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THE STEREOSELECTIVE ADDITION OF PHENYLDIMETHYLSILANE TO PHENYLACETYLENE CATALYZED BY RHODIUM TRIPHENYLPHOSPHINE COMPLEXES

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Summary

Tris(triphenylphosphine)chlororhodium was found to be an effective catalyst for the hydrosilylation of phenylacetylene. Trans addition of phenyldimethylsilane gave cis products, but concomitant cis addition leading to trans products occurred to some extent. Under certain conditions, complete isomerization of the cis to the trans isomer of the product was also observed during the hydrosilylation.

In the hydrosilylation employing bis(triphenylphosphine)-carbonylchlororhodium as catalyst the stereoselective reaction proceeded at faster rates than those using the above rhodium complex and no isomerization occurred.

Introduction

The hydrosilylation of acetylene, catalyzed by peroxide, platinum, chloroplatinic acid or bases, has been studied extensively by many workers over a period of years [1]. Benkeser and co-workers [2,3] reported that the addition of trichlorosilane to alkylacetylenes, catalyzed by platinized charcoal or chloro-

Table 1

ADDITION OF PHENYLDIMETHYLSILANE TO PHENYLACETYLENE WITH RHODIUM TRIPHENYLPHOSPHINE COMPLEX CATALYSTS[a]

Run	Catalyst	Conditions			Products				
		Temp. (°C)	Cat. (M%)[b]	Time (h)	Yield[c] (%)	Isomer distribution[d] cis	trans	α	ratio of cis/trans
1	$RhCl(PPh_3)_3$	40	0.05	8	45	75	23	2	77/23
				24	65	76	20	4	79/21
				52	84	76	19	5	80/20
2	"	40	0.1	8	82	76	21	3	78/22
				24	92	77	20	3	79/21
3	"	80	0.05	2	58	60	31	9	66/34
				4	76	54	34	12	64/36
				8	94	23	63	14	27/73
				24	100	0	83	17	0/100
4	$RhCl(CO)(PPh_3)_2$	40	0.05	3	57	75	25	+	75/25
				24	91	79	21	+	79/21
5	"	80	0.05	1	92	73	24	3	75/25
				3	94	70	26	4	73/27

[a] Equimolar amounts of the substrates (5 mmol each) were used. [b] Relative to the amount of the acetylene used. [c] GLC yield and thermal conductivity correction using an internal standard ($\underline{n}$-$C_{16}H_{34}$) was made. [d] Composition percentages of the isomers.

platinic acid, proceeded *via* stereoselective *cis* addition to yield *trans* products, while the benzoyl peroxide-catalyzed hydrosilylation of alkylacetylenes gave *cis* adducts stereoselectively. More recently, Ojima, Kumagai and Nagai [4] have shown that the hydrosilylation of alkylacetylenes with tris(triphenylphosphine) chlororhodium as catalyst gave *cis* products predominantly.

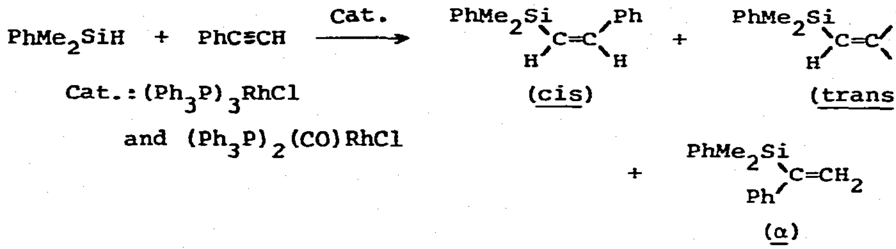
However, there are only limited reports on the hydrosilylation of phenylacetylene. Although the addition of trichlorosilane to phenylacetylene, catalyzed by platinized charcoal or chloroplatinic acid, had been shown to give *trans* products [2], attempts to realize peroxide-catalyzed addition of trichlorosilane to phenylacetylene did not succeed, resulting only in recovery of the starting materials [3]. Further, rhodium complex-catalyzed hydrosilylation of phenylacetylene has not yet been reported. We describe here the stereochemistry of the hydrosilylation of the acetylene with rhodium triphenylphosphine complex catalysts.

Two rhodium(I) complexes were found to catalyze the stereoselective hydrosilylation of phenylacetylene by phenyldimethylsilane. *Trans* addition occurred, giving *cis* organosilylstyrene derivatives, which are not readily accessible by other methods, under mild conditions in good yields.

Results and Discussion

In a typical example, tris(triphenylphosphine)chlororhodium (0.05 or 0.1 mole percent relative to the acetylene used) was added to a mixture of phenylacetylene and phenyldimethylsilane and the mixture was heated for an appropriate period of time. The results are summarized in Table 1.

It is seen from Table 1 that the reaction at 40 °C (Run 1) gave a mixture of *cis* and *trans* adducts in which the *cis* to *trans* ratio was ca. 78/22, along with a small amount of *α* product (eq. 1)



(eq. 1).

This ratio remained unchanged even after heating for a prolonged period of time with a doubled catalyst concentration (Run 2). These facts clearly indicate that the hydrosilylation of phenylacetylene involves stereoselective *trans* addition to yield the *cis* products. However, the result in the reaction carried out at 80 °C (Run 3) was different from that at 40 °C; after 2 h, the *cis/trans* ratio was 66/34, with a conversion of 58%, but was 0/100 after 24 h with a conversion of 100%. Obviously, the *cis* product isomerized to the *trans* during hydrosilylation under these conditions.

In order to check the *cis/trans* isomerization during the hydrosilylation, control experiments were made. Thus, a mixture of 83% *cis*/17% *trans* phenyldimethylsilylstyrene was heated with 0.1 mole percent of the rhodium complex at 40 °C for 48 h: No isomerization occurred. However, heating an identical sample at 80 °C for 22 h with 0.05 mole percent of the catalyst gave a mixture containing 78% *cis* and 22% *trans* isomer. After heating a mixture of 82% *cis*/18% *trans* isomer with phenyldimethylsilane and the catalyst (0.05 mole percent) at 80 °C for 16 min., no *cis* isomer was detected in the mixture, but only the *trans* isomer. Thus, the isomerization which occurred at 40-80 °C in the absence of a hydrosilane is far less important than that which took place during the hydrosilylation. In other words, the *cis* isomer is very readily isomerized *in the presence of both the hydrosilane and the catalyst*. Previously, Benkeser and co-workers [3] had performed similar tests employing *cis*-1-trimethylsilyl-3,3-dimethyl-1-butene in the presence of benzoyl peroxide and of trichlorosilane separately, and in the presence of a mixture of the two reagents. They cocluded that both the hydrosilane and the catalyst were necessary to cause the isomerization of cis to trans isomer. Therefore, it is very likely that the isomerization during the present hydrosilylation involves an insertion of cis silylstyrene formed into the Rh-H bond, rotation around the C-C bond of the intermediate to form the trans isomer.

We found bis(triphenylphosphine)carbonylchlororhodium to be a better catalyst for the stereoselective hydrosilylation of phenylacetylene. It causes formation of cis adducts exclusively (Runs 4 and 5) and the reaction is essentially complete within 3 h (eq. 1). During such a short reaction time product isomerization is of minor importance.

In contrast, the hydrosilylation of phenylacetylene (at 80 °C; 24-75 h) using benzoyl peroxide as catalyst (10-14 mole percent) gave only a slight amount of the adducts (below 4% yields) and the cis isomer was not formed in an appreciable amount.

Experimental

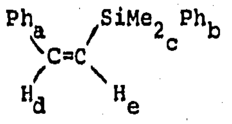
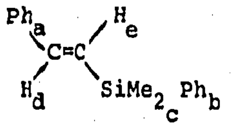
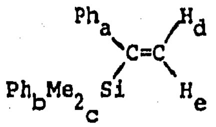
All boiling points are uncorrected. The reactions were carried out under an atmosphere of dry nitrogen. IR spectra were recorded using neat liquid films with a Hitachi EPI-G3 spectrometer, and NMR spectra were measured in CCl_4 solution using a Varian A-60D spectrometer, GLC analyses were conducted using an Ohkura Model 1700 gas chromatograph.

Materials

Phenyldimethylsilane was obtained as described previously [5]. The two rhodium-triphenylphosphine complexes [6,7] were prepared as described in the literature. Other materials were commercially available.

Table 2

SPECTRAL DATA OF PHENYLDIMETHYLSILYLSTYRENES

Compound	NMR (CCl_4, TMS)* (δ, ppm)	IR (neat, sandwich) (cm^{-1})
	7.65-6.9(m, $H_{a,b}$); 7.46(d, H_d)(11H), 5.96(d, H_e, 1H), 0.23(s, H_c, 6H), $J_{H_{d-e}}$ =15.0 Hz.	3060, 3050, 3015 (HC=); 1605sh, 1595, 1573, 1495 (C=C); 1251 (Si-Me); 1430, 1114 (Si-Ph).
	7.8-6.95(m, $H_{a,b}$, 10H), 6.96(d, H_d); 6.46(d, H_e)(2H), 0.40(s, H_c, 6H), $J_{H_{d-e}}$ =19.5 Hz.	3050, 3040, 3015 (HC=); 1600, 1595sh, 1572, 1493 (C=C); 1250 (Si-Me); 990 (<u>trans</u> HC=CH).
	7.75-6.9(m, $H_{a,b}$, 10H), 5.93(d, H_d); 5.62(d, H_e)(2H), 0.38(s, H_c, 6H), $J_{H_{d-e}}$ =2.8 Hz.	3060, 3045, 3020 (HC=); 1597, 1585, 1540, 1490 (C=C); 1251 (Si-Me); 1428, 1113 (Si-Ph).

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*See R. M. Silverstein, G. C. Bassler and T. C. Morrill, "Spectroscopic Identification of Organic Compounds" 3rd ed., John Wiley & Sons, Inc., New York, 1974, P. 226.

Addition of phenyldimethylsilane to phenylacetylene in the presence of the catalysts

A typical reaction is shown by Run 1 (see Table 1). Phenylacetylene (0.52 g, 5 mmol), tris(triphenylphosphine)chlororhodium (2.3 mg, 0.0025 mmol; 0.05 mole percent for the acetylene used) and phenyldimethylsilane (0.68 g, 5 mmol) were placed in a dry, small round-bottomed flask fitted with a reflux condenser which was previously flushed with dry nitrogen. The mixture was immersed in an oil bath maintained at 40 °C and heated with magnetic stirring for 52 h, during which time the mixture was subjected to GLC analysis at suitable intervals (silicone column, 1m X 4mm; 20% SF-96 on Celite 545; column temp., 190-210 °C; He carrier; internal standard, $\underline{n}$-$C_{16}H_{34}$). The products were isolated by preparative GLC. From the elemental analysis and IR and NMR spectra, the three products were identified as $\underline{\beta}$-(cis)-, $\underline{\beta}$-(trans)- and $\underline{\alpha}$-phenyldimethylsilylstyrene, respectively. The combined yield (by GLC) of the products was 84% (based on the acetylene used); the cis/trans/α isomer ratio was 76/19/5, and the cis/trans ratio was 80/20. (cis Isomer; found: C, 80.78; H, 7.36 and trans isomer, found: C, 80.59; H, 7.45. $C_{16}H_{18}Si$ calcd.: C, 80.61; H, 7.61%). The amount of the $\underline{\alpha}$ isomer was too small to be subjected to the analysis. Pertinent spectral data are listed in Table 2.

Isomerization of cis-phenyldimethylsilylstyrene

A mixture of $\underline{\beta}$-phenyldimethylsilylstyrene (2.02 mmol)(82% cis and 18% trans) and phenyldimethylsilane (4.2 mmol) was heated at 80 °C for 16 min. with tris(triphenylphosphine)chlororhodium (9.7×10^{-4} mmol; 0.05 mole percent relative to the styrene derivative used). The resulting mixture was checked by GLC. The presence of only the trans isomer (1.74 mmol, 86% yield) was established.

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