A Simple, New Preparation of α,α-Dimethylallyltrimethylsilane: a Useful Prenylation Reagent

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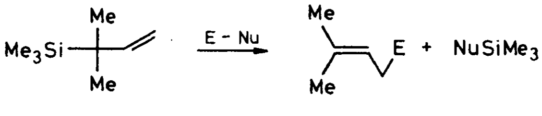
Summary Starting from 3-methylbut-1-yn-3-ol, a short synthesis of α,α-dimethylallyltrimethylsilane (a selective prenylation reagent) has been achieved in 47% overall yield; several other unsaturated organosilicon intermediates of wide potential utility in organic synthesis are also prepared.

THE ability of allylsilanes to induce regiospecific reactions explains the origin of the increasing number of reports concerning the utilization of these compounds as intermediates in organic synthesis. We have used allylsilanes widely and have shown that the trimethylsilyl group is cleaved by electrophiles such as acid chlorides with complete allylic rearrangement.[1] We have also described an expeditious route to the artemisyl skeleton starting from prenyltrimethylsilane,[2] and we expected that 3-trimethylsilyl-3-methylbut-1-ene (**1**) might behave as a prenylating reagent as depicted in Scheme 1.



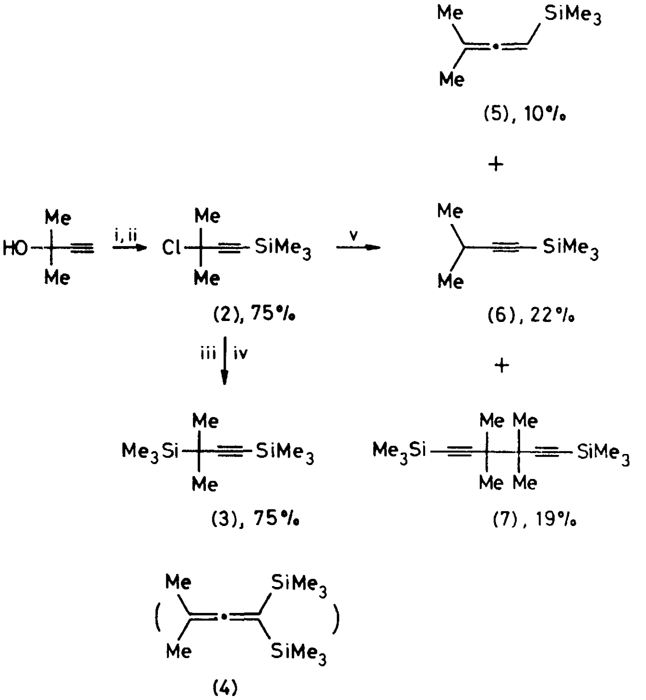
(1)

SCHEME 1

A recent report has described the synthesis and the addition of (**1**) to carbonyl compounds and acetals in the presence of $TiCl_4$ as catalyst,[3] demonstrating that this silylated compound (**2**) behaves as a useful and selective reagent for prenylation.

For our work on the applications of organosilicon derivatives in organic synthesis, we required a reasonable quantity of compound (**1**). From our initial attempts, the reported procedure,[3] involving as the first step the monosubstitution of one chlorine atom in trichlorosilane by one α,α-dimethylallyl moiety, appeared complicated (involving too many steps and large amounts of solvent). We report herein an original and highly efficient preparation of (**1**) in a few simple steps *via* the bistrimethylsilyl compound (**3**), starting from 3-methylbut-1-yn-3-ol which is commercially available and cheap. We have also synthesized several other silicon derivatives bearing allyl-, vinyl-, ethynyl-, or propynyl groups.[4] These compounds possess branched skeletons of five carbon atoms and can serve as potential intermediates for organic synthesis.

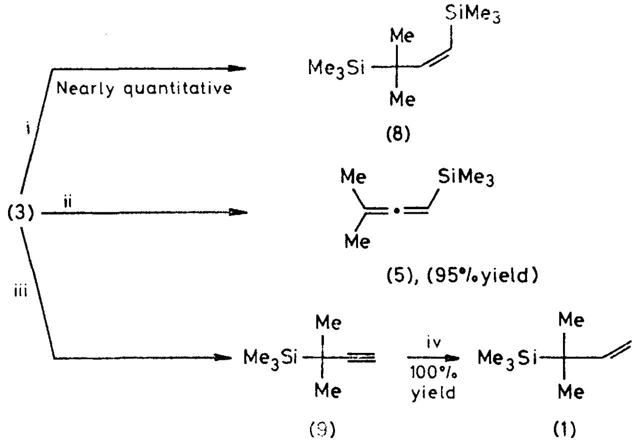
Acetylenic alcohols or their *C*-silylated derivatives[5] are readily chlorinated (in *ca.* 75% yield). We have shown that the Grignard reagent prepared from (**2**) can be silylated in fair yields (75%) to give 1,3-bis(trimethylsilyl)-3-methylbut-1-yne (**3**) which contains both prop-2-ynyl and ethynyl silicon groups; the allenic isomer (**4**) was not detected (Scheme 2).



Scheme 2. Reagents: i, EtMgBr (excess), Me_3SiCl, then hydrolysis; ii, conc. HCl; iii, Mg, tetrahydrofuran (THF), Me_3SiCl, room temp.; iv, H_3O^+; v, Mg, THF, then H_3O^+; composition of the mixture of (**5**)—(**7**) determined by n.m.r. spectroscopy.

Of particular interest is compound (**3**), which had previously been obtained by treatment of isopropylacetylene, a very expensive starting material, with a large excess of BuLi followed by silylation.[6] The key step in our method is the silylation of (**2**), as it permits us to introduce the desired trimethylsilyl group at the more substituted carbon atom; other methods employing allylic systems for instance would generally lead to the less substituted product as the major component.

The two silicon groups of (**3**) can be selectively cleaved under nucleophilic or electrophilic conditions to give, respectively, the prop-2-ynylsilane (**9**) or the allenylsilane (**5**) (Scheme 3).



Scheme 3. Reagents: i, Bu^i_2AlH, then mild hydrolysis; ii, CF_3CO_2H, 0 °C, 5 min; iii, aq. $AgNO_3$–KCN[7] (85% yield) or EtONa–EtOH (70% yield) at room temp.; iv, H_2/Pd–$BaSO_4$ + quinoline.

Reduction of (**9**) with di-isobutylaluminium hydride followed by mild hydrolysis, or hydrogenation in the presence of Lindlar catalyst, led directly to the desired α,α-dimethylallyltrimethylsilane (**1**).

3-Methylbut-1-yn-3-ol thus appears to be a convenient precursor of the three trimethylsilylated C_5 synthons (**1**), (**5**), and (**8**).

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[1] For a review see R. Calas, *J. Organomet. Chem.*, 1980, **200**, 11, and references cited therein.

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