New β-Acylcarbanion Equivalent Based on Allyltrimethylsilane Chemistry

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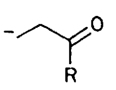
Summary The allylanion (**4**) derived from allyltrimethylsilane reacts with carbonyl compounds to give δ-hydroxyvinylsilanes which can be readily converted into γ-lactols and γ-lactones.

β-Acylcarbanion equivalents (**1**) and their enone analogues (**2**) are synthon units that have attracted a considerable amount of interest because of their potential as synthetic reagents.[1] Many approaches to equivalents



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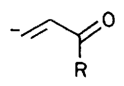

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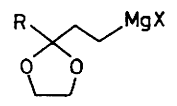
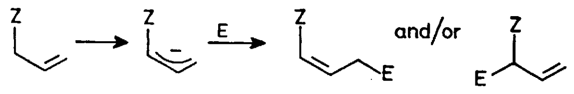


(3)

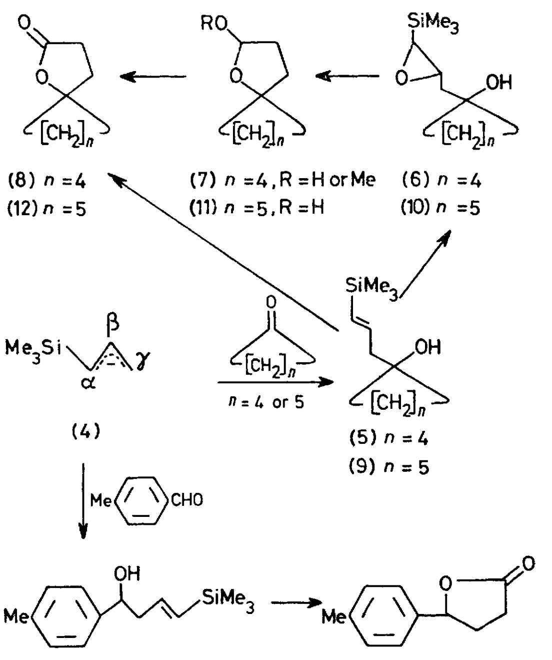
of (**1**) and (**2**) have been based upon allylanion chemistry (Scheme).[2] Recently Grignard reagents of the general type (**3**) have been developed as β-acylcarbanion equivalents.[3]



Scheme

Surprisingly, whilst allylsilane chemistry has had several applications to synthesis,[4] it has not been recognized that the carbanion derived from allyltrimethylsilane[5] can function as a useful and versatile β-acylcarbanion equivalent. As part of our general interest in organosilicon reagents in synthesis[6] we report some reactions of the carbanion (**4**) that establish it as a useful β-acylcarbanion equivalent. Deprotonation of allyltrimethylsilane (commercially available from Petrarch Systems, Inc.) using BuLi in tetrahydrofuran at −78 °C gave (**4**) [for complete formation of (**4**) the mixture was warmed to −40 °C then cooled to −78 °C]. Treatment of (**4**) with cyclohexanone gave (**5**) (73%, b.p. 61—67 °C at 0·15 mmHg), δ 0·18 (9H, s), 1·7—2·0 (10H, m), 2·48 (2H, d, $J_{\rm BX}$ 6 Hz), 5·87 (1H, d, $J_{\rm AB}$ 19 Hz), 6·32 (1H, m, $J_{\rm AB}$ 19 Hz, $J_{\rm BX}$ 6 Hz, ABX_2 system). It should be noted that only the γ-isomer is formed and that the resulting vinylsilane is the *E*-isomer, a result that contrasts with other allylanion systems.[2] Epoxidation of (**5**) [*m*-chloroperoxybenzoic acid (MCPBA) 0 °C in CH_2Cl_2] gave the $\alpha\beta$-epoxysilane (**6**) (94%) which, on mild acid treatment ($MeOH–BF_3.OEt_2$, 0 °C), gave the acetal (**7**, R = Me), whereas aqueous acid treatment of (**6**) gave the lactol (**7**, R = H).

Cyclopentanone reacts with (**4**) to give the adduct (77%, b.p. 55—58 °C at 0·05 mmHg), δ 0·18 (9H, s), 1·5—2·0 (8H, m), 2·21 (1H, s, OH), 2·48 (1H, d, $J_{\rm BX}$ 6 Hz), 5·81 (1H, d, $J_{\rm AB}$ 18·0 Hz), and 6·23 (1H, m, $J_{\rm AB}$ 18·0 Hz, $J_{\rm BX}$ 6 Hz, ABX_2 system), which on epoxidation (MCPBA, 0 °C, CH_2Cl_2) gave (**10**). Mild acid hydrolysis and Jones oxidation of (**10**) gave the lactone (**12**), $\nu_{\rm max}$ 1780 cm^{-1}. The epoxide (**10**) can be converted into (**12**) by treatment with acetic acid–hydrogen peroxide (30%)–sulphuric acid (conc., 3 drops). Furthermore the initial adducts (**5**) and (**9**) can be converted cleanly and rapidly into the lactones (**8**) and (**12**), respectively, by treatment with peracetic acid (30%; 3 equiv.) in acetic acid containing a few drops of sulphuric acid (conc.). A similar sequence of reactions, when applied to *p*-tolualdehyde, gave the lactone (**13**).



(13)

All new compounds gave satisfactory i.r. and n.m.r. spectra, and microanalytical and/or accurate mass spectral data in agreement with assigned structures.

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