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FLUORINATED POLYSILANES. PALLADIUM CATALYZED 1,4-ADDITION OF FLUORODISILANES TO CONJUGATED DIENE AND ENONE SYSTEMS

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Summary

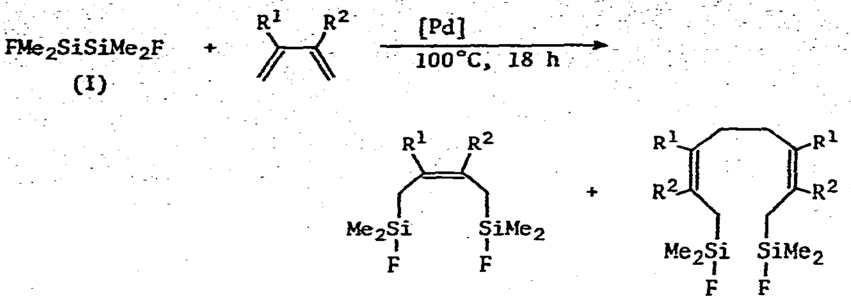
In the presence of palladium complexes as catalysts, fluorinated disilanes add to 1,3-dienes, methyl vinyl ketone and *p*-benzoquinone to give mainly 1,4-addition products.

Introduction

Novel reactivities of the silicon-silicon bond of fluorinated disilanes have recently been recognized [1]. In our previous paper [1] describing the double silylation of acetylenes and the disilane metathesis catalyzed by palladium complexes, we pointed out that there is some similarity in reactivity toward palladium complexes between strained electron-rich Si-Si compounds and those which are strain-free but electron-deficient. The addition of strained Si-Si compounds to 1,3-dienes has been reported recently by Sakurai et al. [2]. In the present report, we describe 1,4-addition reactions of 1,2-difluorodisilanes to conjugated systems such as 1,3-dienes, methyl vinyl ketone and *p*-benzoquinone. Results obtained with the last two afford the first examples of palladium-catalyzed addition of an organosilicon compound across the conjugated enone systems.

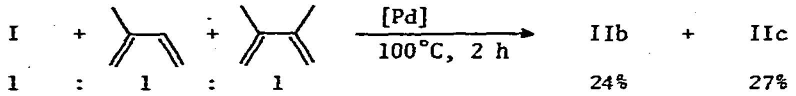
Results and discussion

Reactions are carried out in degassed sealed glass tubes. Addition reactions of 1,2-difluorotetramethyldisilane (I) [3] to 1,3-dienes (molar ratio ca. 1/2) proceeded smoothly at 100°C in the presence of $Pd(PPh_3)_2Cl_2$ or $Pd(PPh_3)_4$ as a catalyst (ca. 1 mol%), as shown by the following equation.

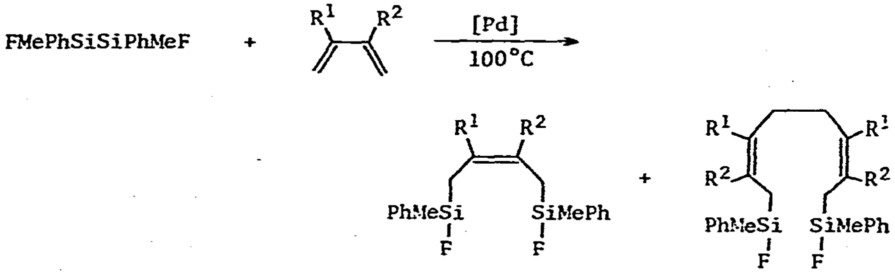


(II)	(III)
a, $R^1=R^2=H$ (73%)	a, (23%)
b, $R^1=Me$, $R^2=H$ (66%)	b, (25%)
c, $R^1=R^2=Me$ (97%)	c, (0%)

There is no significant difference in the reactivities of isoprene and 2,3-dimethyl-1,3-butadiene toward fluorinated disilane I, as shown by the following competition reaction:

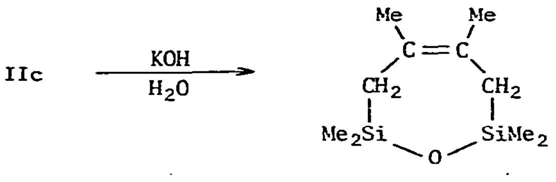


1,2-Difluoro-1,2-dimethyl-1,2-diphenyldisilane, prepared by heating the corresponding chloride [4] with zinc fluoride in the absence of solvent, also was found to react with 1,3-butadienes.



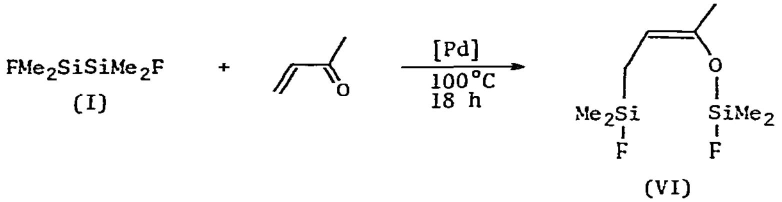
(IV)	(V)
a, $R^1=Me$, $R^2=H$ (43%)	a, (43%)
b, $R^1=R^2=Me$ (76%)	b, (0%)

Novel features of the present reaction are: (1) A highly selective 1/1 addition was observed. In particular, 2,3-dimethyl-1,3-butadiene gave exclusively 1/1 addition products. These results contrast with the selective formation of 1/2 addition products of types III and V in the palladium-catalyzed reaction of rather electron-rich disilanes with 1,3-dienes [2]. (2) The 1,4-addition is highly stereoselective. IIa has a *Z* configuration characterizable by its IR spectrum (no band around 965 cm^{-1}) while IIIa consists of a mixture of isomers. The Z configuration of IIc could be confirmed by its conversion by alkaline hydrolysis to a known cyclic siloxane [5].



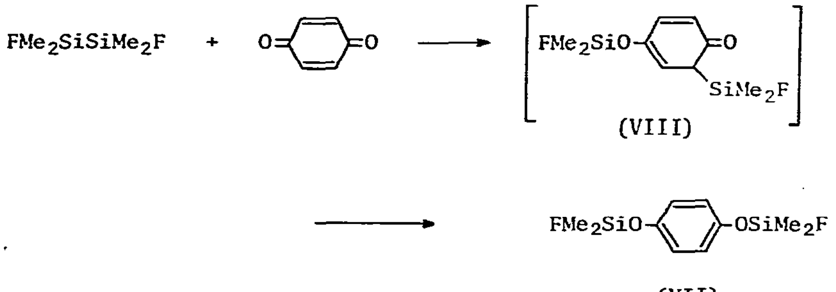
Therefore, it seems reasonable to assign the Z configuration to products IIb and IV. (3) A regioselective head-to-head coupling of diene moieties was observed for the 1/2 addition products III and V [2]. (4) Palladium-(II) and -(0) complexes exhibited essentially the same catalytic activity, which contrasts with Sakurai's observations [2].

Under similar conditions, disilane I added to methyl vinyl ketone to give a 1,4-addition product (VI) selectively, possibly with Z configuration, in 81% yield.



(VI)

p-Benzoquinone also reacted with I under the same conditions, except that benzene was used as solvent, to form *p*-bis(fluorodimethylsiloxy)-benzene (VII) in 41% yield. It seems reasonable to consider that a 1,4-addition product (VIII) may occur initially and that subsequent migration of the silyl group from carbon to oxygen gives rise to the observed product as a result of the large energy gain due to the aromatization and Si-O bond formation. Such a silyl group migration is characteristic of α-silyl ketones [6]. Alternatively, a direct 1,6-addition is also possible. These two mechanisms can not be distinguished at the present time.



(VII)

TABLE 1

^{1}H NMR SPECTRAL AND ANALYTICAL DATA OF REACTION PRODUCTS I - VII

Compound	^{1}H NMR (δ, ppm)[a]	Analysis, found (calcd.) C(%)	H(%)
IIa	0.10 (d, 12H, J=7.5), 1.60 (t, 4H, J=6.5), 5.23 (t, 2H, J=6.5)	46.40 (46.11)	8.74 (8.71)
IIb	0.08 (d, 6H, J=7.5), 0.12 (d, 6H, J=7.5), 1.40 (t, 2H, J=7.0), 1.54 (d, 2H, J=7.0), 1.67 (br. s, 3H), 6.06 (t, 1H, J=7.0)	49.24 (48.60)	9.26 (9.06)
IIc	0.10 (d, 12H, J=7.5), 1.50 (d, 4H, J=8.0), 1.59 (s, 6H)	51.06 (50.80)	9.68 (9.38)
IIIa[b]	0.08 (d, 12H, J=7.5), 1.45 (triplet like m, 4H), 1.96 (br., 4H), 5.24 (triplet like m, 4H)	54.63 (54.91)	9.34 (9.22)
IIIb	0.05 (d, 12H, J=7.5), 1.40 (triplet like m, 4H), 1.48 (s, 6H), 2.00 (s, 4H), 5.08 (t, 2H, J=7.5)	57.65 (57.88)	9.81 (9.71)
IVa	0.40 (d, 3H, J=7.5), 0.43 (d, 3H, J=7.5), 1.65 (s, 3H), 1.76 (d, 4H, J=8.0), 5.10 (t, 1H, J=8.0), 7.20-7.55 (m, 10H)	65.46 (65.85)	6.88 (6.98)
IVb	0.55 (d, 6H, J=7.5), 1.76 (s, 6H), 1.85 (d, 4H, J=8.0) 7.35-7.70 (m, 10H)	66.52 (66.62)	7.17 (7.27)

TABLE 1 (continued)

Compound	^{1}H NMR (δ, ppm)[a]	Analysis, found (calcd.)	
		C(%)	H(%)
Va	0.45 (d, 6H, J=7.5), 1.50 (s, 6H), 1.82 (triplet like m, 4H), 2.04 (s, 4H), 5.16 (t, 2H, J=8.0), 7.2-7.65 (m, 10H)	70.24 (69.51)	7.55 (7.78)
VI[c]	0.07 (d, 6H, J=7.5), 0.15 (d, 6H, J=6.0), 1.41 (br., 2H), 1.77 (s, 3H), 4.38 (t, 1H, J=8.0)	43.03 (42.82)	8.26 (8.09)
VII	0.10 (d, 12H, J=6.0), 6.62 (s, 4H)	45.99 (45.77)	6.31 (6.15)

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[a] 100 MHz, CCl_4, TMS. Coupling constants are given in Hz. [b] A *cis* and *trans* mixture.

[c] IR spectrum (neat); 1682 cm^{-1} (enol ether).

The mechanism proposed for the palladium-catalyzed hydrosilylation of 1,3-dienes [7] may apply to the present double silylation of dienes. The double silylation of *p*-benzoquinone may resemble mechanistically the reductive addition of various covalent compounds to a quinone coordinated to a palladium(0) complex, as reported by Ugo *et al.* [8].

The present reactions provide a new method for the introduction of silicon-functional groups into various types of conjugated systems. Investigations are continuing into the extention of these novel reactions of fluorinated polysilanes to other unsaturated compounds.

Experimental

^{1}H NMR spectra were recorded on a JEOL Model MH 100 spectrometer in carbon tetrachloride solution with TMS as internal standard and IR spectra were measured on a Hitachi EPI-G3 grating spectrophotometer. A Varian Aerograph Model 920 equipped with a 3 or 6 m column packed with Silicone DC 550 (30%) on Celite 545 was used for the purification of products.

Preparation of fluorodisilanes

1,2-Difluorotetramethyldisilane (I) was prepared according to the method reported previously [3].

1,2-Difluoro-1,2-dimethyl-1,2-diphenyldisilane. Under a nitrogen atmosphere, a mixture of 12 g (38.6 mmol) of 1,2-dichloro-1,2-dimethyl-1,2-diphenyldisilane [4] and 12 g (142 mmol) of zinc fluoride tetrahydrate was heated at 50-60°C for 0.5 h. The resulting upper layer was separated and distilled under reduced pressure to give a colorless crystalline product, 6 g (54% yield), bp 106°C/3 torr, m.p. 59-62°C. In the ^{1}H NMR spectrum, the methyl protons appear as a complex multiplet owing to the symmetrical multi-spin systems and a mixture of *meso* and *dl* isomers; δ (ppm) 0.5-0.72 (m, 6H), 7.23-7.57 (m, 10H). (Found: C, 60.15; H, 5.85. $C_{14}H_{16}F_2Si_2$ calcd.: C, 60.39; H, 5.79%.)

Reactions of fluorodisilanes

$Pd(PPh_3)_2Cl_2$ [9] and $Pd(PPh_3)_4$ [10] were prepared according to the established method.

A difluorodisilane, an unsaturated substrate and a palladium catalyst were combined in a glass tube. The mixture was degassed by means of three freeze-degas-thaw cycles. After degassing, the tube was sealed at the constriction, heated at 100°C for 18 h, cooled to -78°C, and then opened. Yields of the products were determined by GLC using an internal standard. For the isolation of the product, the mixture was filtered, flash-distilled, and then subjected to preparative GLC. Products were characterized by ^{1}H NMR and IR spectra and elementary analysis (see Table 1).

Alkaline hydrolysis of IIc

To a solution of IIc (0.42 g) in ether was added a ca. 0.1 *M* aqueous solution of potassium hydroxide at 0°C with stirring. After additional stirring at room temperature for 0.5 h, the organic layer was separated, washed with water, dried and evaporated to give essentially pure cyclic siloxane (0.34 g), 2,2,4,5,7,7-hexamethyl-1-oxa-2,7-disilacyclohept-4-ene; δ (ppm), 0.06 (s, 12H), 1.47 (s, 4H), 1.69 (s, 6H) [5].

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