Me_3Si)_2C=X$ (X=O,S) systems, we report here the results of an investigation on the oxidation of the tris(trimethylsilyl)-(IV)[4] and of the bis(trimethylsilyl)methylthio-methane (VI)[5].

The silylated sulphides were oxidized with m-chloroperoxybenzoic acid (MCPBA) in dichloromethane at -78°C.

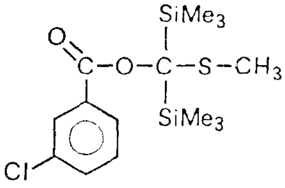
In a typical experiment, to a cooled (dry ice/acetone) solution of (IV) (1.5 g, 5.4 mmol) in dry dichloromethane (10 ml), MCPBA (5.5 mmol) in dry dichloromethane (10 ml), was slowly added under nitrogen. After being stirred for 10 min, the mixture was diluted with ether (100 ml), washed with an aqueous solution of sodium bisulphite, three times with aqueous sodium hydrogen carbonate, dried and carefully concentrated. The GC/MS analysis of the reaction mixture showed a 1:1 ratio of the bis(trimethylsilyl)ketone ($(Me_3Si)_2C=O$ (I)[6] and of the thioketal (II)[6]. Minor amounts of the silylated ester (III) were also detected[7]. Column chromatography on Florisil with degassed n-pentane as the eluent, afforded product (I) as a strawberry coloured oil (424 mg, 45%).



(I)

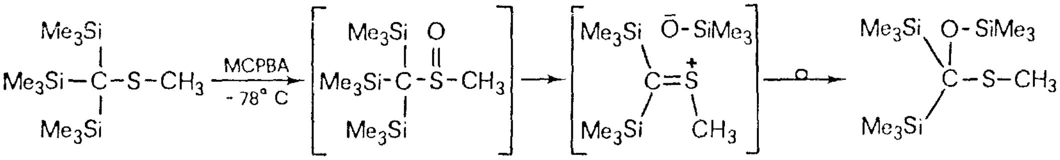


(II)



(III)

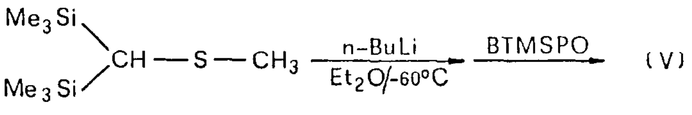
The lack of any evidence for the sulphoxide in the crude, might not be unexpected in consideration of the special features of the tris(trimethylsilyl)methyl ("trisyl") mojety[8]: the high steric compression between the three Me_3Si groups, coupled with the high affinity of the Si atom for the highly polarized oxygen of the sulphinyl group, likely make a Brook-type migration in the sulphoxide particularly favourable. The siloxysulphonium ylid so formed, would then rearrange by the usual Pummerer pathway[9].



(IV) (V)

The intermediacy of the O-Si hemithioacetal (V) being supported however by the presence in the reaction mixture of (II) and (III), there remains the question of why (V) could not be detected in the crude product: even though the lability of the C-S bond in these compounds is well known[1,10] to be fairly high, on first approximation neither hydrolytic quench nor the presence of m-chlorobenzoic acid (MCBA) should allow rapid conversion of (V) into(I).

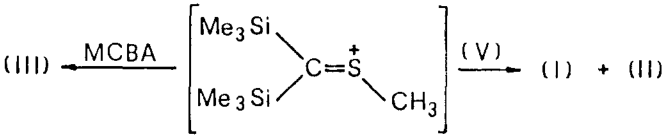
To work out this problem, the O-Si hemithioacetal (V) was synthesised: a novel procedure, based on the bis(trimethylsilyl)peroxide (BTMSPO) as a suitable reagent for electrophilic oxysilylation[11], was employed[12].



(VI)

However, when added to an equimolar amount of MCBA in dichloromethane, (V) did not show any change at GC/MS analysis, even on standing at room temperature for prolonged time.

An hydrolytic key step leading to the observed reaction products being thus unlikely, their formation is best explained by an intermolecular S-alkylation reaction of the thionium ion generated under Pummerer conditions: consistent with work reported by Vedejs and Mullins[13], this highly efficient electrophilic species is able to interact rapidly with O-Si hemithioacetals but, as shown in our reaction, also with the carboxylate ion coming from MCBA.



Preliminary experiments performed on compound (VI) with a 1:1 molar ratio of MCPBA, finally led to the formation of the expected $Me_3SiCH(OSiMe_3)SCH_3$, stable in the reaction conditions, thus showing how a decreased steric crowding of the Me_3Si groups, brings back the oxidation reaction to the usual Pummerer pathway. However again the sulphoxide was undetectable in the reaction mixture.

This hemithioacetal being a suitable precursor for the synthesis of the still unknown Me_3SiCHO, further experiments are currently underway directed to its isolation from the reaction mixture or to its independent synthesis through the previously mentioned oxysilylation procedure.

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4. Lithiation of $(Me_3Si)_3CSH$, prepared according to reference 2, with MeLi in n-hexane at -78°C, followed by treatment with an equimolar amount of MeI, afforded compound (IV) in 95% yield.
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6. The spectral properties of (I) perfectly matched those previously reported (see reference 3); the MS and NMR analysis appear perfectly consistent with the proposed structure of (II): mass spectrum, m/z (%): 252 (M^+, 6), 237 (24), 117 (100), 105 (35), 73 (60); NMR ($CDCl_3$) 0.14 (s, 18H), 2.16 (s, 6H).
7. The same reaction pattern occurred avoiding the hydrolytic quench after the oxidation.
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11. For a more comprehensive study of the synthetic applications of this reaction see: A. Ricci and M. Taddei, Synthesis, 8, 633 (1986).
12. Compound (V) was prepared according to the following procedure: to a solution of (VI) (1.3 g, 63 mmol) in ether (10 ml), at -60° C, a solution of n-BuLi in n-hexane (4.2 ml of a 1.5 molar solution) were added and the reaction mixture stirred for 30 min at -60°C. After 3 h at room T, the mixture was cooled again at -50°C and BTMSFO (1.12 g, 63 mmol) was added. The reaction was left under stirring at room T overnight; the ether was then removed and n-hexane added. After removal by centrifugation of the thin white solid formed, the organic solvent was evaporated and the yellowish oil was distilled under vacuum; the intermediate fraction (b.p. 120-122° C at 20mmHg) submitted to GC/MS analysis resulted to be a 1:1 mixture of unreacted (IV) and of hemithioacetal (V); mass spectrum, m/z (%): 294 (M^+, 1.9), 279 (12), 178 (10), 147 (100), 133 (22), 117 (31), 75 (18), 73 (88). No further attempts have been done so far to improve this separation or the yields of the reaction.
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