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Preliminary communication

A NOVEL DOUBLE SILYLATION OF DIMETHYL ACETYLENEDICARBOXYLATE CATALYZED BY PHOSPHINEPALLADIUM(II) COMPLEXES*

HIROSHIGE OKINOSHIMA, KEIJI YAMAMOTO and MAKOTO KUMADA**
Department of Synthetic Chemistry, Kyoto University, Kyoto 606 (Japan)

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Symmary

A novel double silylation of dimethyl acetylenedicarboxylate using disilicon hydrides and phosphinepalladium(II) complexes as catalysts is reported. This reaction constitutes a third type of trapping of dimethylsilylene with an acetylenic compound.

We have previously reported a facile disproportionation reaction of disilicon hydrides into the homologous members of polysilanes that is effected by a catalytic amount of phosphine-platinum or -nickel complexes [1,2]. Evidence for intervention of a "silylenoid" species has been presented by trapping it with added diphenylacetylene or related compounds. Thus with a platinum catalyst and diphenylacetylene the tetraphenyl derivative of 1,4-disilacyclohexadiene was obtained [1b], whilst in the case of a nickel catalyst with certain of disubstituted acetylenes the respective derivatives of silacyclopentadiene were produced in high yields [2].

The observed difference in the role of metal complexes in the presence of acetylenic compounds prompted us to investigate the palladium-catalyzed reaction of *sym*-tetramethyldisilane or pentamethyldisilane with an added acetylene. We now report a novel double silylation of dimethyl acetylenedicarboxylate using disilicon hydrides and phosphinepalladium complexes as catalyst. This constitutes a third type of dimethylsilylene trapping with an acetylenic compound.

A mixture of 0.70 g (5.9 mmol) of *sym*-tetramethyldisilane (Ia), 0.70 g (5.9 mmol) of dimethyl acetylenedicarboxylate (II), and 1 mg (2.4×10^{-3} mmol) of $PdCl_2(PEt_3)_2$, dissolved in 5 ml of dry benzene, was heated to reflux for 2 h under a nitrogen atmosphere. After removal of solvent from the result-

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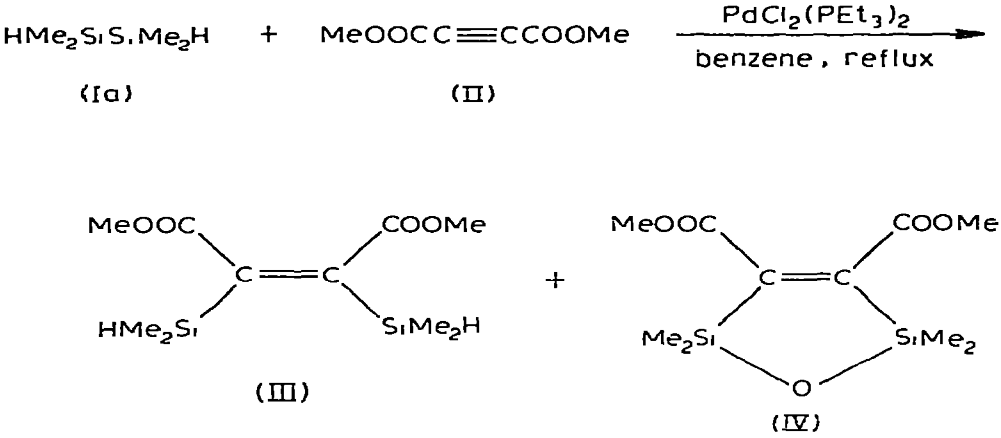
[**] To whom correspondence and requests for reprints should be addressed.



(1)

ing deep-red solution under reduced pressure, the residue was distilled to give 0.56 g (40% yield) of dimethyl α,α'-bis(dimethylsilyl)maleate (III) and a small amount of cyclic disiloxane (IV) (eqn. 1). Similarly, a reaction with pentamethyldisilane (Ib) gave dimethyl α-trimethylsilyl-α'-dimethylsilylmaleate (V) in 43% yield along with 7% yield of dimethyl α-pentamethyldisilanylmaleate (VI).

When another catalyst $PdCl_2(PPh_3)_2$ was used, III was obtained in 20% yield from Ia, while V and VI were produced from Ib in 52 and 8% yield, respectively. All new compounds, III, IV, V, and VI gave satisfactory elemental analyses, and their IR and NMR spectral data are in accord with assigned structures (Table 1).

TABLE 1

NMR AND IR SPECTRAL DATA FOR THE COMPOUNDS III-VIII AND IX

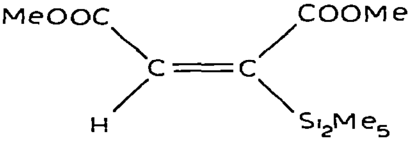
Compound	NMR [a] δ (ppm)					IR (cm^{-1})	
	C=CH	SiH	OMe	$SiMe_2$	$SiMe_3$	(C=O)	(Si—H)
III		4.27 (sep)	3.62 (s)	0.32 (d)		1740	2150
IV [b]			3.56 (s)	0.38 (s)		1730	—
V		4.35 (sep)	3.63 (s)	0.29 (d)	0.27 (s)	1730	2163
VI	5.97 (s)		3.68 (s) 3.71 (s)	0.21 (s)	0.12 (s)	1730	—
VII [c]	6.07 (s)		3.75 (s)	0.29 (s)		1730	—
VIII	5.94 (s)		3.68 (s) 3.71 (s)		0.21 (s)	1730	—
IX	6.58 (s)		3.70 (s)		0.21 (s)	1730	—

[a] s, singlet; d, doublet; sep, septet; coupling constant $J(H-Si-CH_3)$ 4 Hz. [b] IR: 945s cm^{-1} ((Si—O—Si)). [c] NMR δ (ppm) 1.17 (q, OCH_2CH_3, J 7 Hz), and 1.19 (t, OCH_2CH_3, J 7 Hz).

Attempted reactions of hexamethyldisilane with II in the presence of either palladium complex failed to occur under the conditions employed.

It is noticeable that the double silylation of the acetylene yields only *cis*-adducts. Formation of IV is attributable to hydrolysis of III by a trace of water in the starting material. In fact, IV was obtained in 80% yield by treating III with water in the presence of excess II and $PdCl_2(PEt_3)_2$ as catalyst, indicating unequivocally the *cis*-configuration of III.

The observed reactions between a disilicon hydride (Ia or Ib) and acetylenic compound II with a phosphinepalladium(II) catalyst are again likely to involve the generation of dimethylsilylene species, which is effectively trapped by the added acetylene. The resulting highly reactive "silacyclopropene", if not isolated [3,4], would be very sensitive to an attack of dimethylsilane or trimethylsilane, formed as a result of the silylene elimination, to afford *cis*-adduct III or V, respectively.



(VI)

The latter reaction is reminiscent of alcoholysis of the silacyclopropene* and silacyclopropane derivatives [6-8]. Accordingly, an equimolar mixture of Ib and II, dissolved in ethanol/benzene, was heated to reflux in the presence of the $PdCl_2(PPh_3)_2$ catalyst. Dimethyl α-ethoxydimethylsilylmaleate (VII), dimethyl α-trimethylsilylmaleate (VIII) and -fumarate (IX) were obtained in a 4/4/3 ratio, and in 60% combined yield. No double-silylation products could be detected. The IR and NMR spectral data for VII, VIII, and IX are also given in Table 1.

It should be noted that without an added acetylene the reaction of Ib leads to formation of diethoxydimethylsilane and ethoxytrimethylsilane with concomitant evolution of hydrogen under the same conditions [9]. The formation of VII, therefore, may well be implicated with the intervention of the silacyclopropene species. After this investigation had been completed, a similar palladium complex-catalyzed double silylation of acetylenes using certain of hexaorganodisilanes and 1,1,2,2-tetramethyl-1,2-disilacycloalkanes was reported by Sakurai et al., who proposed a mechanism involving bis(triorganosilyl)metal intermediates [10].

The fate of the silacyclopropene intermediates seems to be dependent highly on the nature of added acetylenes. When phenylacetylene was added in place of II in the aforementioned reaction of Ia, 1,1-dimethyl-3,4-diphenyl-1-silacyclopentadiene (X) was obtained in 45% yield along with a doubly silylated styrene derivative in 25% yield (eqn. 2).

The new compound X is hardly accessible by other reaction systems

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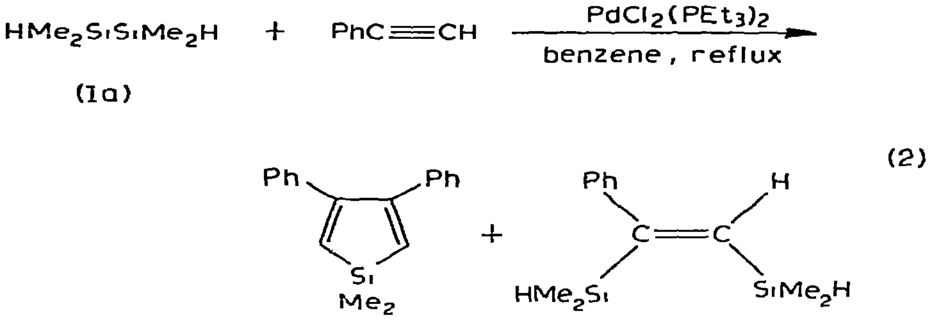
*Atwell and Weyenberg have found that the reactive intermediate, silacyclopropene, reacts with methanol to afford an alkoxysilylalkene, with ring-opening [5].



(2)

(X)

than the present palladium-catalyzed one. The results of our further work in this respect will be reported in due course.

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