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Preliminary communication

Palladium-catalyzed synthesis of silyl-substituted enynes

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Abstract

Treatment of 1-ethynyl-1-phenyltetramethyldisilane, ethynyldimethylphenylsilane and ethynylmethyldiphenylsilane with tetrakis(triphenylphosphine)palladium(0) at 100 °C gave the corresponding enyne by head-to-head coupling, as the single regioisomer in high yield. Ethynyl-substituted mono- and di-silanes that have no phenyl group on the ethynyl silicon atom, however, afforded the enynes only in low yields.

The C–H bond activation of 1-alkynes with a transition metal catalyst offers a convenient route to enynes which can be used as precursors for the synthesis of natural products. Many papers on the enyne synthesis by the direct coupling of 1-alkynes in the presence of a transition metal catalyst have been published to date [1–5]. Most of the papers, however, are concerned with head-to-tail coupling [2–5]. Up to now, no convenient route for head-to-head dimerization has been known, although the rhodium-catalyzed reaction of 1-alkynes bearing a 3-hydroxy group affords the products derived from head-to-head coupling in high yields [2]. In this paper, we report on the palladium-catalyzed dimerization of ethynyl-substituted mono- and di-silanes to give the enyne by head-to-head coupling, as a single regioisomer in high yields.

When a mixture of 1-ethynyl-1-phenyltetramethyldisilane (I) [6] and a catalytic amount of tetrakis(triphenylphosphine)palladium(0) (7 mol%) was heated in benzene at 100 °C for 20 h in a sealed glass tube, (*E*)-1,4-bis(phenyltetramethyldisilanyl)but-3-ene-1-yne (II) was obtained in 65% yield as the sole volatile product.

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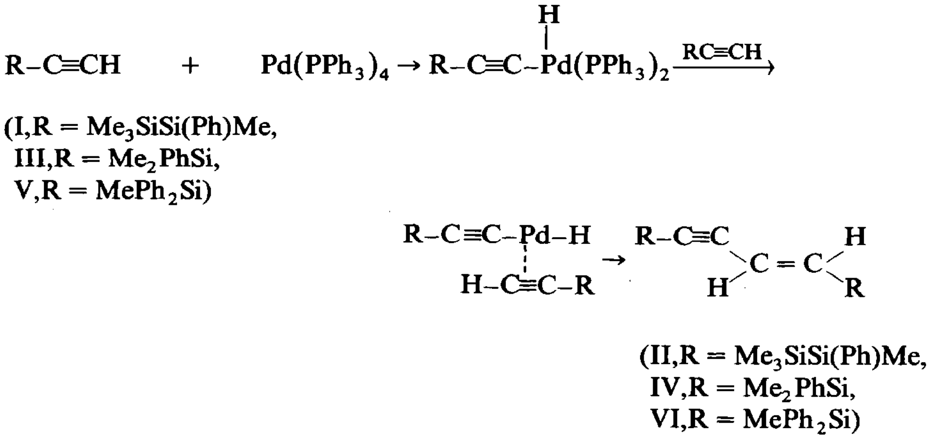
No regio- and stereo-isomers were detected in the reaction mixture by either VPC or spectrometric analysis. The structure of the product II was confirmed by IR, mass and ^{1}H and ^{13}C NMR spectrometry *. The proton coupling constant (J 20 Hz) at δ 6.02 and 6.66 ppm, due to olefinic protons for II clearly indicates that II must have the (E)-configuration. The IR spectrum of II shows strong absorptions at 2150 cm^{-1}, attributable to the stretching vibration of a carbon–carbon triple bond.

Ethynyl-substituted phenylmonosilanes can also be used as convenient precursors for enyne synthesis. Thus, when ethynyldimethylphenylsilane (III) is heated in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) at 100 ° C for 20 h, (E)-1,4-bis(dimethylphenylsilyl)but-3-ene-1-yne (IV) ** can be isolated in 50% yield as the sole volatile product. Similarly, reaction of ethynylmethyldiphenylsilane (V) with a catalytic amount of palladium complex also gave VI but in 62% yield. In both cases, no other volatile products were detected by either VPC or spectroscopic analysis. Products, II, IV and VI were readily isolated by LPC.

Scheme 1 shows a possible mechanism. The mechanism involves the insertion of a palladium(0) complex into an acetylenic C–H bond leading to a palladium(II) intermediate, followed by regiospecific addition of the palladium hydride across the triple bond of the coordinated ethynylsilane and finally reductive elimination takes place.

Scheme 1



(I,R = Me$_3$SiSi(Ph)Me,
III,R = Me$_2$PhSi,
V,R = MePh$_2$Si)

(II,R = Me$_3$SiSi(Ph)Me,
IV,R = Me$_2$PhSi,
VI,R = MePh$_2$Si)

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* Compound II: ^{1}H NMR 0.11 (18H, s, Me$_3$Si), 0.31 (3H, s, MeSi), 0.35 (3H, s, MeSi), 6.02 (1H, d, J 20 Hz, HC=C), 6.66 (1H, d, J 20 Hz, HC=C), 7.17–7.68 (10H, m, phenyl ring protons); ^{13}C NMR −5.9, −4.1, −2.3, −1.9 (C–Si), 91.7, 109.2 (C≡C), 125.1 (C=C), 128.0 (2C), 128.8 (2C), 134.1, 134.4, 135.9, 136.4 (phenyl ring carbons), 143.6 (C=C); IR: ν(C≡C) 2150 cm^{-1}; mass m/e 436 (M^+).

** Compound IV: ^{1}H NMR 0.38 (6H, s, Me$_2$Si), 0.43 (6H, s, Me$_2$Si), 5.90 (1H, d, J 19 Hz, HC=C), 6.59 (1H, d, J 19 Hz, HC=C), 7.21–7.64 (10H, m, phenyl ring protons); ^{13}C NMR −0.30, −0.9 (C–Si), 93.4, 106.7 (C≡C), 125.0 (C=C), 127.7, 127.9, 129.3, 129.4, 133.7, 133.9, 136.9, 137.1 (phenyl ring carbons), 145.1 (C=C); IR: ν(C≡C) 2160 cm^{-1}; mass m/e 320 (M^+). Compound VI: ^{1}H NMR 0.63 (3H, s, MeSi), 0.69 (3H, s, MeSi), 5.93 (1H, d, J 19 Hz, HC=C), 6.75 (1H, d, J 19 Hz, HC=C), 6.96–7.66 (20H, m, phenyl ring protons); ^{13}C NMR −4.1, −2.1 (C–Si), 92.3, 108.0 (C≡C), 126.8 (C=C), 127.9 (2C), 129.7 (2C), 133.9, 134.5, 134.8, 135.1 (phenyl ring carbons), 143.3 (C=C); IR: ν(C≡C) 2160 cm^{-1}; mass m/e 444 (M^+).

In the present system, the introduction of at least one phenyl group to the ethynylsilicon atom is very important for obtaining the enynes in high yields. In fact, ethynyl-mono- and -di-silanes that have no phenyl group on the ethynylsilicon atom gave the enynes, only in low yields. For example, ethynyltrimethylsilane and ethynylpentamethyldisilane underwent head-to-head coupling under the same conditions, to give the enynes in 3 and 22% yields, respectively. The formation of large amounts of unidentified non-volatile substances was observed in these reactions.

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