Tetrahedron Letters Vol. 21, pp 3783 - 3786
©Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/0922-3783$02.00/0

PENTADIENYLSILANES AS NEW REAGENTS OF THE SITESELECTIVE DIENYLMETHYLATION OF ELECTROPHILES PROMOTED BY A LEWIS ACID[1,2]

Akira Hosomi, Masaki Saito and Hideki Sakurai
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Summary: (2,4-Pentadienyl)- and (2,4-hexadienyl)trimethylsilanes, prepared from the corresponding pentadienylpotassiums and trimethylchlorosilane, react smoothly with various electrophiles such as acetals, aldehydes and acid halides to give pentadienylation products, with regiospecific transposition of the pentadienyl group.

We have demonstrated that allylsilane is a versatile synthetic reagent for the regiospecific allylation with allylic transposition as shown in the following equation, where E and N denote electrophilic and nucleophilic moieties of a reagent, respectively.[3]

$$\underset{1}{Me_3SiCR^1R^2CR^3{=}CR^4R^5} + E\text{-}N \longrightarrow CR^1R^2{=}CR^3CR^4R^5E + Me_3SiN$$

An example of substituted allylsilanes is isoprenyltrimethylsilane (1a; $R^1=R^2=R^4=R^5=H$, $R^3=CH_2=CH$-) which has been shown to be a useful reagent for isoprenylation.[4] An obvious and interesting extension of the reagent should be straight-chain dienylmethylsilanes such as (2,4-pentadienyl)trimethylsilane (1b; $R^1=R^2=R^3=R^4=H$, $R^5=CH_2=CH$-) and (2,4-hexadienyl)trimethylsilane (1c; $R^1=R^2=R^3=R^4=H$, $R^5=CH_3$-$CH=CH$-), the preparation and reactions of which are the subject of this paper. Dienylmethylation with the reagents is not only important as a synthetic method,[5] but creates an interesting problem of siteselectivity in the product. The reaction of 1c could be expected to make the problem clear. Recently, Seyferth and Pornet have reported the preparation and some reactions of 1b briefly.[6]

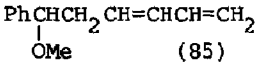
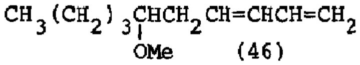
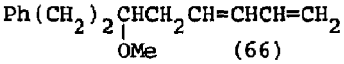
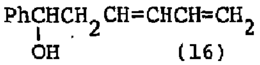
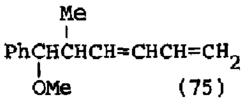
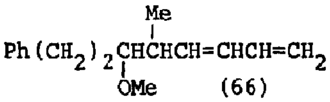
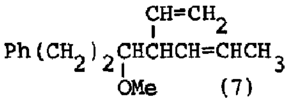
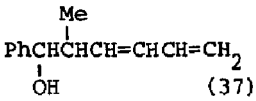
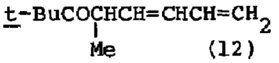
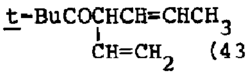
Pentadienylsilanes, (1b)[7] and (1c)[8], are prepared in 50 and 61% yield, respectively, by the reaction of the corresponding pentadienylpotassiums[9] as shown in the following scheme.

$$CH_2{=}CHCH{=}CHCH_3 \xrightarrow{a,b,c} \underset{1b,\ 50\%}{Me_3SiCH_2CH{=}CHCH{=}CH_2} + \underset{2,\ 23\%}{Me_3SiCH(CH{=}CH_2)_2}$$

$$(CH_2{=}CHCH_2)_2 \xrightarrow[61\%]{a,b,c} \underset{1c}{Me_3SiCH_2CH{=}CHCH{=}CHCH_3}$$

a. K, Et_3N, THF, rt, 0.5h then reflux, 5h; b. Me_3SiCl, 0°, 1h;
c. Saturated aq NH_4Cl.

Table 1. Reactions of pentadienylsilanes, (**1b**) and (**1c**), with electrophiles[a]

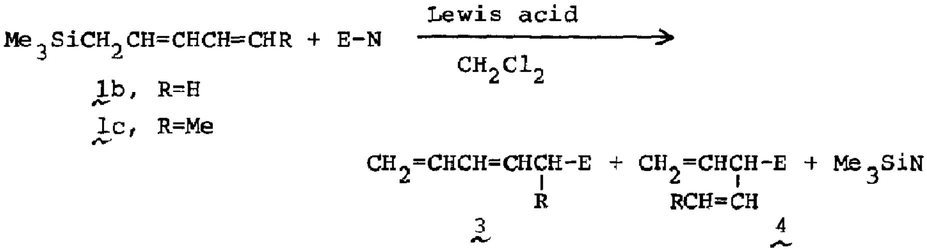
Entry	Pentadienylsilane	Electrophile	Lewis acid	Reaction time (min)	Products (%yield)[b]
1	$\text{Me}_3\text{SiCH}_2\text{CH=CHCH=CH}_2$ (**1b**)	PhCH(OMe)_2	$\text{BF}_3\cdot\text{OEt}_2$	60	 $\underset{\text{OMe}}{\text{PhCH}}\text{CH}_2\text{CH=CHCH=CH}_2$ (85)
2	**1b**	$\text{CH}_3(\text{CH}_2)_3\text{CH(OMe)}_2$	TiCl_4	10	 $\text{CH}_3(\text{CH}_2)_3\underset{\text{OMe}}{\text{CH}}\text{CH}_2\text{CH=CHCH=CH}_2$ (46)
3	**1b**	$\text{Ph(CH}_2)_2\text{CH(OMe)}_2$	TiCl_4	3	 $\text{Ph(CH}_2)_2\underset{\text{OMe}}{\text{CH}}\text{CH}_2\text{CH=CHCH=CH}_2$ (66)
4	**1b**	PhCHO	$\text{BF}_3\cdot\text{OEt}_2$	60[c]	 $\underset{\text{OH}}{\text{PhCH}}\text{CH}_2\text{CH=CHCH=CH}_2$ (16)
5	**1b**	*t*-BuCOCl	TiCl_4	1	*t*-$\text{BuCOCH}_2\text{CH=CHCH=CH}_2$ (34) *t*-$\text{BuCOCH(CH=CH}_2)_2$ (25)
6	$\text{Me}_3\text{SiCH}_2\text{CH=CHCH=CHCH}_3$ (**1c**)	PhCH(OMe)_2	$\text{BF}_3\cdot\text{OEt}_2$	60	 $\underset{\text{OMe}}{\text{PhCH}}\overset{\text{Me}}{\text{CH}}\text{CH=CHCH=CH}_2$ (75)
7	**1c**	$\text{Ph(CH}_2)_2\text{CH(OMe)}_2$	TiCl_4	3	 $\text{Ph(CH}_2)_2\underset{\text{OMe}}{\text{CH}}\overset{\text{Me}}{\text{CH}}\text{CH=CHCH=CH}_2$ (66)  $\text{Ph(CH}_2)_2\underset{\text{OMe}}{\text{CH}}\overset{\text{CH=CH}_2}{\text{CH}}\text{CH=CHCH}_3$ (7)
8	**1c**	PhCHO	$\text{BF}_3\cdot\text{OEt}_2$	120	 $\underset{\text{OH}}{\text{PhCH}}\overset{\text{Me}}{\text{CH}}\text{CH=CHCH=CH}_2$ (37)
9	**1c**	*t*-BuCOCl	TiCl_4	1	 *t*-$\text{BuCO}\underset{\text{Me}}{\text{CH}}\text{CH=CHCH=CH}_2$ (12)  *t*-$\text{BuCO}\underset{\text{CH=CH}_2}{\text{CH}}\text{CH=CHCH}_3$ (43)

---

[a] All reactions were carried out in dichloromethane at -78° unless otherwise noted. [b] Yield after isolation. [c] At -40°.

(Pentadienyl)trimethylsilanes (**1b**) and (**1c**), thus obtained, reveal high reactivity toward various electrophiles such as acetals, aldehydes and acid halides promoted by a Lewis acid to afford the corresponding pentadienylation products regioselectively.[10] The representative results are listed in Table 1.

In all cases, the reaction of **1b** with acetals and aldehydes proceeds very smoothly to afford the corresponding pentadienylation products (**3**) selectively in good yield, except for the cases with acid chlorides where the reaction takes place at the γ-carbon of **1b** in a considerable extent to give **4**. (eq.1) In order



$$\mathrm{Me_3SiCH_2CH{=}CHCH{=}CHR} + \mathrm{E{-}N} \xrightarrow[\mathrm{CH_2Cl_2}]{\text{Lewis acid}} \underset{\mathbf{3}}{\mathrm{CH_2{=}CHCH{=}CH\underset{R}{C}H{-}E}} + \underset{\mathbf{4}}{\mathrm{CH_2{=}CH\underset{RCH=CH}{C}H{-}E}} + \mathrm{Me_3SiN} \qquad (1)$$

1b, R=H

1c, R=Me

to examine whether the reaction proceeds in a regiospecific manner with concomitant rearrangement of the pentadienyl group, (2,4-hexadienyl)trimethylsilane (**1c**) was employed as a diagnostic reagent in the reaction. The reaction of **1c** also took place very smoothly to give pentadienylation products (**3**, R=CH_3) in which the new carbon-carbon linkage occurred specifically at the ε-carbon of the pentadienyl group of **1c**. In these cases, the electrophilic attack at the γ-carbon of the pentadienyl group of **1c** took place in a greater extent to afford **4**, presumably due to the greater steric hindrance at the ε-carbon of **1c** than of **1b**.

The synthetic utility of the present reagents is displayed by the selective introduction of the pentadienyl group to various electrophiles as shown in the Table. In addition, because handling and keeping of the reagents are easy due to the great stability in air, the present reaction is of advantage over other pentadienylation reactions with alkali or alkaline-earth metal derivatives.[9,11]

The following experimental procedure is typical. To a solution of a Lewis acid (1 mmol) and dichloromethane (10 ml) at -78° under nitrogen was added a mixture of a pentadienylsilane (1 mmol) and an electrophile (1 mmol) in dichloromethane (10 ml). The mixture was stirred under a given condition in the Table and hydrolyzed. The organic layer was separated and the aqueous layer was extracted with ether (20ml×2). After the combined mixture was dried over sodium sulfate, the solvent was evaporated. From the residue, pure products were isolated by TLC.

Acknowledgement: We thank to Toshiba Silicone Co., Ltd., and the Mitsubishi Foundation for gifts of chlorosilanes and a partial support to the work. Our thanks are also due to Dr. H. Yasuda, Osaka University, for communication on the detailed manipulation of the preparation of pentadienylpotassiums.

References and Notes

1. Chemistry of Organosilicon Compounds. 141.
2. This work is presented in part at the 37th Annual Meeting of the Chemical Society of Japan, Yokohama, April 1978, Abstract II, p949, and at the Symposium on the Synthetic Organic Chemistry, Tokyo, Nov. 1978, Abstract p5.
3. For recent reports, see a) A. Hosomi and H. Sakurai, Tetrahedron Lett., 2589 (1978); b) idem, J. Am. Chem. Soc., **99**, 1673 (1977); c) A. Hosomi, H. Hashimoto, H. Kobayashi, and H. Sakurai, Chem. Lett., 245 (1979); d) A. Hosomi, H. Kobayashi, and H. Sakurai, Tetrahedron Lett., **21**, 955 (1980) and references cited therein.
4. A. Hosomi, M. Saito, and H. Sakurai, Tetrahedron Lett., 429 (1979).
5. For a review, see C. A. Henrick, Tetrahedron, **33**, 1845 (1977).
6. a) D. Seyferth and J. Pornet, J. Org. Chem., **45**, 1721 (1980); b) J. Pornet Tetrahedron Lett., **21**, 2049 (1980).
7. **1b**: bp 81° (97 mmHg); NMR(CCl_4)δ 0.00(9H, s, $SiCH_3$), 1.40-1.80(2H, m, $SiCH_2$), 4.80-6.80(5H, m, olefinic protons); IR (neat) 3100, 3020, 2960, 1636, 1587, 1230, 991, 954, 898, 754, 699 cm^{-1}; UV λ_{max} 237.5 nm(ε=5.6×10^3). *Anal*. Calcd for $C_8H_{16}Si$: C, 68.49; H, 11.50. Found: C, 68.74; H, 11.68. **2**: NMR (CCl_4)δ 0.05(9H, s, $SiCH_3$), 2.50(1H, tq, J=9.0, 1.0Hz, SiCH), 4.85(2H, ddd, J=17.0, 2.0, 1.0Hz, Z proton in $=CH_2$), 4.90(2H, ddd, 10.0, 2.0, 1.0Hz, E proton in $=CH_2$), 5.85(2H, ddd, J=17.0, 10.0, 9.0Hz, CH=), IR (neat) 3060, 2930, 1625, 1222, 992, 900 cm^{-1}. *Anal*. Calcd for $C_8H_{16}Si$: C, 68.49; H, 11.50. Found: C, 68.67; H, 11.65.
8. **1c**: bp 89° (67 mmHg); NMR(CCl_4)δ 0.10(1H, s, $SiCH_3$), 1.50-1.95(5H, $SiCH_2$, CH_3), 5.10-6.45(4H, m, olefinic protons); IR (neat) 3007, 2957, 1642, 1606, 1249, 1148, 980, 944, 854 cm^{-1}; UR λ_{max} 238.5 nm (ε=1.3×10^4). *Anal*. Calcd for $C_9H_{18}Si$: C, 70.05: H, 11.76. Found: C, 70.25; H, 11.83.
9. a) H. Yasuda and H. Tani, J. Macromol. Sci. Chem., **A9**, 1007 (1975); b) H. Yasuda, T. Narita, and H. Tani, Tetrahedron Lett., 2443 (1973); c) H. Yasuda and H. Tani, ibid., 11 (1975); d) M. Yamauchi, M. Hiramatsu, H. Yasuda, and H. Tani, 24th Symposium on Organometallic Chemistry, Kyoto, 1976, Preprint p4.
10. All new compounds obtained in this work gave correct elemental analyses and satisfactory spectral data.
11. a) R. Paul and S. Tchelitcheff, Bull. Soc. Chim. Fr., 108 (1948); b) F. Gerad and P. Miginiac, ibid., 1924 (1974); c) idem, ibid., 2527 (1974); d) P. Miginiac, Ann. Chim. (Paris), [13] **7**, 446 (1962).

(Received in Japan 28 June 1980)