from acetic acid to give yellow needles, mp 193—195°, which were identified with an authentic sample of lawsone (**24**) by mixed mp and comparisons of IR and NMR spectra.

[3-^{2}H]-3-(2′-Carbomethoxyethyl)-phthalide (15-d$_1$)——Reduction of **17** (250 mg) with $NaBD_4$ in the same manner as described above for the conversion of **17** to **15** gave **15**-d$_1$ as crystals (215 mg), the NMR spectrum of which was identical with that of **15** except for the absence of a signal at δ 5.58 assignable to a proton on C-3 of **15**. Mass Spectrum *m/e*: 221 (M^+).

[4-^{2}H]-2-Carbomethoxy-4-hydroxy-α-tetralone (19-d$_1$)——Dieckmann condensation of **15**-d$_1$ (120 mg) was carried out using the same procedure as described for the preparation of **19**. The crude product (108 mg) was purified by preparative TLC (C_6H_6–ether 7: 3). From the zone corresponding to that of **19**, **19**-d$_1$ (35 mg) was obtained as crystals.

[4-^{2}H]-2-Carboxy-4-hydroxy-α-tetralone (CHT-d$_1$)——Hydrolysis of CHT-d$_1$ methyl ester (**19**-d$_1$) in the same manner as described for **19** gave CHT-d$_1$ (20 mg) as colorless prisms. The NMR spectrum of this substance showed the deuteration of 40% of the proton on C-4.

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Selective Reduction of Conjugated Enones and Dienones with Trialkylsilane and Titanium Tetrachloride

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The reaction of conjugated enones and dienones with trimethyl- or triethyl-silane in the presence of titanium tetrachloride followed aqueous workup produced the corresponding α,β-saturated ketones. This particular Lewis acid catalysis has advantage over Rh(I) complex catalysis which fails for sterically hindered substrates.

Keywords——hydrogenation enone; hydrogenation dienone; hydrosilylation titanium catalyst; hydrosilylation trialkylsilane; silane trialkyl

Catalytic hydrosilylation of α,β-unsaturated carbonyl compounds has been employed as a synthetic tool for obtaining silyl enol ethers[2] (or ketene alkyl silyl acetals[3]) or saturated carbonyl compounds which are readily formed on hydrolytic workup.[3a,4] Among a variety of catalysts,[5] classical Speier catalyst (chloroplatinic acid in isopropanol)[6] and tris(triphenyl-

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[1] Location: *Gofuku, Toyama 930, Japan.*

[2] *a*) A.D. Petrov and S.I. Sadykh-Zade, *Doklady Akad. Nauk SSSR*, **121**, 119 (1958) [*Chem. Abstr.*, **53**, 1207 (1959)]; *b*) I. Ojima, M. Nihonyanagi, T. Kogure, M. Kumagai, S. Horiuchi, K. Nakatsugawa, and Y. Nagai, *J. Organometal. Chem.*, **94**, 449 (1975); *c*) G. Stork and T.L. Macdonald, *J. Am. Chem. Soc.*, **97**, 1264 (1975).

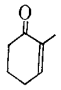
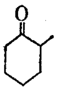
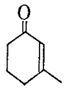
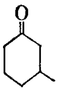
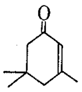
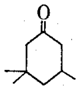
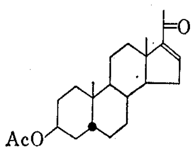
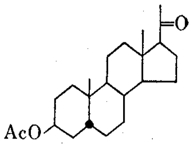
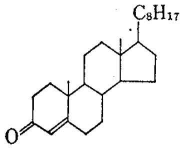
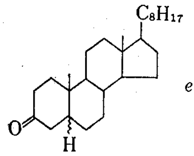
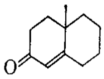
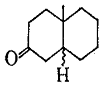
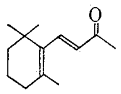
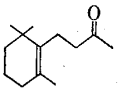
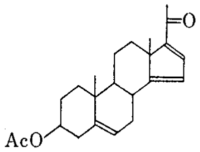
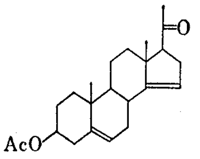
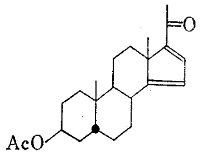
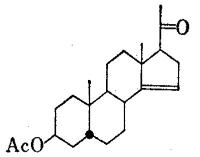
[3] *a*) E. Yoshii, Y. Kobayashi, T. Koizumi, and T. Oribe, *Chem. Pharm. Bull.* (Tokyo), **22**, 2767 (1974); E. Yoshii, T. Koizumi, and T. Kawazoe, *ibid.*, **24**, 1957 (1976); *b*) A.D. Petrov, S.I. Sadykh-Zade, and E.I. Filatova, *J. Gen. Chem. USSR*, **29**, 2896 (1959) [*Chem. Abstr.*, **54**, 11984 (1960)].

[4] *a*) I. Ojima and T. Kogure, *Tetrahedron Letters*, **1972**, 5035; *b*) E. Yoshii, T. Koizumi, H. Ikeshima, K. Ozaki, and I. Hayashi, *Chem. Pharm. Bull.* (Tokyo), **23**, 2496 (1975).

[5] C. Eaborn, "Organometallic Compounds of the Group IV Elements," Vol. I, Part 1, ed. by A.G. MacDiarmid, Marcel Dekker, Inc., New York, 1968.

[6] J.L. Speier, J.A. Webster, and G.H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

Table I. Reduction of Conjugated Enones and Dienones with Trialkylsilane–Titanium Tetrachloride

Entry	Substrate	Silane	Temp. (hr)	Yield[a]	Product[b]
1	$C_6H_5CH{=}CHCOCH_3$	$(C_2H_5)_3SiH$	0° (1)	(36)	$C_6H_5CH_2CH_2COCH_3$
2	$(CH_3)_2C{=}CHCOCH_3$	$(CH_3)_3SiH$	−5° (1)	(75)	$(CH_3)_2CHCH_2COCH_3$
3		$(CH_3)_3SiH$ $(C_2H_5)_3SiH$	−78° (1) −5° (1)	73 (72)	
4		$(CH_3)_3SiH$	−5° (1)	(74)	
5		$(CH_3)_3SiH$ $(C_2H_5)_3SiH$	−5° (1) −5° (1)	(66), [25] (53), [38]	
6		$(C_2H_5)_3SiH$	room temp. (½)	80	
7		$(CH_3)_3SiH$	room temp. (1/6)	81 $(5\beta H/5\alpha H=3)$[c]	 e)
8		$(C_2H_5)_3SiH$	0° (1) −78° (1)	53 (*cis*/*trans*=9)[d] (50), [23]	 f)
9		$(CH_3)_3SiH$	0° (1)	78	 g)
10		$(C_2H_5)_3SiH$	room temp. (1)	76	 h)
11		$(C_2H_5)_3SiH$	room temp. (1)	70—80	 h)

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a) Yield in parenthesis was obtained by gas chromatographic determination using appropriate alkane as internal standard. Value bracketed indicates the yield of recovered enone.

b) Identification of product was carried out by direct comparison of the sample isolated by gas chromatography or silica gel chromatography with authentic sample which was obtained commercially or prepared according to literature as cited.

c) Gas chromatographic determination using a glass column (4 mm × 2 m) packed with 2% OV-17 on Chromosorb W (80/100 mesh) and at 260° with Shimadzu GC-6AF apparatus. Relative retention time: $5\alpha/5\beta=1.21$(N_2 gas flow rate, 35 ml/min).

d) NMR determination by integration of peak areas of angular methyls. δ^{TMS}_{ppm} ($CDCl_3$): *cis*, 1.20; *trans*, 1.03. *cf.*) K.L. Williamson, L.R. Sloan, T. Howell, and T.A. Spencer, *J. Org. Chem.*, **31**, 436 (1966).

e) S. Nishimura, M. Shimahara, and M. Shiota, *J. Org. Chem.*, **31**, 2394 (1966).

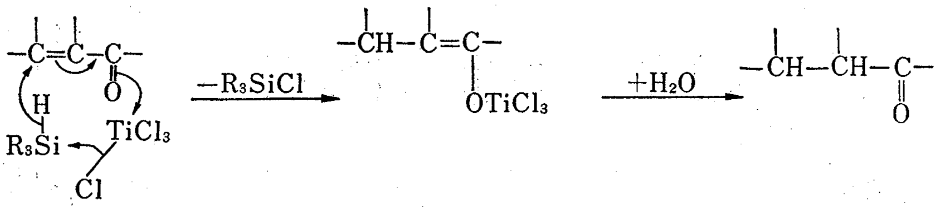
f) W. G. Dauben, J. B. Rogan, and E. J. Blanz, Jr., *J. Am. Chem. Soc.*, **76**, 6384 (1954).

g) ref. 7)

h) ref. 4*b*)

phosphine)rhodium chloride[2b,3] have been most widely used under the combination with triethylsilane. However, our experimentation associated with the selective reduction of conjugated enones through hydrosilylation revealed that those catalysts, especially the rhodium complex, were ineffectual to sterically hindered substrates. In order to solve this problem we have investigated Lewis acid catalyzed hydrosilylation with trialkylsilane (trimethyl- and triethylsilane).

Although boron trifluoride etherate did not induce the reaction at all, stannic and titanium tetrachloride proved to be highly effective in dichloromethane solvent. Of the two reagents, titanium chloride showed up general use. Stannic chloride had the tendency to form insoluble complex with some substrates which no longer entered in the reaction. The course of the reaction was believed to be expressed as depicted in eq 1. The intermediate titanium enolate was hydrolyzed during working to give α,β-saturated ketones.



(eq 1)

The experimental results obtained with representative substrates (Table I) showed that both acyclic and cyclic enones and dienones underwent saturation of α,β-double bond in good yields. Exceptional cases were entries 1 and 8 where low yields were responsible to the formation of high boiling byproduct presumably arising from the condensation of the reduction products. Characteristic features to be emphasized should be (1) α,β-unsaturated esters which undergo transition metal catalyzed hydrosilylation[3a] remained unreacted, (2) smooth reduction of $\alpha,\beta;\gamma,\delta$-dienone to γ,δ-enone (entries 9 to 11) which previously has been accomplished either with triphenylstannane[4b,7] or with phenyldimethylsilane—Rh(I) complex,[4a] and (3) predominant formation of A/B *cis* product in the cases of bicyclic enones (entries 7 and 8).

The present method which apparently compensate the drawback of Rh(I) complex catalysis should extend the applicability of hydrosilylation method for the selective reduction of conjugated enones.

Experimental

General Procedure——The reaction temperature and period were indicated in the Table I. A stirred solution of 1 mmol of conjugated enone (and an appropriate alkane as internal standard for gas chromatographic determination) in 5 to 10 ml of dry dichloromethane was treated with 1.2 ml of 1M $TiCl_4$ in dichloromethane (2.4 ml for the compounds bearing acetate group) under argon atmosphere. After stirring the solution for about 10 min, 1.2 mmol of triethylsilane (neat) or 1.2 ml of 1M trimethylsilane in dichloromethane was added and the stirring of the resulting brown to purple brown solution was continued until no progress of the reaction was indicated by thin-layer chromatography. Ice was added to the reaction mixture and the dichloromethane layer was washed with water and saturated sodium bicarbonate, and dried on $MgSO_4$. It was then concentrated at atmospheric pressure or by a rotary evaporator depending on the volatility of the product. When the product was contaminated with small amount of the corresponding saturated alcohol (evidenced by gas chromatography),[8] Jones oxidation was performed at this point. The yield was determined gas chromatographically or by isolation of the product by evaporative distillation or by preparative thin-layer chromatography using silica gel.

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7) H.R. Wolf and M.P. Zink, *Helv. Chim. Acta.*, **56**, 1062 (1973); M. Yamasaki, *Chem. Comm.*, **1972**, 606.

8) This overreduction should most probably be responsible to the liberation of free ketone from titanium enolate with moisture (see eq 1). The extent of alcohol production depends on the dryness of whole experimental procedure.