Silyl Alkenyl Ethers as the Synthetic Equivalent of Enols. New Syntheses of β-Keto-sulphides and 1,3-Diketones

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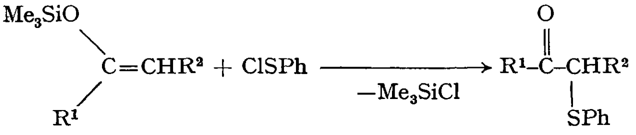
Summary New syntheses of β-keto-sulphides and 1,3-diketones *via* the addition of a sulphenyl chloride and polychloroacetyl chlorides to trimethylsilyl alkenyl ethers are described.

Recently we have shown that silyl alkenyl ethers can be used as the synthetic equivalent of enols.[1,2] We report here that electrophilic addition of a sulphur–halogen bond, as well as a carbon–halogen bond, can also provide new synthetic methods *via* readily available silyl alkenyl ethers[3] (Schemes 1 and 2).

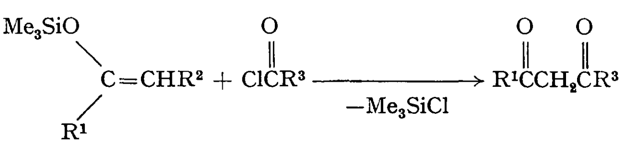


(1) **(2)**

a; $R^1 = Ph, R^2 = Me$. **b**; $R^1 = Bu^t, R^2 = H$
c; $R^1, R^2 = -[CH_2]_4-$

Scheme 1

The β-keto sulphides[4] (Scheme 1) were synthesised as ollows. Phenylsulphenyl chloride (25 mmol) in CH_2Cl_2 20 ml) was added slowly to a stirred solution of the trimethylsilyl alkenyl ethers[5] (**1**; 25 mmol) in CH_2Cl_2 (15 ml) at −40 to −60°. The red colour (PhSCl) disappeared instantly. The solution was then stirred at a room temperature for 1 h. Distillation gave the β-keto-sulphides (**2a**), (**2b**), and (**2c**) in 78, 60, and 68% yields respectively.

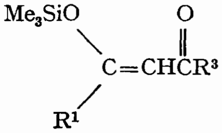


(1) **(3)** **(4)**

1; R^1=Ph or Bu^t; R^2=H **3**; $R^3=CCl_3, CHCl_2$
4a; R^1=Ph, $R^3=CCl_3$ **4b**; R^1=Ph, $R^3=CHCl_2$
4c; $R^1=Bu^t$, $R^3=CCl_3$ **4d**; $R^1=Bu^t$, $R^3=CHCl_2$

Scheme 2

1,3-Diketones were synthesised (Scheme 2) as follows. To a solution of the trimethylsilyl alkenyl ether[5] (**1**; 25 mmol in CH_2Cl_2 (25 ml) was added the polychloroacetyl chloride (**3**; 25 mmol) in CH_2Cl_2 (25 ml) at 25° and the mixture was stirred for 24 h at this temperature. Methanol (20 ml) was then added and the solution was refluxed for 1 h. Distillation gave pure polychloromethyl 1,3-diketones (**4**) (**a**, 67%; **b**, 47%; **c**, 41%; and **d**, 40%) showing i.r. absorptions at *ca.* 1600 br, s cm^{-1} typical of 1,3-diketones. Methanolysis



(5)

was necessary to obtain (**4**) pure and in better yield because silylation of (**4**) took place to give (**5**) by trimethylsilyl chloride formed during the reaction.

Preliminary experiments show that (**4c**) forms a europium complex[6] having high solubility in nonpolar solvents.

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