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CATALYZED HYDROSILYLATION OF 2-METHYL-1-BUTEN-3-YNE WITH METHYLDICHLOROSILANE; PROMOTIONAL EFFECT IMPARTED BY THE PRESENCE OF A DIFFERENT CHLOROSILANE

Maurizio Licchelli and Alberto Greco
ENICHEM SINTESI S.p.A. - R&D Laboratories
Via Maritano 26, 20097 San Donato Milanese, Milan, Italy

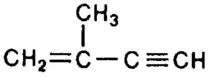
Abstract: Chloroplatinic acid catalyzed hydrosilylation of 2-Methyl-1-buten-3-yne with chlorosilanes is reinvestigated; the results can't be satisfactorily explained by Chalk and Harrod mechanism.

Alkene and alkyne hydrosilylation promoted by chloroplatinic acid or platinum organometallics is now explained on the basis of the commonly accepted coordinative mechanism proposed by Chalk and Harrod[1-3]. This mechanism involves the coordination of alkene or alkyne on a Pt (II), followed by oxidative addition of the silane to the metal to give a Pt (IV); this species is able to rearrange reversibly to a σ bonded Pt (IV) which can split the hydrosilylation product and regenerate the original Pt (II).

In an attempt to prepare some silicon-organics we reinvestigated the hydrosilylation of 2-Methyl-1-buten-3-yne (**1**)[4] with chlorosilanes[5], a reaction already described by Greber for the case of chlorosilane **2c**[6]; Greber however did not give in his work the experimental conditions in detail, for instance temperature and (Pt) concentration. For hydrosilylation of **1**, we adopted $H_2PtCl_6.6H_2O$ in isopropanol as catalyst[7,8] and the typical hydrosilylation conditions specified in Table 1. Quite surprisingly any attempt to hydrosilylate **1** with **2b** at molar ratio **2b**:**1** = 1:1, in normal conditions or with a higher level of catalyst, failed (exp. 1 and 2 of Table 1); but when we tried the hydrosilylation of **1** with a mixture of **2a** and **2b** at a molar ratio **1**:**2a**:**2b** = 1:1:1, it occurred normally, giving the monosilylated products 3-Methyl-1-trichlorosilyl-trans-buta-1,3-diene (**3a**) and 3-Methyl-1-Methydichlorosilyl-trans-buta-1,3-diene (**3b**) in a ratio **3a**:**3b** = 1:4 (exp. 3 of Table 1)[9]; the expected product (**3a**) was only formed in a minor proportion.

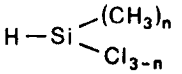
With a different behaviour from **2b**, **2a** and **2c** reacted with **1** in a molar ratio **2**:**1** = 1:1, regularly giving the expected products **3a** and **3c**[10] (exp. 4 and 5 of Table 1).

The unexpected result obtained in the synthesis of **3b** pushed us to attempt the hydrosilylation of **1** with a mixture of **2b** and **2c** in a molar ratio **1**:**2b**:**2c** = 1:1:1, still



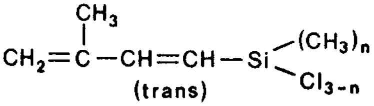
$CH_2=C(CH_3)-C\equiv CH$

1



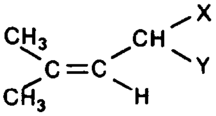
$H-Si(CH_3)_nCl_{3-n}$

n = 0 : **2a**
n = 1 : **2b**
n = 2 : **2c**



$CH_2=C(CH_3)-CH=CH-Si(CH_3)_nCl_{3-n}$ (trans)

n = 0 : **3a**
n = 1 : **3b**
n = 2 : **3c**



$X = Y = SiCH_3Cl_2$: **4a**
$X = Y = Si(CH_3)_2Cl$: **4b**
$X = SiCH_3Cl$; $Y = Si(CH_3)Cl$: **4c**

mantaining unchanged experimental condition. Once again hydrosilylation worked well, but, in this case, double addition occurred and 1-bis (Methylchlorosilyl)-3-Methyl-2-butenes **4a**, **4b** and **4c** were produced in the ratio 18:29:53 (exp. 6 of Table 1)[11].

The reluctance of **2b** to hydrosilylate **1** and the results we got by using chlorosilanes in couple cannot be explained by Chalk and Harrod coordinative mechanism. Particularly chlorosilanes reactivity seems to follow the order $HSiMe_2Cl > HSiMeCl_2 > HSiCl_3$, which is the opposite of that commonly found[2, 12].

Our results suggest that, also in presence of soluble transition metals, hydrosilylation requires an "initial push" to be performed. We carried out the following experiments to check our hypothesis:

i) **1** was hydrosilylated with **2b** in presence of H_2PtCl_6 and a very small amount of benzoylperoxide. The reaction afforded the expected product **3b**[13] (exp. 7 of Table 1).

ii) **1** was hydrosilylated with **2b** in the presence of H_2PtCl_6 and a very small amount of **2a**; yet practically pure **3b** was obtained (exp. 8 of Table 1).

iii) **2a** was used in the presence of H_2PtCl_6 for hydrosilylation of divinylbenzene (DVB), a substrate very sensitive towards radicals. In this case polymer was always produced[14].

We think that hydrosilylation of **1** is promoted by radicals which probably operate in the transition metal environment.

When chlorosilane/H_2PtCl_6 system is used, radicals can be produced by H-Si splitting; silicon radicals generation seems to be the rate determining step of reaction.

If chlorosilanes are used in couple, the main hydrosilylation product is determined by the relative reactivity of two different silicon radicals towards **1**. Now we are working to collect other experimental proofs which support our hypothesis.

TABLE 1 - Hydrosilylation of **1** catalyzed by H_2PtCl_6 [a]

Exp. n°	Molar ratios				Products
	2a/1	**2b/1**	**2c/1**	catal./**1**	
1	-	1	-	10^{-5}	-
2	-	1	-	10^{-3}	-
3	1	1	-	$1.25\ 10^{-4}$	**3a** (20%), **3b** (80%)
4	1	-	-	$1.25\ 10^{-4}$	**3a**
5	-	-	1	$1.25\ 10^{-4}$	**3c**
6	-	1	1	$1.25\ 10^{-4}$	**4a**(18%),**4b**(29%),**4c**(53%)[b]
7[c]	-	1	-	$1.25\ 10^{-4}$	**3b**
8	10^{-1}	1	-	$1.25\ 10^{-4}$	**3b**

[a] Reactions were normally carried out with 0.08 mol of **1** in sealed tubes at 80°C for 6 hours under magnetic stirring. [b] GC results. [c] Hydrosilylation in presence of benzoyl peroxide (moles peroxide/moles **1** = 10^{-3}), 18 hours.

References and notes

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2. J.L. Speier, Advances in Organometallic Chemistry, 17, 407, (1979) and references quoted therein.
3. M. Green, J.L. Spencer, F.G.A. Stone, C.A. Tsipis, J. Chem. Soc. Dalton, 1977, 1519 and 1977, 1525.
4. (1) was prepared by dehydrating ethynyl-dimethyl-carbinol with p-toluene sulfonic-acid; see W.H. Carothers and D.D. Coffmann, J. Am. Chem. Soc., 54 (1932), 4071.
5. Commercial chlorosilanes were used without further purification.
6. G. Greber, Makrom. Chemie, 53, (1962), 192.
7. The catalyst was prepared according to Speier ; see J.L. Speier, J.A. Webster and G.H. Barnes, J. Am. Chem. Soc. 79, (1957), 974.

8. R.A. Benkeser and J. Kang, J. Organomet. Chem., 185, (1980), C9.
9. The 3a-3b mixture (total yield 70%) gave pure 3b after repeated distillation (b.p. 43°C at 10 torr). IR (film):νSi-CH$_3$ 1255 cm.$^{-1}$ ^{1}H-NMR (60 MHz, C_6D_6): δ = 0,6, s, 3 H (-Si-CH$_3$); 1,6, s, 3 H (=C-CH$_3$);5.0, s broad, 2 H (CH$_2$=C); 5.7, d, 1 H, J = 16 Hz (-CH=CH-trans); 6.8, d, 1 H, J = 16 Hz (-CH=CH-trans).
10. 3a (yield 65%) and 3c (yield 80%) were characterized without further purification after stripping of unreacted products.
    ^{1}H-NMR (60 MHz, CDCl$_3$); 3a: δ = 1.9, s, 3 H (=C-CH$_3$); 5.4, s broad, 2 H (CH$_2$=C); 5.9, d, 1 H, J = 18 Hz (-CH=CH-trans); 7.1, d, 1 H, J = 18 Hz (-CH=CH-trans);
    3c: δ = 0.4, s, 6 H (Si-(CH$_3$)$_2$); 1.8, s, 3 H (=C-CH$_3$); 5.1, s broad, 2 H (CH$_2$=C); 5.8, d, 1 H, J = 17 Hz (-CH=CH-trans); 6.7, d, 1 H, J = 17 Hz (-CH=CH-trans).
11. The mixture was distilled (b.p. 57-59°C at 0,1 torr) but we did not succeed in separating the products.
    The composition was determined by GLC analysis (siliconic columns were used) which was carried out onto methoxy-derivatives obtained by treating the mixture with MeOH + propilene-oxide. Identity of components was proved by mass-spectra. ^{1}H-NMR (100 MHz, CDCl$_3$), 4c: δ = 0,5, s, 6 H (Si-(CH$_3$)$_2$); 0.8, s, 3 H, (Si-CH$_3$); 1.6, s, 3 H (CH$_3$-C=); 1,8, s, 3 H (CH$_3$-C=); 2,1, d, 1 H, J = 6 Hz (=C-CH$<$); 5.1, d, 1 H, J = 6 Hz ($>$C=CH-).
12. M. Copka, P. Svoboda, V. Bazant, V. Chvalovsky, Coll. Czech. Chem. Comm., 36, (1971), 2785.
13. 3b (yield 75%) was purified by distillation (b.p. 44°C at 10 torr). ^{1}H-NMR (60 MHz, CDCl$_3$): δ = 0.8, s, 3 H (Si-CH$_3$); 1.8, s, 3 H (CH$_3$—C=); 5.2, s broad, 2 H, (H$_2$C=C); 5.9, d, 1 H, J = 17 Hz (-HC=CH-trans); 7.0, d, 1 H, J = 17 Hz (-CH=CH-trans).
14. The addition of 2a to DVB gave, even at 30°C , a very fast exothermic reaction which produced in few minutes a highly insoluble polymer.

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