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Peterson Olefination of (α-Methoxybenzyl)silane with Aldehydes and Ketones Leading to Vinyl Ethers

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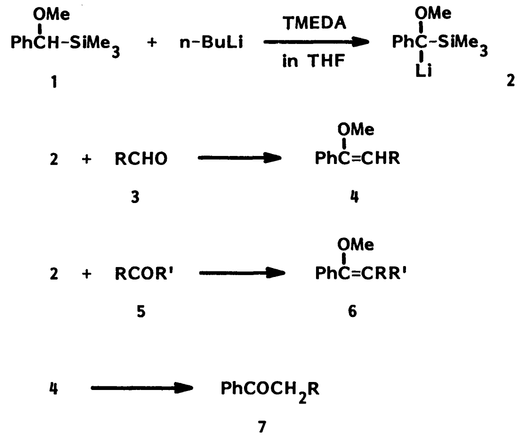
Synopsis. (α-Methoxybenzyl)trimethylsilane is deprotonated with butyllithium and then allowed to react with a variety of carbonyl compounds giving vinyl ethers which are convertible into methyl ketones under mild conditions.

Although a variety of α-hetero-substituted organosilanes have been utilized in organic synthesis as an attracting member of isolable α-hetero organometallics, only limited applications of α-hydroxy or α-alkoxy alkylsilanes are known.[1] The present paper describes the vinyl ether synthesis using (α-methoxybenzyl)trimethylsilane **1** which is readily available through the 1,2-anionic rearrangement of silyl moiety of benzyl silyl ether.[2]

When the silane **1** was treated with a mixture of butyllithium and *N*,*N*,*N'*,*N'*-tetramethyl-1,2-ethanediamine (TMEDA) in dry THF at 0 °C, the solution immediately began to color and became deep red in 5 min. In this solution, the silyl-stabilized carbanion **2** was found to form in an excellent yield. Benzaldehyde **3a** was added and the mixture was allowed to stir at 0 °C and then at room temperature until all the silane **1** was consumed (checked on TLC). From the above procedure, 83% yield of **4a** was given as 7:2 mixture of E and Z isomers.

As shown in Scheme 1 and Table 1, the silyl-stabilized carbanion **2** was allowed to react with several carbonyl compounds. The reactions with aromatic aldehydes **3b—f**, heteroaromatic aldehydes **3g—h**, an α,β-unsaturated aldehyde **3i**, aliphatic aldehydes **3j—k**, and ketones **5a—d** gave the corresponding vinyl ethers in good yields as mixtures of E and Z isomers. Their structures were determined on the basis of the spectral data and elementary analyses.

Some of the vinyl ethers thus obtained were readily hydrolyzed under mild conditions. When the vinyl ethers **4** were heated in methanol in the presence of a catalytic amount of hydrochloric acid the correspond-



Scheme 1.

Table 1. Peterson olefination of (α-methoxybenzyl)trimethylsilane **1**

Carbonyl compound	Reaction time/h[a)]	Product			Yield[b)]	E/Z[c)]	OMe[d)]		=CH-[d)]		others[d)]	C=C	M+
					%		E	Z	E	Z			*m/z*
			R										
3a	5.5	**4a**	Ph		83	7/2	3.74	3.57	5.77	5.65		1630	210
3b	20	**4b**	*o*-MeC_6H_4		78	7/2	3.77	3.52	5.75	6.16	2.25E 2.32Z (*p*-Me)	1625	224
3c	19.5	**4c**	*m*-MeC_6H_4		83	7/2	3.72	3.57	5.76	6.05	2.16E 2.34Z (*m*-Me)	1630	224
3d	6.5	**4d**	*p*-MeC_6H_4		71	7/2	3.72	3.58	5.76	6.07	2.22E 2.32Z (*p*-Me)	1630	224
3e	20	**4e**	*o*-ClC_6H_4		68	1/1	3.76	3.51	5.85	6.39		1630	244, 246
3f	19.5	**4f**	*m*-ClC_6H_4		92	7/2	3.76	3.59	5.70	5.93		1630	244, 246
3g	15.5	**4g**	2-Furyl		65	3/1	3.71	3.62	5.69	6.20		1630	200
3h	16	**4h**	2-Thienyl		62	6/1	3.73	3.65	5.98	6.48		1630	216
3i	18	**4i**	PhCH=CH (t)		76	3/1	3.64	3.57	5.65^d	6.06^d		1625	236
3j	20	**4j**	*n*-Pr		70	1/1	3.60	3.50	4.71^t	5.29^t		1660	176
3k	20	**4k**	*i*-Pr		77	1/1	3.55	3.48	4.52^d	5.12^d		1650	176
3l	20.5	**4l**	*t*-Bu		76	3/2	3.52	3.39	4.79	5.04	0.92E 1.19Z (*t*-Bu)	1650	190
			R	R'									
5a	6	**6a**	Ph	Ph	70	—	3.36		—			1610	286
5b	5.5	**6b**	Ph	Me	94	2/1	3.34	3.18	—		1.92E 2.14Z (Me)	1630	224
5c	6	**6c**	Et	Et	79	—	3.18		—			1650	190
5d	13	**6d**	$(CH_2)_4$		60	—	3.39		—			1660	188

a) All the reactions were performed by using each 1.5 equivalent amounts of butyllithium, carbonyl compounds, and TMEDA in dry THF under nitrogen. In the beginning the reaction mixture was stirred at 0 °C for 1 h and then at room temperature for the time shown in Table. b) All isolated yields as mixtures of E and Z isomers. c) Determined by ^{1}H-NMR spectra. d) Measured in deuteriochloroform. All the signals appear as singlets otherwise cited. d: doublet; t: triplet.

TABLE 2. HYDROLYSIS OF THE VINYL ETHERS

Vinyl ether	Conditions[a)]		Product	R	Yield/%[b)]
4a	reflux in MeOH	3 h	**7a**	Ph	86
4f	reflux in MeOH	6 h	**7b**	*m*-$\mathrm{ClC_6H_4}$	91
4i	reflux in MeOH	5 h	**7c**	PhCH=CH (t)	86[c)]
	rt in HCOOH	5 h	**7c**		35
4l	reflux in MeOH	3 h	**7d**	*t*-Bu	78

a) The reaction in MeOH was carried out in the presence of a catalytic amount of HCl. b) All isolated yields. c) Containing 42% of 3-methoxy-1,4-diphenyl-1-butanone.

ing methyl ketones **7a—d** were given as shown in Scheme 1 and Table 2. A part of **7c** underwent the double bond migration into a conjugated ketone and the subsequent methanol addition gave 3-methoxy-1,4-diphenyl-1-butanone (42%).

Experimental

General Procedure for the Reaction of 1 with Carbonyl Compounds 3 and 5. To the solution of TMEDA (2.3 ml, 1.5 mmol) in dry THF (distilled over lithium aluminum hydride immediately before use, 2 ml) was added at 0 °C under nitrogen butyllithium (15% content in hexane, 0.94 ml, 1.5 mmol). After 5 min, the silane **1** (0.194 g, 1.5 mmol in 0.5 ml of THF) was added slowly by the use of a syringe, the color of solution turning deep red. After an additional 5 min at the same temperature, carbonyl compounds **3** or **5** (1.5 mmol for **3a—f**, **3i**, **5a—d**, and 2.0 mmol for **3g—h**, **3j—l** in 1 ml of THF) were added dropwise. The resulting mixture was stirred at 0 °C under nitrogen for 1 h and then at room temperature for the time shown in Table 1. Aqueous ammonium chloride solution (**3—5** ml) was added and the mixture was extracted with ether (20 ml×2). The ether extracts were combined and washed with saturated sodium chloride three times, and finally dried over anhydrous magnesium sulfate. The residue obtained by evaporation of the ether *in vacuo* was chromatographed over silica gel using hexane–benzene (5:1) as an eluent giving viscous oil of vinyl ethers **4** and **6**. The yields, E/Z ratios, ^{1}H-NMR, IR, and mass spectral data are listed in Table 1. As the separation of the E and Z isomers by repeated column chromatography were unsuccessful, purified E/Z mixtures were submitted to elementary analyses.

Other data for the vinyl ethers **4** and **6** are as follows: **4a**: colorless oil (E/Z=7/2), Found: C, 85.49; H, 6.64%. Calcd for $\mathrm{C_{15}H_{14}O}$: C, 85.68; H, 6.71%. **4b**: colorless oil (E/Z=7/2), Found: C, 85.83; H, 7.13%. Calcd for $\mathrm{C_{16}H_{16}O}$: C, 85.68; H, 7.19%. **4c**: colorless oil (E/Z=7/2), Found: C, 85.62; H, 7.27%. Calcd for $\mathrm{C_{16}H_{16}O}$: C, 85.68; H, 7.19%. **4d**: pale yellow oil (E/Z=7/2), Found: C, 85.55; H, 7.10%. Calcd for $\mathrm{C_{16}H_{16}O}$: C, 85.68; H, 7.19%. **4e**: colorless oil (E/Z=1/1), Found: C, 73.75; H, 5.55%. Calcd for $\mathrm{C_{15}H_{13}OCl}$: C, 73.62; H, 5.35%. **4f**: colorless oil (E/Z=7/2), Found: C, 73.82; H, 5.55%. Calcd for $\mathrm{C_{15}H_{13}OCl}$: C, 73.62; H, 5.35%. **4g**: pale yellow oil (E/Z=3/1), ^{1}H-NMR ($\mathrm{CDCl_3}$) δ=5.53, 6.72 (1H, 3:1, d, *J*=3.0 Hz, 3-H of furyl), 6.15, 6.43 ppm (1H, 3:1, m, 4-H of furyl), Found: *m/z* 200.0840. Calcd for $\mathrm{C_{13}H_{12}O_2}$: M, 200.0837. **4h**: pale yellow oil (E/Z=6/1), Found: C, 72.06; H, 5.57%. Calcd for $\mathrm{C_{13}H_{12}OS}$: C, 72.19; H, 5.59%. **4i**: pale yellow oil (E/Z=3/1), ^{1}H-NMR ($\mathrm{CDCl_3}$) δ=5.65 (3/4H, d, *J*=9.0 Hz, $\mathrm{C\underline{H}{=}C(OMe)Ph}$ of E isomer), 6.06 (1/4H, d, *J*=9.5 Hz, $\mathrm{C\underline{H}{=}C(OMe)Ph}$ of Z isomer), 6.37 (3/4H, d, *J*=17.0 Hz, $\mathrm{PhC\underline{H}{=}CHCH{=}}$ of E isomer), 6.50 (1/4H, d, *J*=17.5 Hz, $\mathrm{PhC\underline{H}{=}CHCH{=}}$ of Z isomer), and 6.84 ppm (3/4H, dd, *J*=9.0 and 17.0 Hz, $\mathrm{PhCH{=}C\underline{H}CH{=}}$ of E isomer). **4j**: colorless oil (E/Z=1/1), ^{1}H-NMR ($\mathrm{CDCl_3}$) δ=0.89, 0.98 (each 3/2H, t, $\mathrm{CH_3}$), 1.28—1.70 (2H, m, $\mathrm{CH_2C\underline{H}_2CH_3}$), 2.07, 2.26 (each 2/2H, q, $\mathrm{{=}CHC\underline{H}_2{-}}$), 4.71 (1/2H, t, *J*=7.5 Hz, $\mathrm{{=}C\underline{H}CH_2}$ of E isomer), and 5.29 ppm (1/2H, t, *J*=8.0 Hz, $\mathrm{{=}C\underline{H}CH_2}$ of Z isomer), Found: *m/z* 176.1200. Calcd for $\mathrm{C_{12}H_{16}O}$: M, 176.1207. **4k**: colorless oil (E/Z=1/1), ^{1}H-NMR ($\mathrm{CDCl_3}$) δ=0.97, 1.06 (each 3/2H, d, $\mathrm{\underline{Me}_2CH}$), 2.26 (1/2H, m, $\mathrm{Me_2C\underline{H}}$ of E isomer), 3.20 (1/2H, m, $\mathrm{Me_2C\underline{H}}$ of Z isomer), 4.52 (1/2H, d, *J*=9.5 Hz, =CH– of E isomer), and 5.12 ppm (1/2H, d, *J*=9.5 Hz, of Z isomer), Found: *m/z* 176.1202. Calcd for $\mathrm{C_{12}H_{16}O}$: M, 176.1202. **4l**: the E and Z isomers were separated through the column chromatography over silica gel using hexane–benzene (5:1). *E*-**4l**: colorless oil, Found: *m/z* 190.1307. Calcd for $\mathrm{C_{13}H_{18}O}$: M, 190.1357; *Z*-**4l**: colorless oil, Found: *m/z* 190.1352. Calcd for $\mathrm{C_{13}H_{18}O}$: M, 190.1357. **6a**: colorless prisms from benzene–hexane, mp 110—111 °C, Found: C, 88.08; H, 6.34%. Calcd for $\mathrm{C_{12}H_{18}O}$: C, 87.92; H, 6.31%. **6b**: colorless oil (E/Z=2/1), Found: C, 85.51; H, 7.11%. Calcd for $\mathrm{C_{16}H_{16}O}$: C, 85.68; H, 7.19%. **6c**: colorless oil, ^{1}H-NMR ($\mathrm{CDCl_3}$) δ=0.92, 1.03 (each 3H, t, $\mathrm{C\underline{H}_3CH_2}$), 1.93, 2.23 (each 2H, q, $\mathrm{CH_3C\underline{H}_2}$), and 7.18 ppm (5H, br.s, ArH), Found: *m/z* 190.1295. Calcd for $\mathrm{C_{13}H_{18}O}$: M, 190.1357. **6d**: colorless oil, ^{1}H-NMR ($\mathrm{CDCl_3}$) δ=1.55—1.90 and 2.20—2.70 ppm (each 4H, m, $\mathrm{CH_2}$), Found: *m/z* 188.0830. Calcd for $\mathrm{C_{13}H_{16}O}$: M, 188.1119.

General Procedure for the Hydrolysis of 4. The vinyl ether **4** was heated under reflux in methanol containing a catalytic amount of hydrochloric acid until **4** was completely consumed (checked on TLC). The methanol was evaporated *in vacuo*, the residue was treated with water, extracted with ether (twice), the ether was washed with aqueous sodium hydrogencarbonate, and dried over magnesium sulfate. The residue obtained by the removal of the ether *in vacuo* was chromatographed over silica gel using hexane–benzene (2:1) as an eluent. The reaction conditions and yields are listed in Table 2. All the methyl ketones **7** are known compounds, therefore their structures were confirmed by the comparison of melting points and/or spectral data with those of authentic samples. **7b**: colorless prisms; mp 43 °C;[3)] IR (neat) 1690 cm^{-1}; ^{1}H-NMR ($\mathrm{CDCl_3}$) δ=4.13 (2H, s, $\mathrm{CH_2}$) and 6.98—7.55 ppm (9H, m, ArH); MS *m/z* 230, 232 (M$^+$) and 105 (base peak). **7c**: colorless prisms (benzene–hexane), mp 88—89 °C,[4)] IR (KBr) 1660 cm^{-1}, ^{1}H-NMR ($\mathrm{CDCl_3}$) δ=3.79 (2H, m, $\mathrm{CH_2}$), 6.35 (2H, m, $\mathrm{C\underline{H}{=}C\underline{H}}$), and 7.00—8.00 ppm (10H, m, ArH), MS *m/z* 222 (M$^+$) and 105 (base peak). **7d**: colorless oil,[5)] IR (neat) 1660 cm^{-1}; ^{1}H-NMR ($\mathrm{CDCl_3}$) δ=1.03 (9H, s, *t*-Bu), 2.79 (2H, s, $\mathrm{CH_2}$), and 7.20—7.88 ppm (5H, m, ArH), MS *m/z* 176 (M$^+$) and 77 (base peak).

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