Tetrahedron Letters, Vol.31, No.4, pp 543-544, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

A NEW ONE-POT SYNTHESIS OF SILYLATED 1,3-DIENES

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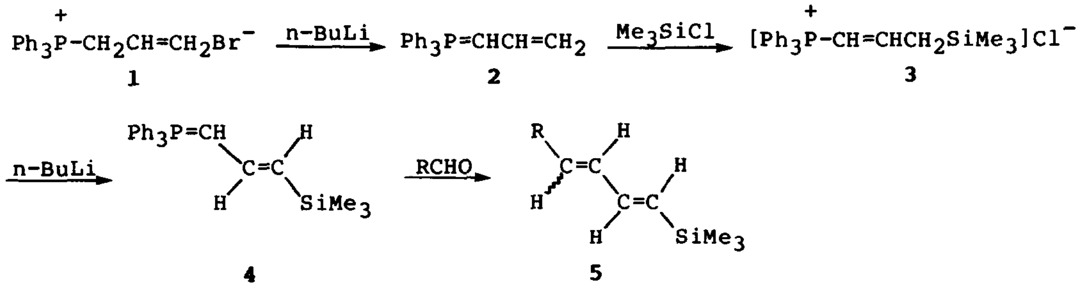
Summary. A new convenient one-pot synthesis of substituted silylated 1,3-dienes starting from the commercial available substances is described.

Since the widespread upsurge of interest in organosilicon reagents, vinyl and allyl silanes have begun to be employed as a useful reagents in numerous electrophilic carbon-carbon bond forming reactions.[1] Many natural products with biological activity, such as insect pheromones, leukotrienes, bearing the butadiene structure have attracted much attention and the synthetic methods leading to the formation of butadienes may be desirable. Silylated 1,3-dienes could convert to functionalized 1,3-dienes which was potentially useful intermediates in organic synthesis.[2] However, the synthetic application of silylated 1,3-dienes seems to remain limited, and there are only few preparative methods[3] in which the starting materials are not easily available,[4] the procedures are troublesome,[5] and the yields are lower.[2]

We now wish to report a convenient one-pot synthesis of substituted silylated 1,3-dienes starting from commercial available substances in 70-94% yields (4 steps) based on the sequence of reactions shown as follows:



$$\underset{\mathbf{1}}{Ph_3\overset{+}{P}\text{-}CH_2CH\text{=}CH_2Br^-} \xrightarrow{n\text{-}BuLi} \underset{\mathbf{2}}{Ph_3P\text{=}CHCH\text{=}CH_2} \xrightarrow{Me_3SiCl} \underset{\mathbf{3}}{[Ph_3\overset{+}{P}\text{-}CH\text{=}CHCH_2SiMe_3]Cl^-}$$

Allylidenetriphenylphosphorane (**2**) generated from the corresponding phosphonium salt (**1**) and n-butyllithium could react regiospecifically with chlorotrimethylsilane at γ-position to give trimethylsilylallyltriphenylphosphonium chloride (**3**). Without isolation treatment of **3** with n-butyllithium gives trimethylsilylallylidenetriphenylphosphorane exclusively in E-isomer as judged on the basis of NMR spectra, and the phosphorane reacts with aldehydes to afford silylated 1,3-dienes (**5**).

In a general procedure n-butyllithium (2 mmol) is added dropwise with stirring to a suspension of allyltriphenylphosphonium bromide (**1**) (0.77g, 2 mmol) and absolute tetrahydrofuran (20 ml) at 0 °C under nitrogen. The reaction mixture is stirred for 0.5 h at 0 °C and the chlorotrimethylsilane is slowly added. After stirring at 0 °C for 1 h and cooling to -70 °C, a second portion of n-butyllithium (2 mmol) is added. The mixture is allowed to warm to 0 °C, stirred for 1 h and the aldehyde (2 mmol) is added. After this addition, it is stirred at 20 °C for several hours (see Table 1). Work-up is by the usual procedure to afford the products (**5**). The results are shown in Table 1.

Table 1. Preparation of Substituted Silylated 1,3-Dienes

Compound	R	Reaction Time (h)	B.P. (°C/mmHg)	Yield[a] (%)	1E,3E:1E,3Z[b]
5a	$4\text{-}NO_2C_6H_4$	2	87-88[c]	94	100:0
5b	$C_6H_5CH{=}CH$	2	136-138/0.5	70	100:0
5c	$n\text{-}C_6H_{13}$	4	75/0.5	82	80:20
5d	$n\text{-}C_9H_{19}$	4	96-97/0.5	78	75:25
5e	$4\text{-}FC_6H_4$	4	81-83/0.5	80	76:24
5f	$4\text{-}ClC_6H_4$	2	59-60[c]	81	56:44
5g	$4\text{-}MeOC_6H_4$	4	134-136/0.5	70	56:44
5h	2-furfyl	4	76-78/0.5	76	54:46

[a] Isolated yields. All compounds are new and characterized by microanalyses, IR, NMR and mass spectroscopy.

[b] The ratios of 1E,3E- and 1E,3Z-isomers are estimated on the basis of NMR spectra and GLC.

[c] M.P./°C.

The reaction is of wide scope. The aldehydes may be aliphatic, aromatic or heterocyclic. It may contain double bond. Double bond conjugated with the carbonyl group does not interfere the reaction, the attack being at the carbonyl carbon. Thus this methodology provides a convenient synthesis of the title compounds.

Acknowledgement

The authors thank the National Natural Science Foundation of China and Academia Sinica for financial support.

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(Received in Japan 4 November 1989)