Dehydrosilylation of Alkenylsilanes Utilizing Polyvalent Organoiodine Compounds

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Alkenylsilanes, on treatment with iodosylbenzene activated by co-ordination of boron trifluoride–diethyl ether to the oxygen atom, give the corresponding alkynes in good to excellent yields, presumably *via* vinyliodine(III) intermediates.

Hydrosilylation of alkynes utilizing transition metal catalysts such as hexachloroplatinic acid provides one of the major routes to vinylsilanes [(**1**) → (**2**)].[1] However, there are no efficient, direct methods for the reverse reaction, that is, dehydrosilylation of vinylsilanes to give the corresponding alkynes [(**2**) → (**1**)]. Halogenodesilylation of vinylsilanes affording vinyl halides is a well known process.[2] This reaction, when combined with the β-elimination of vinyl halides,[3] may provide a procedure for the dehydrosilylation of vinylsilanes. We now report a new iodine(III)-mediated β-elimination of vinylsilanes (**2**) to form alkynes (**1**).

Vinylsilanes readily react with a wide range of electrophiles to give substitution or addition products. Iodosylbenzene†

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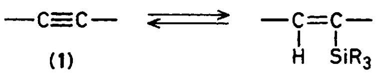
† It has been proposed that iodosylbenzene is polymeric, linked by I–O–I bonds.[4]

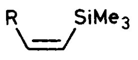
was shown not to react readily with vinylsilanes, but boron trifluoride–diethyl ether was found to be an effective catalyst for this reaction. When (*Z*)-1-trimethylsilyldec-1-ene (**3a**) was treated with iodosylbenzene (1.2 mol. equiv.) and BF_3–Et_2O (1 mol. equiv.) in dichloromethane at room temperature for 5 h, dehydrosilylation occurred and dec-1-yne was directly obtained in 99% yield. The dehydrosilylation also proceeded smoothly in benzene, dioxane, or acetonitrile in 87—90% yields, whereas reaction in diethyl ether or tetrahydrofuran resulted in the recovery of a large amount of (**3a**).

Similarly, (*Z*)-monosubstituted (**3b**—**d**) and (*E*)- and (*Z*)-α,β-disubstituted (**5**)[5] vinyltrimethylsilanes gave rise to terminal and internal alkynes, respectively, in good yields. However, (*E*)-monosubstituted vinylsilanes (**4**)[6] gave only a small amount of the corresponding alkynes directly. For the dehydrosilylation of (**4**), further treatment with base was found to be required; after treatment of (*E*)-1-trimethylsilyldec-1-ene (**4a**) with iodosylbenzene (1.2 mol. equiv.) and BF_3–Et_2O (1 mol. equiv.) in dichloromethane at room temperature for 19 h, g.l.c. showed the presence of small amounts of dec-1-yne (12%) and unchanged (**4a**) (41%). When the reaction mixture was treated with excess of aqueous sodium hydroxide at room temperature, the yield of dec-1-yne increased to 51%. By using 2.5 mol. equiv. of both iodosylbenzene and BF_3–Et_2O from the beginning of the reaction, a 98% yield of dec-1-yne was obtained after treatment of the reaction mixture with base. Similarly, (**4b**) and (**4c**) afforded the corresponding alkynes in 73 and 84% yields, respectively. The results are summarized in Table 1.

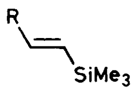
The boron trifluoride-catalysed dehydrosilylation of vinylsilanes using iodosylbenzene may occur through the replacement of the silyl group by the iodine(III) species, which is presumably an iodosylbenzene activated by the co-ordination of BF_3–Et_2O to the oxygen atom. The difference between the reactivity of the (*E*)- and (*Z*)-vinylsilanes (**3**) and (**4**) in the dehydrosilylation can be reasonably explained by the stereospecific formation of the (*E*)- and (*Z*)-vinyliodine(III) compounds (**6**) and (**7**), respectively, as intermediates (Scheme 1). In the protodesilylation or Friedel–Crafts acylation of alkenylsilanes, retention of the configuration was usually observed.[2] The successive *anti*-β-elimination of (*Z*)-(**6**) derived from (*Z*)-vinylsilanes (**3**) seems to proceed smoothly, with concomitant loss of iodobenzene, because iodine(III), in its hypervalent state, is known to be a good leaving group.[7] For the *syn*-β-elimination of (*E*)-(**7**) derived from (*E*)-(**4**), however,



(**1**) (**2**)

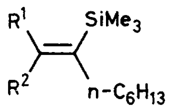


(**3a-d**)



(**4a-c**)

a; R = n-C_8H_{17}
b; R = Ph
c; R = $PhCH_2$
d; R = $Ph(CH_2)_2$

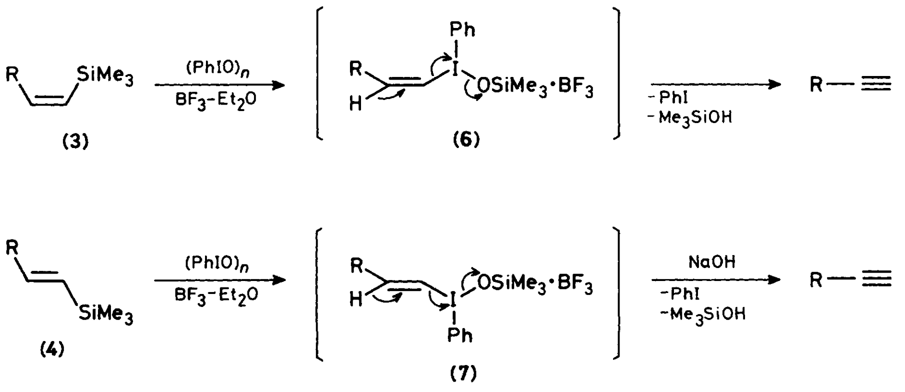


(**5a**) R^1 = n-C_6H_{13}, R^2 = H
(**5b**) R^1 = H, R^2 = n-C_6H_{13}

Table 1. Dehydrosilylation of alkenylsilanes using iodosylbenzene and BF_3–Et_2O in CH_2Cl_2 unless otherwise noted.

Alkenylsilane	Reaction time/h	Product	Yield[a]/%
(**3a**)	5	Dec-1-yne	99
(**3b**)	3	Phenylacetylene	61
(**3c**)[b]	5	3-Phenylprop-1-yne	85
(**3d**)[b]	5	4-Phenylbut-1-yne	85
(**4a**)[c,d]	3	Dec-1-yne	98
(**4b**)[c,d]	3	Phenylacetylene	73
(**4c**)[c,d]	2	3-Phenylprop-1-yne	84
(**5a**)[c]	2.5	Tetradec-7-yne	79
(**5b**)[c]	3	Tetradec-7-yne	52[e]

[a] Yields were determined by g.l.c. unless otherwise noted. [b] In MeCN. [c] 2—2.5 mol. equiv. of iodosylbenzene and of BF_3–Et_2O were used. [d] The reaction mixture was treated with excess of aqueous sodium hydroxide at room temperature as described in the text. [e] Isolated yield.



Scheme 1

the presence of an additional base may be required because of its unfavourable steric arrangement. In fact, *anti*-dehydrohalogenation of vinyl halides by using bases has been shown to be much faster than *syn*-β-elimination.[8]

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