CHEMISTRY LETTERS, pp. 481-484, 1988.

Bis(η^5-cyclopentadienyl)diphenyltitanium-catalyzed Hydrosilylation of Ketones

Taichi NAKANO and Yoichiro NAGAI
Department of Chemistry, Gunma University, Kiryu, Gunma 376

Bis(η^5-cyclopentadienyl)diphenyltitanium activated a Si-H bond of diphenylsilane, methylphenylsilane, and phenylsilane effectively to bring about the reaction with ketones giving hydrosilylation products, alkoxysilanes, in good yields with good selectivity.

The hydrosilylation of carbonyl compounds is known to be effected by various catalytic systems such as metal halides(e.g., $ZnCl_2$[1)] and H_2PtCl_6[2)]), UV light,[3)] and Group VIII metal phosphine complexes(e.g., $[(PhMe_2P)PtCl_2]_2$,[4)] $RhCl(PPh_3)_3$,[5)] and $RuCl_2(PPh_3)_3$[6)]). However, to date, no report has been published for the hydrosilylation of carbonyl compounds employing bis(η^5-cyclopentadienyl)diphenyltitanium as a catalyst. Bis(η^5-cyclopentadienyl)diphenyltitanium[7)] is known to be stable in air and decompose to o-phenylene titanocene[8)] at temperatures of 70-90 °C, which is further subject to attack of reagents such as CO_2,[9)] N_2,[10)] and RC≡CR'[8,11)] giving the corresponding titanacarbocycles. We wish to report herein the first example that diphenyltitanocene did catalyze the hydrosilylation of ketones efficiently at higher temperatures than the decomposition temperatures of the titanium complex to give the corresponding adducts in good yields with good selectivity(Scheme 1).

$$R^1R^2SiH_2 \quad + \quad R^3R^4C{=}O \xrightarrow{Cp_2TiPh_2} R^1R^2HSi\text{-}OCHR^3R^4 \qquad (1)$$

$$R^1{=}R^2{=}Ph;\ R^1{=}Me,\ R^2{=}Ph$$

Typically, a 1:1:0.016 mixture of diphenylsilane, 2-heptanone, and the titanium complex was introduced into a glass ampoule. The mixture was degassed through several freeze-evacuate-thaw cycles prior to sealing in vacuo.

Then, the mixture was stirred at 120 °C for 11 h. GLC analysis of the resulting mixture disclosed that 84% of the ketone charged was consumed and (1-methylhexyloxy)diphenylsilane was produced in 91% yield based on the ketone consumed. The product was identified by comparing its IR, ^{1}H NMR, and MS spectra with those of an authentic sample. Other examples are summarized in Table 1.[12)]

Table 1. Bis(η^5-cyclopentadienyl)diphenyltitanium-catalyzed Hydrosilylation of Ketones

Run	Silane(mmol)	Ketone(mmol)	Conditions temp /°C,time/h	Conv.[a)]	Product	Yield[b)] %
1	Ph_2SiH_2(6)	2-Heptanone(6)	120, 11	87	$Ph_2HSi\text{-}OCHMe(C_5H_{11})$	91
2	Ph_2SiH_2(6)	2-Heptanone(12)	120, 20	65[c)]	$Ph_2HSi\text{-}OCHMe(C_5H_{11})$	88
3	Ph_2SiH_2(6)	3-Pentanone(6)	120, 11	67	$Ph_2HSi\text{-}OCHEt_2$	91
4	Ph_2SiH_2(6)	Cyclopentanone(6)	120, 11	93	$Ph_2HSi\text{-}OC_5H_9$	76
5	$MePhSiH_2$(6)	3-Pentanone(6)	90, 8	87	$MePhHSi\text{-}OCHEt_2$	66[d,e)]
6	$PhSiH_3$(6)	2-Heptanone(12)	120, 5	100[c)]	$PhHSi(\text{-}OCHMe(C_5H_{11}))_2$	60[e)]

a) Conversion of the ketone, %.
b) Yields were determined by GLC. Correction for thermal conductivity was made.
c) Conversion of the silane, %.
d) Uncorrected.
e) Any other products were not detected by GLC analysis.[13)]

As is seen from tha Table, the reaction of diphenylsilane with 3-pentanone and cyclopentanone under conditions described in the Table gave (1-ethylpropoxy)-diphenylsilane and cyclopentyloxydiphenylsilane in 91 and 76% yield based on the ketone consumed, respectively. Rather surprisingly the reaction of diphenylsilane with two equivalents of 2-heptanone under similar conditions produced only (1-methylhexyloxy)diphenylsilane in 88% yield. The hydrosilylation of 3-pentanone with methylphenylsilane proceeded under even milder conditions than did the reaction with diphenylsilane and occurred at 90-100 °C to form methyl(1-ethylpropoxy)-phenylsilane selectively. On the other hand, phenylsilane entered into the reaction with two equivalents of 2-heptanone in the presence of the titanium catalyst to give bis(1-methylhexyloxy)phenylsilane in 61% yield. The difference in selectivity between the dihydrosilane and the trihydrosilane has been found in

$RhCl(PPh_3)_3$-catalyzed hydrosilylation of conjugated enones.[5b)]

A possible mechanism for the present reaction can be tentatively illustrated in Fig. 1. Harrod et al.[14)] have recently shown that while dialkyltitanocenes such as Cp_2TiMe_2 and $Cp_2Ti(Bz)_2$ react with various hydrosilanes(e.g., trihydrosilanes, dihydrosilanes, and alkoxymonohydrosilanes) at room temperature to give

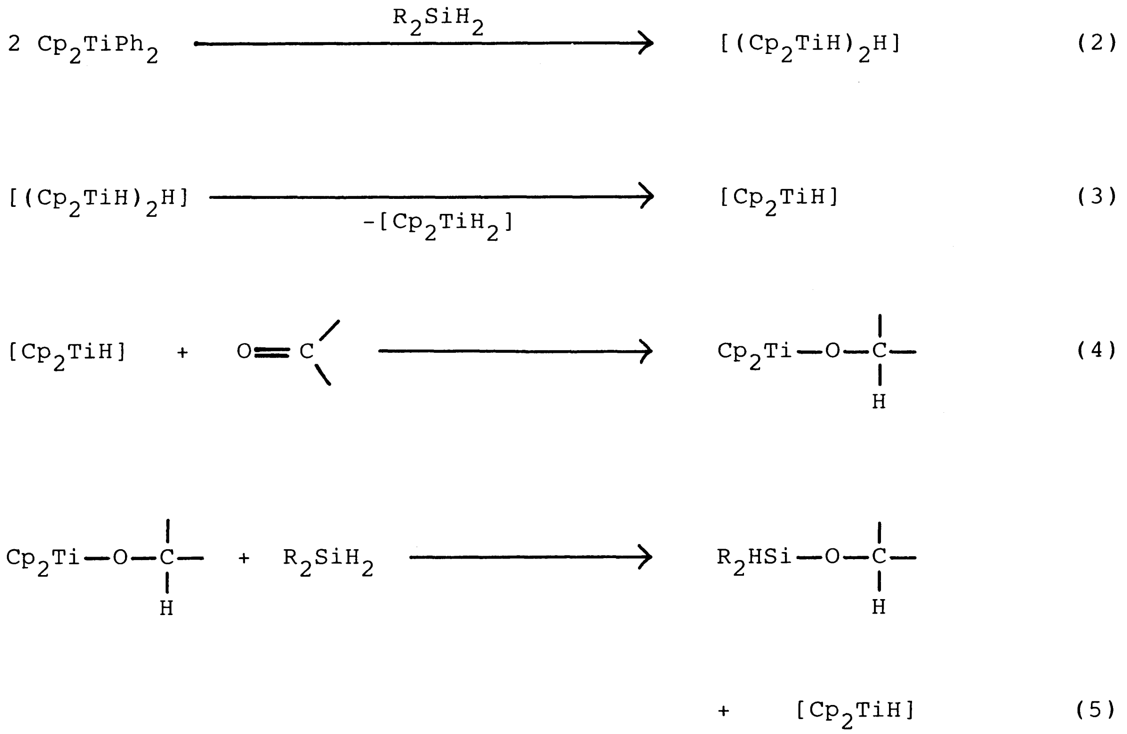

Fig. 1.

bis(η^5-cyclopentadienyl)titanium hydride complex, $[(Cp_2TiH)_2H]$, Cp_2TiPh_2 does not. However, successful hydrosilylation of ketones using the dihydrosilanes and phenysilane in the presence of diphenyltitanocene as a catalyst seems to be understood in terms of the formation of some titanium hydride complex,[15)] possibly $[(Cp_2TiH)_2H]$, from the reaction of diphenyltitanocene with the dihydrosilanes or phenylsilane under the conditions employed. The addition of $[Cp_2TiH]$ to carbonyl compounds has been reported by Sato et al.[16)]

References

1) R. Calas, E. Frainnet, and J. Bonastre, C. R. Acad. Sci. Paris, 252, 2987 (1960).
2) S. I. Sadykh-Zade and A. D. Petrov, Zh. Obshch. Khim., 29, 3194 (1959).

3) C. Eaborn, "Organosilicon Compounds," Butterworth, London, (1960), p.213.

4) T. Hayashi, K. Yamamoto, and M. Kumada, J. Organomet. Chem., 112, 253 (1976).

5) For example, a) I. Ojima, M. Nihonyanagi, and Y. Nagai, J. Chem. Soc., Chem. Commun., 1972, 938; b) I. Ojima, M. Nihonyanagi, T. Kogure, M. Kumagai, S. Horiuchi, K. Nakatsugawa, and Y. Nagai, J. Organomet. Chem., 94, 449 (1975).

6) C. Eaborn, K. Odel, and A. Pidcock, J. Organomet. Chem., 63, 93 (1973); R. J. P. Corriu and J. J. E. Moreau, ibid., 114, 135 (1976); H. Matsumoto, Y. Hoshino, and Y. Nagai, Bull. Chem. Soc. Jpn., 54, 1279 (1981).

7) L. Summers, R. H. Ultoh, and A. Holmes, J. Am. Chem. Soc., 77, 3604 (1955).

8) J. Dvorak, R. J. O'brien, and W. Santo, J. Chem. Soc., Chem. Commun., 1970, 441.

9) I. S. Kolomnikov, T. S. Lobeeva, V. V. Grorbachevskaya, G. G. Aleksandrov, Yu. T. Struckhov, and M. E. Vol'pin, J. Chem. Soc., Chem. Commun., 1971, 972.

10) V. B. Shur, E. G. Berkovitch, L. B. Vasiljeva, R. V. Kudryavtsev, and M. E. Vol'pin, J. Organomet. Chem., 78, 127 (1974).

11) H. Masai, K. Sonogashira, and N. Hagihara, Bull. Chem. Soc. Jpn., 41, 750 (1968).

12) The hydrosilylation of ketones using monohydrosilanes did not occur. For example, a mixture of dimethylphenylsilane(6 mmol), 2-heptanone(6 mmol), and diphenyltitanocene(0.13 mmol) was stirred at 120 °C for 45 h. The resulting mixture was subjected to GLC analysis which indicated that only small amounts of aldol condensation products were produced.

Similar results were obtained in the reaction using triethylsilane as a monohydrosilane.

13) GLC analysis was performed using a Ohkura Model 802 gas chromatograph, with 4 mm x 1.4 m columns packed with Silicone SE-30 or Silicone DCQF-1(15% by weight) on 60-80 mesh Celite 545AW. The column temperature was 198 °C with a helium flow of 40 cm^3/min.

14) E. Samuel and J. F. Harrod, J. Am. Chem. Soc., 106, 1859 (1984); C. Aitken, J. F. Harrod, and E. Samuel, J. Organomet. Chem., 279, C11 (1985); C. Aitken, J. F. Harrod, and E. Samuel, J. Am. Chem. Soc., 108, 4059 (1986); J. F. Harrod and S. S. Yun, Organometallics, 6, 1381 (1987).

15) The structure is not specified as yet. But, Cp_2TiPh_2-$MePhSiH_2$ system brought about the isomerization of 1-octene to 2-octene under similar conditions. The results may suggest the existence of titanium hydride complexes.

16) F. Sato, T. Jinbo, and M. Sato, Tetrahedron Lett., 21, 2171 (1980).

(Received December 23, 1987)