# Notes

## Acetalization of Carbonyl Compounds with Alkoxysilanes Catalyzed by Iodotrimethylsilane. "One-Pot" Allylation Reactions of Carbonyl Compounds to Homoallyl Ethers Using an Allylsilane[1]

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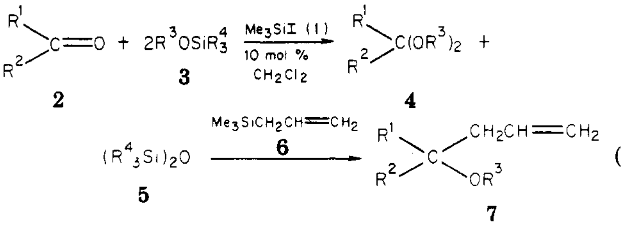
Carbonyl functions of aldehydes and ketones are usually protected as acetals in synthesis and derivatization.[2] We have recently reported that iodotrimethylsilane is an efficient catalyst for silylation of alcohols,[3a] allylation of acetals[3b] and α-chloro ethers[3c] with allylsilanes, α-amino methylation[3d] and α-heteroatom-substituted alkylation of ketones by the reaction of silyl enol ethers, and the stereoselective cross-aldol reaction of silyl enol ethers.[3e]

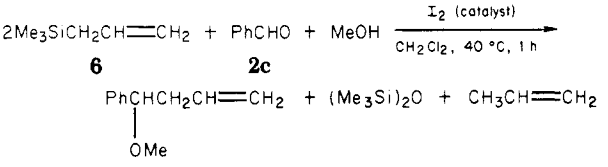
In an extension of the studies, we now report that the acetalization of carbonyl compounds can be successfully achieved by using an alkoxysilane and a catalytic amount of iodotrimethylsilane. It has been known that the effective cleavage of acetals to ketones, alkoxysilanes, and alkyl iodides is promoted by a stoichiometric amount of iodotrimethylsilane in aprotic medium,[4] but the reverse reaction can be carried out by using a catalytic amount of iodotrimethylsilane. Moreover, we found that "one-pot" conversion of carbonyl compounds to homoallyl ethers occurs successively in the presence of an allylsilane (eq 1). Since allylation of carbonyl compounds can be effected only by the use of titanium chloride and related Lewis acids, the present extension of the reaction would be useful.[5]



(1)

Reactions of an alkoxysilane (3) with carbonyl compounds 2 proceeded smoothly in the presence of a catalytic amount (ca. 10 mol %) of iodotrimethylsilane (1) to afford the corresponding acetals 4 which were readily isolated by TLC. Tetramethoxysilane (3a) was used most satisfactorily and conveniently for the acetaliaztion among various alkoxysilanes because 3a was easily accessible and could be readily removed from the reaction mixture as siloxane polymers after hydrolysis. When allyltrimethylsilane (6) was added at the initial stage of the acetalization, the successive allylation of the resulting acetals took place more rapidly than the acetalization to give the homoallyl ethers 7 exclusively in excellent yield. The results are summarized in Table I.

Interestingly, by combining three consecutive reactions, namely, silylation,[3a] acetalization, and allylation,[3b] the iodine-catalyzed synthesis of a homoallyl ether 7a can be achieved all at once from a mixture of methanol, benzaldehyde, and 6, as shown in eq 2. Apparently the iodosilane 1 works as a common catalyst in these three reactions.



$$2Me_3SiCH_2CH{=}CH_2 + PhCHO + MeOH \xrightarrow[CH_2Cl_2,\ 40\ °C,\ 1\ h]{I_2\ (catalyst)} PhCH(OMe)CH_2CH{=}CH_2 + (Me_3Si)_2O + CH_3CH{=}CH_2 \quad (2)$$

6 2c

7a (89%)

### Experimental Section

Infrared spectra were determined on a Hitachi EPI-G2 spectrometer. NMR spectra were recorded on Varian T-60 and EM-390 spectrometers. Mass spectra were taken on a JEOL JMS-300D GC-MS spectometer. Gas chromatographic analyses were carried out on Hitachi Model 063 and 163 gas chromatographs equipped with a thermal conductivity detector.

1,2-Bis(trimethylsiloxy)ethane,[6] allyltrimethylsilane[7] and iodotrimethylsilane[8] were prepared according to the reported procedure. Tetramethoxysilane was gifted from Mitsubishi chemicals Co., Ltd.

**General Procedure for the Acetalization.** Iodotrimethylsilane (1) (0.020 g, 0.10 mmol) was added from a syringe to a mixture of a carbonyl compound (2) (1.0 mmol) and an alkoxysilane (3) (1.1 mmol) in dichloromethane (2 mL). The reaction mixture was stirred under a given condition in Table I. After a few drops of pyridine was added, the reaction mixture was hydrolyzed with saturated aqueous hydrogen sodium carbonate and extracted with ether. The residue was subjected to TLC (silica gel). All products were identified by spectroscopic and elemental analyses as shown below.

A similar procedure was carried out for the conversion of "one-pot" allylation of carbonyl compounds, where allyltrimethylsilane (6) (1.2 mmol) was added to the mixture.

**Spectral Data for Acetals 4 and Homoallyl Ethers 7. Benzaldehyde dimethyl acetal (4a):**[9] TLC (PhH/Hex, 2/3) $R_f$ 0.4; NMR ($CCl_4$) δ 3.20 (s, 6 H), 5.40 (s, 1 H), 7.33 (s, 5 H).

**Heptanal dimethyl acetal (4b):**[10] TLC (PhH/Hex, 1/3) $R_f$ 0.6; NMR ($CCl_4$) δ 0.8–1.0 (m, 3 H), 1.1–1.7 (m, 10 H), 3.20 (s, 6 H), 4.20 (t, $J$ = 5 Hz, 1 H); IR (liquid film, $cm^{-1}$) 2940 (s), 1470 (m), 1390 (m), 1205 (m), 1145 (s), 1075 (s); MS, $m/e$ (relative intensity) 129 ($M^+ - 31$, 6), 75 (65), 71 (100), 58 (12), 55 (18), 45 (11). 41 (52).

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[1] Chemistry of Organosilicon Compounds. 191.

[2] For review articles, see: (a) Loewnthal, H. J. E. In "Protective Groups in Organic Chemistry"; McOmie, J. F. W., Ed.; Plenum Press: New York, 1973; Chapter 9, pp 325–332. (b) Greene, T. W. "Protective Groups in Organic Synthesis"; Wiley-Interscience: New York, 1981; Chapter 4, pp 116–129.

[3] (a) Hosomi, A.; Sakurai, H. *Chem. Lett.* **1981**, 85. (b) Sakurai, H.; Sasaki, K.; Hosomi, A. *Tetrahedron Lett.* **1981**, *22*, 745. (c) Sakurai, H.; Sakata, Y.; Hosomi, A. *Chem. Lett.* **1983**, 409. (d) Hosomi, A.; Iijima, S.; Sakurai, H. *Tetrahedron Lett.* **1982**, *23*, 547. (e) Sakurai, H.; Sasaki, K.; Hosomi, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3195.

[4] Jung, M. E.; Andrus, W. A.; Ornstein, P. L. *Tetrahedron Lett.* **1977**, 4175. For trimethylsilyl triflate mediated acetalization, see: Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron* **1981**, *37*, 3899.

[5] For a review of the reactions of allylsilanes, see: Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1.

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[8] Sakurai, H.; Shirahata, A.; Sasaki, K.; Hosomi, A. *Synthesis* **1979**, 740.

[9] Adams, E. W.; Adkins, H. *J. Am. Chem. Soc.* **1925**, *47*, 1365.

[10] Hori, I.; Hayashi, T.; Midorikawa, H. *Synthesis* **1974**, 704.

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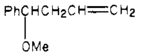
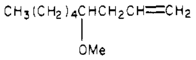
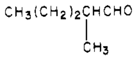
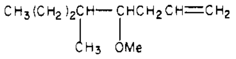
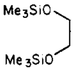
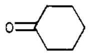
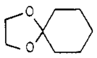
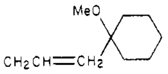
Table I. Acetalization and Allylation of Carbonyl Compounds

| entry | alkoxysilane | carbonyl compound | conditions[a] | product (% yield)[b] |
|---|---|---|---|---|
| 1 | $(MeO)_4Si$ (**3a**) | PhCHO (**2a**) | −78°, 3 h; then rt, 4 h | $PhCH(OMe)_2$<br>(**4a**) (87) |
| 2 | **3a**[c] | **2a** | −30 °C, 6 h; then rt, 3 h |  $\mathrm{Ph\underset{\displaystyle OMe}{C}HCH_2CH{=}CH_2}$<br>(**7a**) (90) |
| 3 | **3a** | $CH_3(CH_2)_2CHO$ | −40 °C, 1 h; then 0 °C, 15 min | $CH_3(CH_2)_2CH(OMe)_2$<br>(**4b**) (91) |
| 4 | **3a**[c] | $CH_3(CH_2)_4CHO$ | −78 °C, 15 min; then 0 °C, 3 h |  $\mathrm{CH_3(CH_2)_4\underset{\displaystyle OMe}{C}HCH_2CH{=}CH_2}$<br>(**7b**) (94) |
| 5 | **3a**[c] |  $\mathrm{CH_3(CH_2)_2\underset{\displaystyle CH_3}{C}HCHO}$ | −40 °C, 30 min; then 0 °C, 4 h |  $\mathrm{CH_3(CH_2)_2\underset{\displaystyle CH_3}{C}H{-}\underset{\displaystyle OMe}{C}HCH_2CH{=}CH_2}$<br>(**7c**) (77) |
| 6 | <br>(**3b**) | <br>(**2b**) | −78 °C, 5 h | <br>(**4c**) (86) |
| 7 | **3a**[c] | **2b** | −40 °C, 30 min; then 0 °C, 4 h | <br>(**7d**) (90) |

[a] All reactions were carried out in dichloromethane in the presence of a catalytic amount of iodotrimethylsilane. [b] Yields after isolation by TLC. [c] A small excess amount (1.2 equiv) of **6** was added. rt = room temperature.

**Cyclohexanone ethylene acetal (4c)**:[11] TLC (PhH/Hex, 2/3) $R_f$ 0.4; NMR ($CCl_4$) δ 1.50 (s, 10 H), 3.85 (s, 4 H).

**4-Methoxy-4-phenyl-1-butene (7a)**:[12] TLC (PhH/Hex, 1/1) $R_f$ 0.5; NMR ($CCl_4$) δ 2.15–2.73 (m, 2 H), 3.15 (s, 3 H), 4.03 (t, $J$ = 6 Hz, 1 H), 4.81–6.10 (m, 3 H), 7.21 (s, 5 H); IR (liquid film, $cm^{-1}$) 2800–3100 (m), 1640 (m), 1450 (m), 1110 (s), 915 (m); MS, $m/e$ (relative intensity) 121 ($M^+ - 41$, 100) 91 (15), 77 (25), 51 (9), 41 (3). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.63; H, 8.75.

**4-Methoxy-1-nonene (7b)**: TLC (PhH/Hex, 1/1) $R_f$ 0.85; NMR ($CCl_4$) δ 0.8–1.0 (m, 3 H), 1.1–1.6 (m, 8 H), 2.20 (t, $J$ = 6 Hz, 2 H), 2.9–3.2 (m, 1 H), 3.30 (s, 3 H), 4.7–5.2 (m, 2 H), 5.4–6.1 (m, 1 H); IR (liquid film, $cm^{-1}$) 2940 (s), 1640 (m), 1460 (w), 1100 (m); MS, $m/e$ (relative intensity) 115 ($M^+ - 41$, 96), 85 (35), 83 (100), 55 (93); high-resolution MS, $C_7H_{15}O$ ($M^+ - 41$) obsd $m/e$ 115.1117 (calcd 115.1122).

**4-Methoxy-5-methyl-1-octene (7c)**: TLC (PhH/Hex, 1/4) $R_f$ 0.8; NMR ($CCl_4$) δ 0.8–1.1 (m, 6 H), 1.2–1.9 (m, 5 H), 2.3 (t, $J$ = 6 Hz, 2 H), 2.9–3.1 (m, 1 H), 3.30 (s, 3 H), 4.9–5.2 (m, 2 H), 5.7–6.1 (m, 1 H); IR (liquid film, $cm^{-1}$) 2960 (s), 1640 (m), 1460 (m), 1380 (w), 1260 (w), 1100 (s), 920 (m), 860 (m); MS, $m/e$ (relative intensity) 115 ($M^+ - 41$, 100), 85 (71), 83 (73), 56 (30), 50 (50), 41 (39); high-resolution MS, $C_7H_{15}O$ ($M^+ - 41$) obsd $m/e$ 115.1124 (calcd 115.1123).

**1-Methoxy-1-(2-propenyl)cyclohexane (7d)**: TLC (PhH/Hex, 1/1) $R_f$ 0.8; NMR ($CCl_4$) δ 1.2–1.9 (m, 10 H), 2.15 (d, $J$ = 7 Hz, 2 H), 3,15 (s, 3 H), 4.9–5.2 (m, 2 H), 5.6–6.1 (m, 1 H); IR (liquid film, $cm^{-1}$) 2940 (s), 1640 (w), 1480 (w), 1260 (m), 1090 (s), 860 (s); MS, $m/e$ (relative intensity) 113 ($M^+ - 41$, 100), 81 (86), 71 (12); high-resolution MS, $C_7H_{13}O$ ($M^+ - 41$) obsd $m/e$ 113.0970 (calcd 113.0967).

**Reaction of Benzaldehyde (2a), Allylsilane (6), and Methanol Catalyzed by Iodine. Synthesis of 7a.** Iodine (6 mg, 0.02 mmol) was added to a mixture of benzaldehyde (53 mg, 0.50 mmol), allyltrimethylsilane (229 mg, 2.0 mmol) and methanol (39 mg, 1.2 mmol) in dichloromethane (0.5 ml) and the resulting mixture was stirred at 40 °C for 1 h. The product **7a** (72 mg, 89% yield) was purified by TLC (silica gel) by using PhH/Hex (1/1) as an eluent.

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**Registry No.** 1, 16029-98-4; **2a**, 100-52-7; **2b**, 108-94-1; **3a**, 681-84-5; **3b**, 7381-30-8; **4a**, 1125-88-8; **4b**, 10032-05-0; **4c**, 177-10-6; **6**, 18191-59-8; **7a**, 22039-97-0; **7b**, 90246-13-2; **7c**, 90246-14-3; **7d**, 60753-94-8; $CH_3(CH_2)_5CHO$, 29381-66-6; $CH_3(CH_2)_4CHO$, 66-25-1; $CH_3(CH_2)_2CH(CH_3)CHO$, 123-15-9; $I_2$, 7553-56-2.

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# An Unusual Oxidative Dimerization of 2-(Vinyloxy)phenols

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Reported here is an unusual oxidative dimerization of 2-(vinyloxy)phenols. Specifically, the phenols **2a** and **2b** were observed to give the respective dimers **3a** and **3b** in nearly quantitative yields when treated with either $Ag_2O$ or AgO under anhydrous conditions at ambient temperature (Scheme I). A particularly interesting feature of this facile transformation is the observation that the vinyloxy group in one of the monomeric units has undergone a migration and conversion to an ethanal moiety, and this all takes place under the mild reaction conditions employed.

In attempts to isolate an intermediate in the transformations of **2a** and **2b** to their respective dimers, **3a** and **3b**, the $Ag_2O$ oxidation of **2a** was carried out at low tem-

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