Facile Synthesis of Alkyl and Aryl Substituted 1,2,3-Butatrienes

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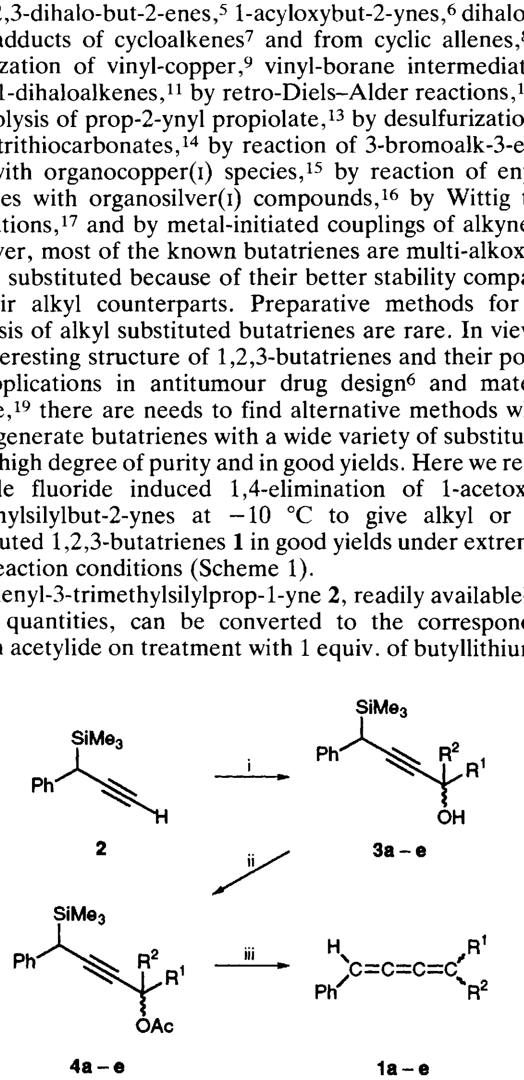
Alkyl and aryl substituted 1,2,3-butatrienes can be prepared in good yields *via* tetrabutylammonium fluoride induced 1,4-eliminations of 1-acetoxy-4-trimethylsilylbut-2-ynes at −10 °C.

Cumulenes are extremely reactive molecules.[1] One of the lower cumulenes, 1,2,3-butatriene, is relatively stable but still polymerizes rapidly at room temperature on exposure to acid, oxygen or light.[2]

Substituted butatrienes have been prepared by elimination from 1,4-dihalo[2] (or 1,4-dihydroxy,[3] 1,4-dialkoxy[4])-but-2-ynes, 2,3-dihalo-but-2-enes,[5] 1-acyloxybut-2-ynes,[6] dihalocarbene adducts of cycloalkenes[7] and from cyclic allenes,[8] by dimerization of vinyl-copper,[9] vinyl-borane intermediates[10] and 1,1-dihaloalkenes,[11] by retro-Diels–Alder reactions,[12] by thermolysis of prop-2-ynyl propiolate,[13] by desulfurization of cyclic trithiocarbonates,[14] by reaction of 3-bromoalk-3-en-1-ynes with organocopper(I) species,[15] by reaction of enynyl epoxides with organosilver(I) compounds,[16] by Wittig type olefinations,[17] and by metal-initiated couplings of alkynes.[18] However, most of the known butatrienes are multi-alkoxy or phenyl substituted because of their better stability compared to their alkyl counterparts. Preparative methods for the synthesis of alkyl substituted butatrienes are rare. In view of the interesting structure of 1,2,3-butatrienes and their potential applications in antitumour drug design[6] and material science,[19] there are needs to find alternative methods which could generate butatrienes with a wide variety of substituents with a high degree of purity and in good yields. Here we report a facile fluoride induced 1,4-elimination of 1-acetoxy-4-trimethylsilylbut-2-ynes at −10 °C to give alkyl or aryl substituted 1,2,3-butatrienes **1** in good yields under extremely mild reaction conditions (Scheme 1).

3-Phenyl-3-trimethylsilylprop-1-yne **2**, readily available[20] in 100 g quantities, can be converted to the corresponding lithium acetylide on treatment with 1 equiv. of butyllithium at −78 °C. The resulting anion can be trapped with ketones or aldehydes to give a diastereomeric mixture of silyl prop-2-ynylic alcohol **3**† in good yields (Table 1). For easily enolizable aldehydes such as heptanal (entry b), the yield of the propargylic alcohol **3b** from this reaction was poor. This is probably due to enolization and self-condensation of the heptanal. However, conversion of the organolithium to organocerium[21] by addition of $CeCl_3$ results in a very clean transformation. The alcohol was then converted (DMAP, NEt_3, Ac_2O) to the thermally labile acetate **4**,† which on treatment with a THF solution of tetrabutylammonium fluoride at −10 °C underwent a facile fluoride-induced 1,4-elimination to afford substituted butatriene **1**‡ in good yield. Upon aqueous workup with sodium carbonate solution and extraction with hexane under nitrogen, followed by flash chromatography on Florisil, the butatriene **1** was isolated in >90% purity.



Scheme 1 *Reagents and conditions* i, BuLi, THF (or BuLi, $CeCl_3$, THF) then $R^1R^2C{=}O$; ii, Ac_2O, NEt_3, DMAP; iii, tetrabutylammonium fluoride, THF

Table 1 Yields[a] of reactions i–iii (%)

Entry	R^1	R^2	**3**	**4**	**1**
a	Ph	H	75	84	83[c]
b	n-C_6H_{13}	H	90[b]	91	70[c]
c	Pr^i	H	78	78	89[d]
d	Bu^t	H	80	90	93[e]
e	Me	Me	83	79	71

[a] Isolated yields after chromatography. [b] Addition of $CeCl_3$. [c] 1 : 1 geometric isomers. [d] 1 : 1.2 geometric isomers. [e] 1 : 1.5 geometric isomers.

The 1,4-disubstituted butatrienes **1a–d** are relatively stable under nitrogen at 0 °C in hexane solution. However, upon concentration or exposure to oxygen, polymerization of **1a–d** takes place very readily with the formation of white precipitates. With contact with silica gel and alumina, the butatrienes underwent extensive decomposition. The 1,1,4-trisubstituted butatriene **1e**, however, is unstable and tends to polymerize rapidly under nitrogen in hexane solution. On contact with Florisil, **1e** partially polymerizes to give a white precipitate. As a result, we were unable to obtain a good quality ^{13}C NMR spectrum of **1e**.

The butatrienes **1a–d** exhibit interesting spectroscopic properties. Thus, the vinylic proton (δ 6.2–6.5) adjacent to the phenyl ring exhibits long range coupling to the other olefinic proton with a coupling constant $^5J_{HH}$ of 7 Hz. There is little difference (<0.5 Hz) between the *cis*- and *trans*-coupling constants in compounds **1a–d**. It is therefore difficult to assign the double bond geometry, although it was claimed previously[22] that the *trans*-isomer should have a larger $^5J_{HH}$ value than that of the corresponding *cis*-isomer. The presence of the butatriene skeleton was also confirmed by the characteristic C–H coupling constants ($^1J_{CH}$ 158–165 Hz) of the terminal olefinic carbons.[14]

This synthetic methodology could, in principle, be extended to compounds other than 3-phenyl substituted propargylic silane **2**. It is well documented that treatment of the dianion of alk-1-ynes with 1 equiv. of trimethylsilyl chloride resulted in exclusive silylation at the 3-position.[20] Our synthetic methodology could therefore be used to synthesize a wide variety of di- or tri-substituted butatrienes.

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Footnotes

† All compounds were characterized by ^1H and ^{13}C NMR, IR and high resolution mass spectra. The acetates **4** decompose slowly on standing at room temperature.

‡ Apart from **1e**, compounds **1a–d** exist as an inseparable mixture of (E)- and (Z)-geometric isomers.

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