

and amide C=O (1701 cm^{-1}) stretching modes. From the results, some alkyl chains were thought to be removed during the acid or/and heat treatment. Meanwhile, the peaks intensity due to the stretching or bending modes of O-H (3348 cm^{-1}), C-O, and C-N ($1000\text{--}1150\text{ cm}^{-1}$, peaks overlapped) groups are increased. Therefore, it is supposed that the amino groups of the melamine ring were hydroxymethylated and their dehydrations resulted in crosslinking in part. However, the quantitative extent of the hydroxymethylation and the crosslinking was not clear at this point.

SEM micrographs of Figure 3 show the surface morphology of the porous fluorocarbon membranes. We can readily observe the original pores, which are seen as longish and somewhat dark appearance (Figure 3a), of the substrate membrane. When the monolayer of NDTOA was deposited on the substrate membrane from pure water subphase, the large defects with sizes of *ca.* $2\text{ }\mu\text{m}$ were seen as dark spots even in 12 layers. However, good covering of the pores was found in the 8 monolayers film which was transferred from acidic (pH=3) aq. formaldehyde subphase (Figure 3b). The covering capability is thought to be enhanced through the partially crosslinking between the melamine moieties at the air-water interface. The surface morphology observed through the SEM micrograph was not changed when the LB film was heat-treated as described above.

In conclusion, we demonstrated a molecularly-thin network film of a melamine-formaldehyde resin which is a well-known thermosetting resin. A modification of a porous sol-

id surface by ultrathin thermoset film could be done by using the LB technique.

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References

1. Tieke, B. *Adv. Polym. Sci.* **1985**, *71*, 79.
2. Fukuda, K.; Shibasaki, Y.; Nakahara, H.; Endo, H. *Thin Solid Films* **1989**, *179*, 103.
3. Hahabusa, K.; Yamasaki, J.; Koyama, T.; Shirai, H.; Hayakawa, T.; Kurose, A. *J. Macromol. Sci., Chem.* **1989**, *A26* (12), 1571.
4. Bauer, S.; Heckman, K.; Six, L.; Strobl, C.; Bloecher, D.; Henkel, H.; Garbe, T.; Ring, K. *Desalination* **1983**, *46*, 369.
5. Jones, R.; Tredgold, R. H.; Davis, F.; Hodge, P. *Thin Solid Films* **1990**, *186*, L51.
6. Shimomura, M.; Kunitake, T. *Thin Solid Films* **1985**, *132*, 243.
7. Ueno, T.; Kunitake, T. *Chem. Lett.* **1990**, 1927.
8. (a) Jeong, H.; Lee, B.-J.; Kwon, Y.-S. *Bull. Korean Chem. Soc.* **1994**, *15*(8), 650. (b) Jeong, H.; Lee, B.-J.; Kwon, Y.-S. *Thin Solid Films* **1994**, *244*, 710. (c) Choi, G.; Lee, B.-J.; Chang, S.-M.; Kwon, Y.-S. *Bull. Korean Chem. Soc.* **1995**, *16*(6), 493. (d) Lee, B.-J.; Choi, G.; Kwon, Y.-S. *Bull. Korean Chem. Soc.* **1995**, *16*(12), 1167.

Hydrosilation of Ketones Catalyzed by Dimethylzirconocene

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While catalytic hydrosilation reactions of a carbonyl group by late transition metal complexes have been reported,¹ few hydrosilation reactions catalyzed by early transition metal complexes are known.² Since catalytic activities of group 4 metallocene derivatives for the dehydrogenative coupling of organosilanes³ have been known, the catalytic activation of organosilanes by the metallocene derivatives has been utilized for the olefin hydrosilation.⁴ We have successfully applied the activation of phenylsilane by dimethylzirconocene to O-silation of various alcohols and aldehydes.⁵ It has also been reported that diphenyltitanocene is effective as a catalyst for the hydrosilation of various ketones to give alkoxy-silanes.^{2a}

In this paper we wish to report the hydrosilation of ketones with phenylsilane catalyzed by dimethylzirconocene under mild conditions. A catalytic amount of dimethylzirconocene (**1**) prepared by the literature procedure⁶ was added to a stoichiometric mixture of a ketone and phenylsilane (**2**) in benzene. The initially colorless solution turned yellow with

evolution of H₂ gas. In a typical procedure, a mixture (0.5 mL) of **1** (0.06 M), **2** (3.7 M), and a ketone (3.7 M) in benzene was stirred under argon for 72 hours at room temperature. The resulting mixture was subjected to the GC/MS analysis.⁷ All manipulations were carried out under argon atmosphere using either standard inert-atmosphere techniques or argon filled glove box. The solvent, phenylsilane, and ketones were saturated with argon before use.

The results of the O-silation reaction catalyzed by **1** are summarized in Table 1. For relatively simple ketones such as 2-butanone and 2-pentanone, bis(alkoxy)phenylsilanes are major products (64-74%) and tris(alkoxy)silanes are minor products (6-15%). In the case of 4-hexene-3-one which is sterically rather bulkier than 2-butanone or 2-pentanone, only bis(alkoxy)phenylsilane is observed in a good yield (84%). The results are comparable with those of the diphenyltitanocene system.^{2a} A similar reaction of phenylsilane and 2-heptanone by a catalytic amount of diphenyltitanocene under

Table 1. Hydrosilation products of ketones with phenylsilane catalyzed by dimethylzirconocene

Ketones	Products	GC yield (%) ^a
2-butanone	[(CH ₃)(C ₂ H ₅)HCO] ₂ SiHPh	61
	[(CH ₃)(C ₂ H ₅)HCO] ₃ SiPh	15
2-pentanone	[(CH ₃)(C ₃ H ₇)HCO] ₂ SiHPh	74
	[(CH ₃)(C ₃ H ₇)HCO] ₃ SiPh	6
4-hexene-3-one	[(CH ₃ CH=CH)(C ₂ H ₅)HCO] ₂ SiHPh	84
	C ₆ H ₁₁ OH	22
cyclohexanone	(C ₆ H ₁₁ O)SiH ₂ Ph	13
	(C ₆ H ₁₁ O) ₂ SiHPh	32
	C ₆ H ₅ C ₂ H ₅	8
acetophenone	C ₆ H ₅ CH=CH ₂	21
	[(C ₆ H ₅)(CH ₃)HCO]SiH ₂ Ph	5
	[(C ₆ H ₅)(CH ₃)HCO] ₂ SiHPh	2

^a yield based on the initial concentration of the ketone.

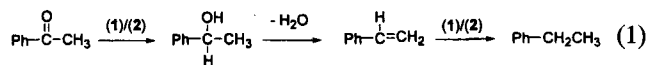
harsh conditions (120 °C) gives only bis(1-methylhexyloxy) phenylsilane as an only product.^{2a}

There seems to be a steric factor in the O-silation reactions of ketones. As the number of carbon atoms of a ketone increases, the yield of tris(alkoxy)silane decreases, while the yield of bis(alkoxy)silane increases. The major products of these reactions are bis(alkoxy)phenylsilanes. The larger steric demand of ketones than that of aldehydes would also hinder further hydrosilations of ketones to produce tris(alkoxy)phenylsilanes which are yet the major products in the reactions with aldehydes.^{5a}

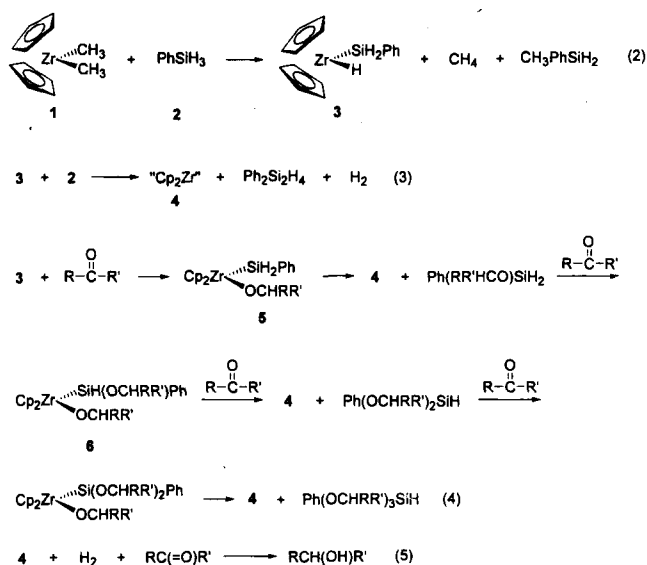
The yields of hydrosilation products of cyclohexanone are significantly decreased. Instead, hydrogenation of the carbonyl group of cyclohexanone by H₂ evolved from the dehydrogenative coupling of phenylsilane gives cyclohexanol. A similar reaction of benzaldehyde to produce benzylalcohol has been observed in the dimethylzirconocene catalysis system.^{5a} In the case of 4-hexene-3-one, a resonance at δ 5.4 ppm assignable to the olefinic hydrogen in NMR spectrum was observed, which is due to neither the hydrogenation nor the hydrosilation of 4-hexene-3-one occurs. It is obvious that the hydrosilation of the carbonyl group occurs preferentially over that of the olefin group in the unsaturated ketone.

Surprisingly major products of the reaction of acetophenone are styrene (21% yield) and ethylbenzene (8% yield). The yield of hydrosilation products of acetophenone is very poor. As shown in equation (1), the hydrogenation of the carbonyl group followed by the dehydration produces styrene. Subsequent hydrogenation of styrene would give ethylbenzene.

It is not clear at the moment why the hydrogenation occurs preferentially over the hydrosilation of the carbonyl group in the reaction of acetophenone. The steric and electronic effects of phenyl group in acetophenone may play roles in the reaction of eq 1.



A plausible mechanism for the hydrosilation of ketones shown in Scheme 1 would be similar to that of aldehydes.^{5a} It has been suggested that hydridosilylzirconocene species 3 formed from the reaction of 1 with 2 is an active species



for the catalytic coupling of 2,⁸ hydrosilation of olefines, and the O-silation of alcohols and aldehydes.^{5a} The hydridosilylzirconocene (3) would act also as the catalyst for the hydrosilation of ketones.

The reaction of 4 with bis(alkoxy)phenylsilane to form a new hydridosilylzirconocene would be retarded due to the steric hindrance with increasing the number of carbon atoms of ketones. This accounts for decreasing yields of tris(alkoxy)phenylsilane in the order of 2-butanone > 2-pentanone > 4-hexene-3-one. For highly bulky ketones such as cyclohexanone and acetophenone, reactions of eq 3 and eq 5 are rather favorable to form the hydrogenation products of the carbonyl group.

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References

- (a) Speier, J. L. *Advances in Organometallic Chemistry*; Stone, F. G. A.; West, R. Eds., Vol. 2, p 407. Academic Press, New York, **1979**. (b) Lukevics, E.; Dzintara, M. *J. Organomet. Chem.* **1985**, 295, 265. (c) Luo, X.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, 111, 2527. (d) Barber, D.; Lu, Z.; Richardson T.; Crabtree, R. H. *Inorg. Chem.* **1992**, 31, 4709.
- (a) Nakano, T.; Nagai, Y. *Chem. Lett.* **1988**, 481. (b) Hasegawa, M.; Suzuki, N.; Saburi; Rousset, M. C.; Fanwick, P.; Negishi, E. *J. Am. Chem. Soc.* **1991**, 113, 8564.
- (a) Aitken, C.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, 279, C11. (b) Aitken, C.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, 108, 4059. (c) Aitken, C.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1986**, 64, 1677.
- (a) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, 6, 1381. (b) Kesti, M. R.; Waymouth, R. M. *Organometallics* **1992**, 11, 1095.

5. (a) Yun, S. S.; Kim, T. S.; Kim, C. H. *Bull. Korean Chem. Soc.* **1994**, *15*, 522. (b) Yun, S. S.; Yang, Y. S. *Reaction Kinetics and Catal. Lett.* **1997**, in press.
6. Hunter, W. E.; Hencir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.
7. The GC analyses were performed on a Hewlett Packard 5890 Chromatography using a HP-5 capillary column. GC/MS analyses were carried out on a Hewlett Packard 5889A equipped with a HP-5 capillary column for gas chromatography and the 70 eV electron ionization mode for mass spectrometer. The column was heated from 30 °C to 250 °C with a heating rate of 10 °C/min.
8. Harrod, J. F. *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*; Laine, R. M., Ed., NATO ASI Series E., No 141, p 103, Martinus Nijhoff, Amsterdam 1988.