# β-Silylketones as Masked αβ-Unsaturated Ketones†

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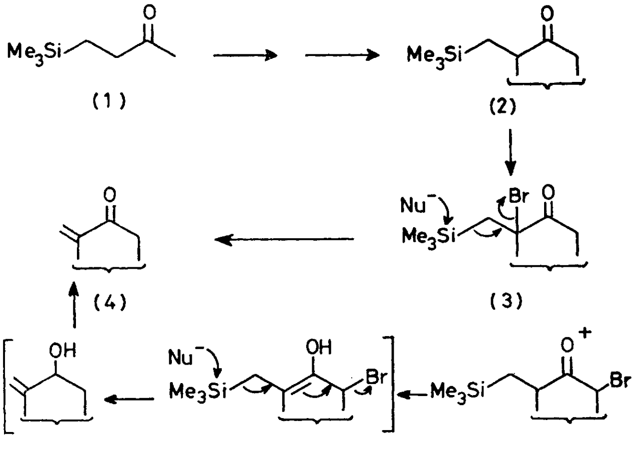
*Summary* β-Silylated ketones can be converted, by bromination followed by desilylbromination, into αβ-unsaturated ketones.

IN this and the following two papers, we show that a β-silyl ketone (**2**) is a masked αβ-unsaturated ketone (**4**).[1] Whereas β-halogeno-, hydroxy-, or amino-ketones undergo elimination on treatment with base, giving αβ-unsaturated ketones, a β-silylketone will not; furthermore, short of dissolving it in concentrated sulphuric acid[2] or treating it with rather special reagents like alkoxide ion in dimethyl sulphoxide[3] it will be stable to most of the reagents commonly used in organic synthesis. It should therefore be possible to use the ketone function of a β-silylketone in synthesis in most of the usual ways, represented schematically as (**1**) → (**2**) in Scheme 1, without any risk that the β-silyl group will drop off. However, bromination, (**2**) → (**3**), will set up the silyl and bromine groups for easy elimination (**3**) → (**4**), and an αβ-unsaturated ketone should be produced. Furthermore, should bromination take place on the 'wrong' side, (**2**) → (**5**), enolisation, (**5**) → (**6**), or equilibration, (**5**) → (**3**), again provide a pathway by which desilylbromination, (**5**) → (**4**), can give the same αβ-unsaturated ketone.



SCHEME 1.

In this paper we present a simple example (Scheme 2) to show that this reasoning is correct, and in the following papers we present some other ways in which β-silylated ketones can be prepared and converted, by bromination, into αβ-unsaturated ketones.

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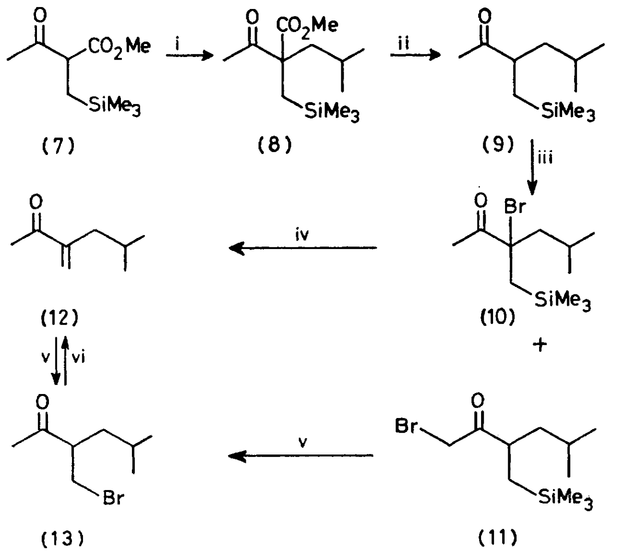
† Reprints of this paper will not be available.



Scheme 2. Reagents: i, NaH–Bu$^t$I-dimethylformamide; ii, NaCN-hexamethylphosphoric triamide–90 °C; iii, Br$_2$–CCl$_4$; iv, NaF–EtOH; v, HBr–CCl$_4$; vi, NaHCO$_3$–EtOH-H$_2$O.

Trimethylsilylmethylation of methyl acetoacetate is essentially a known reaction.[4] The product (**7**) can be alkylated again, (**7**) → (**8**), and the methoxycarbonyl group removed to give the β-silylketone (**9**). Bromination of this ketone gave the two bromides (**10**) (65%) and (**11**) (15%), and some unchanged starting material (**9**) (*ca.* 15%). When this mixture was treated with sodium fluoride in ethanol, the bromide (**10**) rapidly gave the unsaturated ketone (**12**) (55%), which had a definitive $^{1}$H n.m.r. spectrum identical to that reported for it.[5] Evaporation of this product gave a relatively pure sample of the 'wrong' bromide (**11**), identified by the presence of a two-proton singlet at δ 3·88. Treatment of this bromide with hydrogen bromide in carbon tetrachloride at room temperature gave a solution of the β-bromide (**13**), the $^{1}$H n.m.r. spectrum of which was identical with that of a sample prepared by the addition of hydrogen bromide to the unsaturated ketone (**12**). Plainly, the hydrogen bromide had, either by catalysing enolisation or by catalysing the equilibration of the bromides (**11**) and (**10**), allowed desilylbromination to take place, as we had predicted. Since other acids were ineffective, and since it is known that hydrogen bromide equilibrates α-bromoketones by debromination and rebromination,[6] we incline to the second mechanism. The β-bromide (**13**) could, of course, be easily converted into the unsaturated ketone (**12**). Overall, the best procedure for converting the β-silylketone (**9**) into the αβ-unsaturated ketone (**12**) is (i) to add bromine at 0—20 °C in carbon tetrachloride, with a stream of nitrogen to blow off the hydrogen bromide produced, (ii) after the bromine has been consumed, to pass hydrogen bromide through the solution for 0·4 h at 20 °C, and (iii) to add the solution to aqueous ethanol containing sodium hydrogen carbonate and to reflux the mixture for 2·5 h. The overall yield of the rather sensitive αβ-unsaturated ketone (**12**) is 75—80% (by $^{1}$H n.m.r.).

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[1] This idea was present in work of L. Eberson (*Acta Chem. Scand.*, 1956, **10**, 633), but was not developed.

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[4] L. H. Sommer and N. S. Marans, *J. Amer. Chem. Soc.*, 1950, **72**, 1935.

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