

Silation of Alcohols and Aldehydes Catalyzed by Dimethylzirconocene

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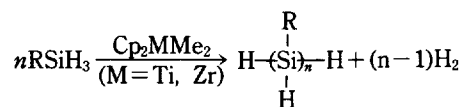
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Received March 14, 1994

Silation reactions catalyzed by homogeneous transition metal complexes has been useful for the preparation of various silyl compounds.¹ Most of the reactions are catalyzed by late transition metal complexes. Very little attention has been paid to early transition metal catalysts.²

Catalytic activities of titanocene and zirconocene derivatives for the dehydrogenative coupling of organosilanes have been described (eq. (1)).³



Recently these catalytic activations of the organosilanes by group 4 metallocene derivatives have been utilized for the olefin hydrosilations.⁴

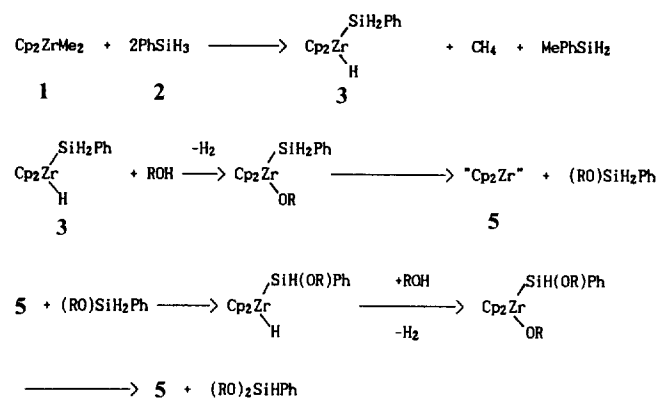
In this study, we have attempted the application of the catalytic reaction system of dimethylzirconocene, **1**, to O-silation of alcohols and aldehydes. O-silations of alcohols and aldehydes are important reactions for the synthesis of silyl ethers.⁵ However, only a few number of complexes have been used as the homogeneous catalysts for the reaction.⁶ Most of the homogeneous catalysts known to date are late transition metal complexes. This work is one of a few examples of O-silation of aldehydes and alcohols catalyzed by early transition metal complex.² O-silation of alcohols or aldehydes catalyzed by **1** occurs preferentially over the olefin group presented in the same molecule.

After the addition of catalytic amount of dimethylzirconocene, **1**, to stoichiometric mixture of alcohols and phenylsilane, **2**, in benzene, the initially colourless solution turned yellow with evolution of H₂.⁷ ¹H-NMR spectrum of the mixture showed no resonances due to the Si-H (δ 4.16) and O-H protons. The chemical shifts and resonance patterns for the alkyl proton of the reaction mixture remained basically same as those for the pure alcohol. In the case of allyl alcohol reaction, the resonance peaks (δ 0.9, 1.5, 3.6) of propyl group appeared weakly, indicating the hydrogenation of allylic C=C of small portion of allyl alcohol to propanol. However the GC/MS analysis⁸ of the reaction mixture showed only trace amounts of propanol and its related compounds. The GC/MS analyses of the reaction mixtures of some alcohols as given in Table 1 indicate the production of alkoxy silanes.⁸ The alcoholysis of phenylsilane produces upto trialkoxyphenylsilane with the yield of about 70%. Other minor products are high-MW products such as alkoxy compounds of various oligomers of the silane. For an example, we have identified the formation of (CH₃CH₂CH₂O)₃(Si)₂H(Ph)₂ and (CH₃CH₂CH₂O)₄(Si)₂(Ph)₂ in the case of propanol.

Table 1. Silation of Alcohols with Phenylsilane catalyzed by Dimethylzirconocene

Alcohol	Product	GC yield (%) ^a
Allyl alcohol	(CH ₂ =CHCH ₂ O)SiH ₂ Ph	1
	(CH ₂ =CHCH ₂ O) ₃ SiPh	78
Propanol	(CH ₃ CH ₂ CH ₂ O) ₂ SiHPh	35
	(CH ₃ CH ₂ CH ₂ O) ₃ SiPh	37

^aYield calculated by GC based on [alcohol],



Scheme 1.

Table 2. Hydrosilation of Aldehydes with Phenylsilane catalyzed by Dimethylzirconocene

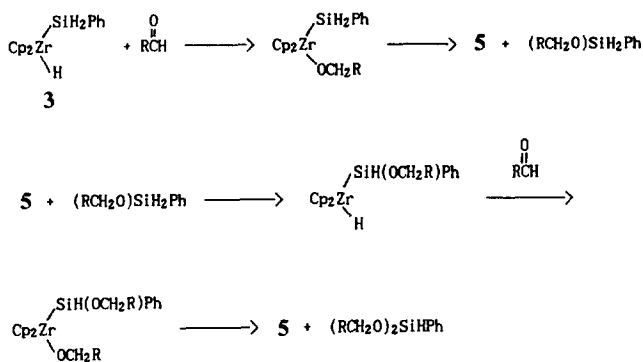
Aldehyde	Product	GC yield (%) ^a
Crotonaldehyde	(CH ₃ CH=CHCH ₂ O) ₂ SiHPh	30
	(CH ₃ CH=CHCH ₂ O) ₃ SiPh	55
Propionaldehyde	(CH ₃ CH ₂ CH ₂ O) ₂ SiHPh	4
	(CH ₃ CH ₂ CH ₂ O) ₃ SiPh	89
Benzaldehyde	PhCH ₂ OH	81

^aYield calculated by GC based on [aldehyde],

It has been suggested⁹ that the hydridosilyltitanocene, **3**, formed by the reaction of **1** with **2** is an active species for the catalytic polymerization of **2**. In this case of O-silation of alcohol, **3** would act also as the catalyst as follows: (Scheme 1).

The procedures for the aldehyde reactions are similar to those for the alcohol reactions.¹⁰ The aldehyde reactions were usually slower than the alcohol reactions. In this case of aldehyde reactions, we could trace the progress of reaction by monitoring ¹H-NMR peak (δ ca 9) of carbonyl CH.¹¹ Table 2 gives the hydrosilation products of some aldehydes.⁸ The alkoxy silanes are produced with over 70% yield. However, no hydrosilation products were detected in the reaction of benzaldehyde. The hydrogenation to C=O group of benzaldehyde with H₂ evolved by the dehydrogenative coupling of phenylsilane eq. (1) occurs to produce benzyl alcohol. At this stage it is obscure why the hydrosilation of benzaldehyde does not go. Further study is under way to clarify the reason.

A plausible mechanism for the hydrosilation of aldehydes is as follows: (Scheme 2). In both of Schemes 1 and 2, the complexation of **5** with monoalkoxyphenylsilane goes further



Scheme 2.

silation to produce the dialkoxyphenylsilane and **5** with dialkoxyphenylsilane to produce the trialkoxysilane. When **5** reacts with **2** to produce **3**, the catalytic cycle begins again.

Acknowledgement. This work was supported by a grant from Korea Science and Engineering Foundation.

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- In a typical procedure, dimethylzirconocene (0.11 mmole), for an example, was added to a mixture of allyl alcohol (4.1 mmole) and phenylsilane (1.1 mmole) in benzene. The mixture was kept at room temperature under argon for more than 24h. All manipulations were carried out under argon (or nitrogen) by using standard inert-atmosphere techniques. All solvents, phenylsilane, alcohols, aldehydes were saturated with argon (or nitrogen) before use.
- The GC analyses were performed on a Varian 3300 chromatograph using 50 cm \times 1/8 inch column packed with 50% OV-101 Chrom G.H.P. 100/120. GC/MS analyses were carried out on a JEOL-JMX-DX 303, with HP 5890 capillary column. [compd, fragment, m/e (% base): (C_3H_5O)₃SiPh, M-H, 275 (7); M-C₃H₅, 235 (39); M-C₃H₅O, 219 (39); M-C₆H₉O₂, 163 (100); M-PhC₆H₁₀, 117 (39); M-PhC₆H₁₀O, 101 (39); (C_3H_7O)₂SiHPh, M-H, 223 (100); M-C₃H₇, 181 (11), M-C₃H₇O, 165 (57); M-PhH, 146 (78); M-C₆H₁₃O, 123 (73); M-C₆H₁₅O₂, 105 (26); (C_3H_7O)₃SiPh, M, 282 (19); M-C₂H₅, 253 (34); M-C₃H₇O, 223 (100); M-PhH,

204 (72); M-C₆H₁₅, 195 (53); M-C₆H₁₅O₂, 163 (15); M-C₉H₂₁O₃, 105 (9); (C_4H_7O)₂SiHPh, M, 248 (27); M-CH₃, 233 (21); M-C₄H₇, 193 (51); M-C₄H₇O, 177 (48); M-C₈H₁₃, 139 (83); M-C₈H₁₃O, 123 (100); (C_4H_7O)₃SiPh, M, 318 (22); M-CH₃, 303 (11), M-C₄H₇, 263 (69); M-C₄H₇O, 247 (11); M-C₆H₁₃O, 193 (28); M-C₈H₁₃O₂, 177 (22); M-C₁₂H₁₉O, 139 (100).]

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- In the case of aldehyde reactions, equimoles (3.5 mmole) of the aldehyde and phenylsilane were reacted to find whether the hydrogenation of C=C or C=O groups occurs preferably. No hydrogenation products to C=C group of crotonaldehyde were detected. However, the amount of alcohol detected was less than 1%, which could stem from the hydrogenation of C=O group.
- About 48h after the beginning of the reaction, ¹H-NMR peak (δ ca 9) of carbonyl CH of the aldehyde usually disappears and the pattern of ¹H-NMR turns completely to that of corresponding alkoxy group.

Bifunctional Diaziridine: Synthesis of Vinylic Diaziridylcarbamate¹

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Received March 14, 1994

Diaziridines, structurally simple three membered heterocycles with two nitrogen atoms, are fairly new class of compounds not only for their structural inertness but also for the unique chemical reactivities.³ With regard to the unique structural aspects, diaziridines exhibit several characteristics, namely i) trans isomer favorability over *cis* isomer so that the preparation of chiral diaziridines is possible by asymmetric induction⁴ ii) relatively low basicity due to the trans orientation of nonbonding electrons on nitrogen atoms⁵ iii) and good stabilities toward high temperature and acidic or basic media compared to their close analogue, oxaziridines.³ Given those attractive features of diaziridines, we have been interested in designing biologically active substances especially new

