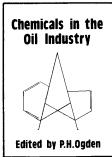
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Edited by P. H. Ogden

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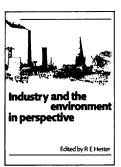
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$$Me_3Si - = - = -SiMe_3$$
 $\frac{RCOCI}{AICI_3}$ $RCO - = - = -SiMe_3$

4-Lithiotrimethylsilylbutadiyne is a more powerful nucleophile than **BTMSBD**. It is easily generated by selective monodesilylation of **BTMSBD** with MeLi LiBr in THF, and reacts readily with carbonyl compounds^{3,4} and primary alkyl halides.

$$Me_3Si - = - = -SiMe_3 \xrightarrow{\text{MeLi LiBr}} Li - = - = -SiMe_3$$

$$R - = - = -SiMe_3$$

$$R^1R^2CO$$

$$R^2R^2C(OH) - = - = -SiMe_3$$

The 4-substituted 1-trimethylsilylbutadiynes can be selectively hydrogenated at the nonsilylated triple bond to give, after desilylation, terminal (Z)-enynes. 6-8 Alternatively, LiAlH₄ reduction of the diynols affords (E)-enyne allylic alcohols. 4,9,10

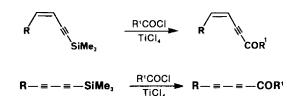
$$R - = - = -SiMe_3 \qquad 5\% \text{ Pd-BaSO}_4/\text{quinofine}$$

$$R^1R^2C(OH) - = - = -SiMe_3 \qquad EiAIH_4$$

$$R^1R^2C(OH) - = - = -SiMe_3 \qquad F \qquad R^1R^2C(OH)$$

$$SiMe_3$$

Both the reduced silyl enyne and the silyl diyne undergo electrophilic replacement of the remaining silyl substituent with Friedel-Crafts reagents. Such transformations have wide applications in natural-product synthesis. 4,11,12



BTMSBD reacts with selenides to give selenophens, ¹³ with tellurides to give tellurophens, ¹⁴ and with hydrazine to give pyrazoles. ¹⁵ It has also been used in [2+4]-cycloaddition/cycloreversion sequences to prepare ethynyl-substituted pyridazines ¹⁶ and furans. ¹⁷

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