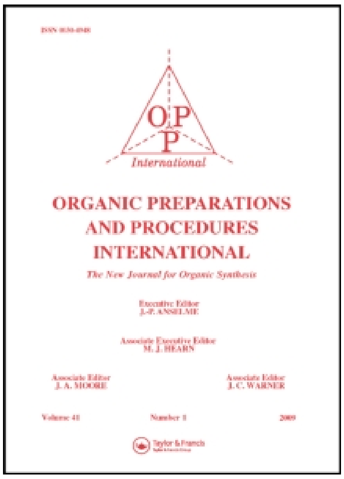

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α,β-UNSATURATED ALDEHYDES BY ONE-STEP VINYLOGATION OF CARBONYL COMPOUNDS

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α,β-UNSATURATED ALDEHYDES BY ONE-STEP VINYLOGATION OF CARBONYL COMPOUNDS

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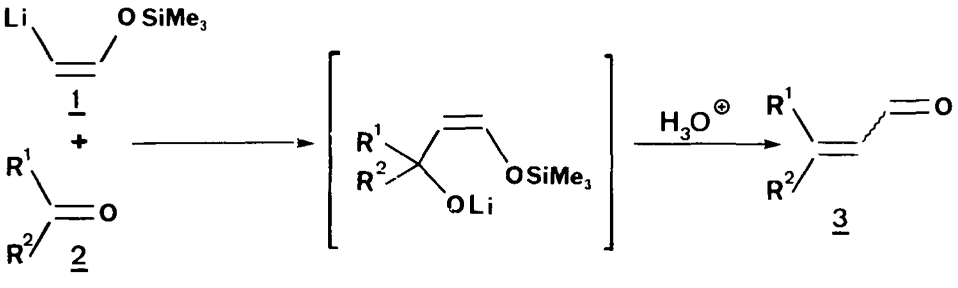
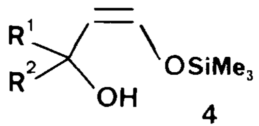
Several recent publications have focused on a new class of functionalized vinyllithium derivatives (Li-C=C-Y, Y= OEt, $OSiR_3$, NR_2),[1-3] which seemed to be synthetically useful for the one-step vinylogation of carbonyl compounds. The present paper describes the conversion of a variety of substrates 2 to their vinylogs 3 in better yields than previously reported by treatment with (Z)-2-(trimethylsiloxy) vinyllithium 1 (Table). The required reagent 1 is easily prepared by halogen-metal exchange between (Z)-2-(trimethylsiloxy) vinyl bromide and one molar equivalent of t-butyllithium at -70° in ether.[2a]



Condensation of 1 with aldehydes and ketones 2 occurred readily at low temperatures. Treatment of the reaction mixture with dilute hydrochloric acid, for a short period of time, produced the α,β-unsaturated carbonyl compounds 3 smoothly, without double bond migration. The condensation of 1 with an α,β-unsaturated carbonyl compound such as 2g afforded only the 1,2-adduct, which upon treatment with a weakly basic aqueous solution afforded only the γ-hydroxysilylenol ether 4 ;[2a-c] these compounds were easily converted into the products 3 in high yield upon simple acidic hydrolysis. In contrast, the table shows that the previously reported attractive one-step methods have some drawbacks. For example, the acetaldehyde procedure[4] (method B) is not applicable to many substrates, and often proceeds with low yields. It has also been reported that while the ylid, Ph$_3$P=CH-CHO, condenses with aldehydes (method C)[5], but it fails to react with ketones. In contrast with these conventional procedures, the new vinylic functionalized reagents such as 1 have a wide application in the preparation of unsaturated carbonyl compounds and offer significant advantages. In addition to its versatility, the ease of work-up, the high yields, the availability of starting material, the simplicity of manipulation and the absence of retro-products, make this procedure extremely attractive.

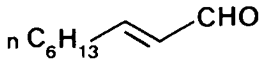
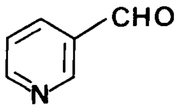
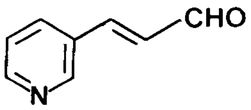
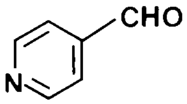
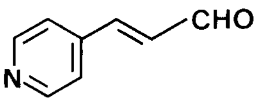
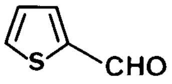
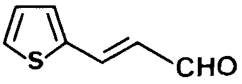
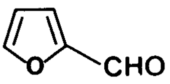
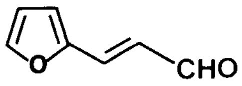
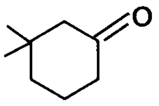
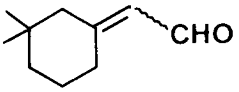
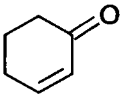
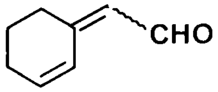
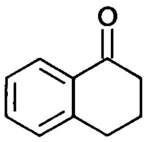
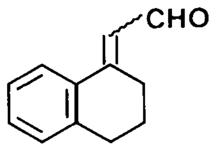


4

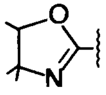
EXPERIMENTAL SECTION

IR spectra were obtained with a Perkin-Elmer Model Infracord 237 spectrometer and ^{1}H NMR spectra were obtained with a Perkin-Elmer R 12 (60 MHz) spectrometer, in CDCl$_3$. Alkyl - lithium titration was carried out according to a recent literature procedure.[9] Ether was distilled from sodium benzophenone ketyl prior to use. The reactions were performed

Table. Yields of Vinylogated Aldehydes

	2	**3**	Yields	
			This work	Lit.[c]
a	n C_6H_{13}—CHO		85% [a]	50% (D,6c) 50% (E,F,6d) 80% (G,1a)
b			quant.[b]	4.5% (B,4a) 55% (C,7) 14% (D,6c)
c			quant.[b]	0.6% (B,4b) 60% (B,4c) 62% (C,7) 23% (D,6e)
d			quant.[b]	54% (B,4d) 30% (B,4c) 55% (C,4e)
e			90% [a]	30% (E,4f)
f			quant.[b]	82% (A,8c) d (A,8a,b) 69% (A,8d) 83% (A,8b) 61% (D,6c) 94% (G,1e)
g			85% [a]	50% (G,1a) 66% (G,1b)
h			70% [a]	d

a) Distilled product; b) crude product; c) A : Multi-step method; B : Crossed aldol condensation with acetaldehyde; C : $Ph_3P=CH-CHO$[5]; D* : $R-CH_2Li$[6a-c]; E* : $R-CH=PPh_3$; F* : $R-CH_2PO(OEt_2)$[6d]; G : Li-CH=CH-OEt; d) No reported yield.

* R 

under an argon atmosphere.

General Procedure For Aldehydes (3a-g).- A solution of 1.5 ml of 1.7N t-butyllithium in pentane (2.5 mmol) was added over a 10 min period to a solution of 1-bromo-2-(trimethylsiloxy) ethylene[10] (0.5 g, 2.5 mmol) in anhydrous ether (16.5 ml) maintained at -70°. The mixture was stirred magnetically for 20 min at -70°, then a solution of the carbonyl compound 2 (2 mmol) in anhydrous ether (0.5 ml) was added dropwise over a 5 min period. The cooling bath was removed and the reaction stirred at -20° for 0.5 hr. The reaction cooled back to -50° was quenched with 1.2N HCl (2.5 ml) solution and the temperature was raised to 10° and stirring was continued for 0.5 hr. After the usual work-up, the ethereal extract gives the crude α,β-unsaturated aldehydes 3, which were recrystallized or distilled in some cases (3a, 3e, 3g, 3h).

(E)-Nonenal(3a), bp. 60° (0.2 mmHg), lit.[11] 56-58° (0.1 mmHg). IR (neat) : 1690, 1635 cm^{-1}. ^1H NMR : δ 0.9 (3 H, t), 1.35 (8 H, m), 2.4 (2 H, m), 6.1 (1 H, ddd, J = 16.0, 7.5, 2.0 Hz), 6.85 (1 H, td, J = 16.0, 7.5 Hz), 9.55 (1 H, d, J = 7.5 Hz).

(E)-3-(3-Pyridyl)propenal(3b), pale yellow oil. IR (neat) : 1680, 1630 cm^{-1}. ^1H NMR : δ 6.85 (1 H, dd, J = 16.0, 7.5 Hz), 7.45 (H_5, q, J = 8.0, 5.0 Hz), 7.6 (1 H, d, J = 16.0 Hz), 8.0 (H_4, m, J = 8.0, 2.0, 2.0 Hz), 8.75 (H_6, dd, J = 5.0, 2.0 Hz), 8.85 (H_2, d, J = 2.0 Hz), 9.75 (1 H, d, J = 7.5 Hz).

(E)-3-(4-Pyridyl)propenal(3c), pale yellow oil. IR (neat) : 1685, 1635 cm^{-1}. ^1H NMR : δ 6.85 (1 H, dd, J = 16.0, 7.5 Hz), 7.35-7.65 (H_3, H_5, m), 7.6 (1 H, d, J = 16.0), 8.7 (H_2, H_6, m), 9.8 (1 H, d, J = 7.5 Hz).

<u>(E)-3-(2-Thienyl)propenal</u>(<u>3d</u>), pale yellow oil. IR (neat) : 1680, 1635 cm^{-1}. ^{1}H NMR : δ 6.4 (1 H, dd, J = 16.0, 8.0 Hz), 7.5 (1 H, d, J = 16.0 Hz), 7.1-7.55 (H_3, H_4, H_5, m), 9.55 (1 H, d, J = 8.0 Hz).

<u>(E)-3-(2-Furanyl)propenal</u>(<u>3e</u>), mp. 48-50°, lit.[4g] 53°. IR (neat) : 1675, 1635 cm^{-1}. ^{1}H NMR : δ 6.5 (H_4, m, J = 3.5, 2.0 Hz), 6.55 (1 H, dd, J = 16.0, 8.0 Hz), 6.8 (H_3, d, 3.5 Hz), 7.25 (1 H, d, J = 16.0 Hz), 7.55 (H_5, d, J = 2.0 Hz), 9.6 (1 H, d, J = 8.0 Hz).

<u>3,3-(Dimethylcyclohexylidene)acetaldehyde</u>(<u>3f</u>), pale yellow oil. IR (neat) : 1675, 1625 cm^{-1}. ^{1}H NMR : δ Z isomer (43%) : 1.0 (6 H, s), 1.6 (4 H, s), 2.15 (2 H, m), 2.45 (2 H, s), 5.9 (1 H, d, J = 8.0 Hz), 10.1 (1 H, d, J = 8.0 Hz), E isomer (57%) : 1.0 (6 H, s), 1.6 (4 H, m), 2.0 (2 H, s), 2.6 (2 H, m), 5.75 (1 H, d, J = 8.0 Hz), 10.15 (1 H, d, J = 8.0 Hz).

<u>2-(Cyclohex-2-en-1-ylidene)acetaldehyde</u>(<u>3g</u>), bp. 65° (0.3 mm Hg). IR (neat) : 1670, 1625 cm^{-1}. ^{1}H NMR : δ Z isomer (37%) : 1.85 (2 H, m), 2.3 (4 H, m), 5.65 (1 H, d, J = 8.0 Hz), 6.25 (1 H, m), 7.15 (1 H, d, J = 10.0 Hz), 10.25 (1 H, d, 8.0 Hz), E isomer (63%) : 1.85 (2 H, m), 2.3 (2 H, m), 2.9 (2 H, m), 5.75 (1 H, d, J = 8.0 Hz), 6.25 (2 H, m), 10.2 (1 H, d, J = 8.0 Hz).

<u>1,2,3,4,-(Tetrahydronaphtalen-1-ylidene)acetaldehyde</u>(<u>3h</u>).- A solution of 2.65 ml of <u>t</u>-butyllithium 1.7N in pentane (4.5 mmol) was added over a 10 min period to a solution of 1-bromo-2-(trimethylsiloxy) ethylene (0.5 g, 2.5 mmol) in anhydrous ether (16.5 ml) maintained at -70°. The mixture was magnetically stirred for 1.5 hr at -70°, then a solution of α-tetra-

lone (2 mmol) in anhydrous ether (0.5 ml) was added. After 3 hrs at -50°, the reaction mixture was quenched at -50° with 5 ml of 1.2N HCl and treated as above to give the product, bp. 110° (0.05 mmHg). IR (neat) : 1655, 1640 cm^{-1}. ^{1}H NMR : δ Z isomer (94%) : 2.0 (2 H, m), 2.55 (2 H, m), 2.85 (2 H, m),6.5 (1 H, d, J = 8.0 Hz), 7.25 (3 H, m), 8.0 (1 H, m), 10.15 (1 H, d, J = 8.0 Hz), E isomer (6%) : 9.85 (1 H, d, J = 8.0 Hz).

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