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Preliminary communication

A CONVENIENT SYNTHESIS OF SILACYCLOBUTENES

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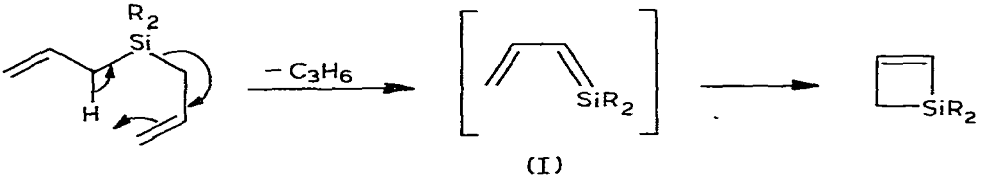
Summary

Flash vacuum pyrolysis of 1,3-bis(trimethylsilyl)-3-methoxysilylpropenes has been found to be an efficient route to silacyclobutenes. The thermolysis is viewed as proceeding through initial β-elimination of trimethylmethoxysilane followed by cyclization of the resulting 1-sila-1,3-butadiene.

Introduction

Until 1978 silacyclobutenes were available only through NBS-bromination of 2-phenylsilacyclobutanes followed by base-induced dehydrobromination [1]. A major synthetic breakthrough came when Block [2] discovered that flash vacuum pyrolysis (FVP) of diallylsilanes afforded silacyclobutenes in yields of 9—36%. This reaction was viewed as proceeding through a retroene elimination of propene to produce a transient 1-sila-1,3-butadiene (I) which closed to the unsaturated ring. However, a radical pathway involving initial Si-allyl homolysis cannot be ruled out from existing data, particularly in view of the accumulating evidence for gas-phase silyl radicals to undergo disproportionation to silenes [3].

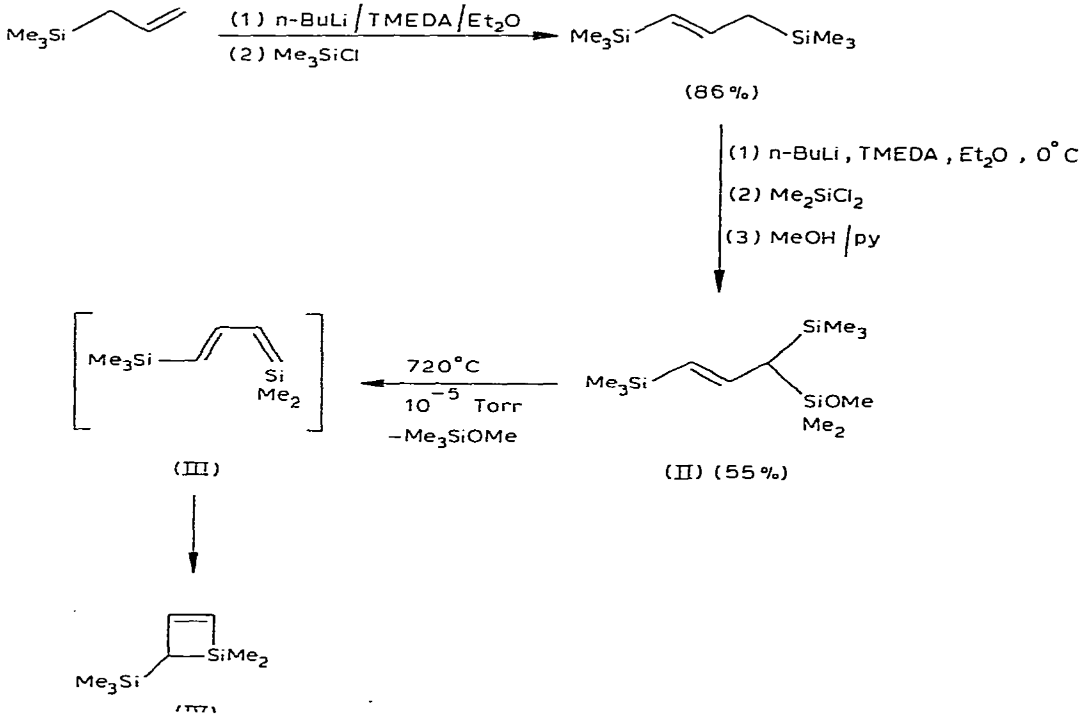


(I)

That the availability of this novel synthetic route has not produced a notable surge of interest in the chemistry of silacyclobutenes is perhaps due to the relatively low yields and tedious product separations. We report here a major modification of this route which employs readily available starting materials, affords very good yields, produces very clean product mixtures separable by distillation, and tolerates functionality on silicon.

Results and discussion

Our recent success in the generation of silenes through the thermally-induced β-elimination of Me$_3$SiOMe [4] suggested that this method could be utilized in the synthesis of 1-sila-1,3-butadienes. Thus, 1,3-bis(trimethylsilyl)-3-dimethylmethoxysilylpropene (II) was synthesized from allyltrimethylsilane via sequential metallation [5] chlorosilane quenching as shown in Scheme 1. The overall yield of II was 47%, and the sequence can be run on a large scale if desired. (II, NMR (CCl$_4$) δ (ppm) 0.0 (s, 2 SiMe$_3$, 18 H), 0.03 (s, SiMe$_2$, 6H), 1.23 (d, J 10 Hz, Si—CH—Si, 1H), 3.3 (s, OMe, 3H), 5.18 (d, Me$_3$Si—*CH*=, J 18 Hz), 5.82 (d of d, Me$_3$Si—C=*CH*, J 10 and 18 Hz, $h\nu$ at δ 1.23 ppm collapses to d J 18 Hz); calcd. for $C_{12}H_{30}Si_3O$ m/e 274.1605, measured m/e 274.1607). FVP* of II (700—720°C, 10^{-5} Torr) afforded (in addition to Me$_3$SiOMe) 3,3-dimethyl-4-trimethylsilyl-3-silacyclobutene (IV) in 56% isolated yield** after distillation as a colorless liquid. (IV, NMR (CCl$_4$)



SCHEME 1

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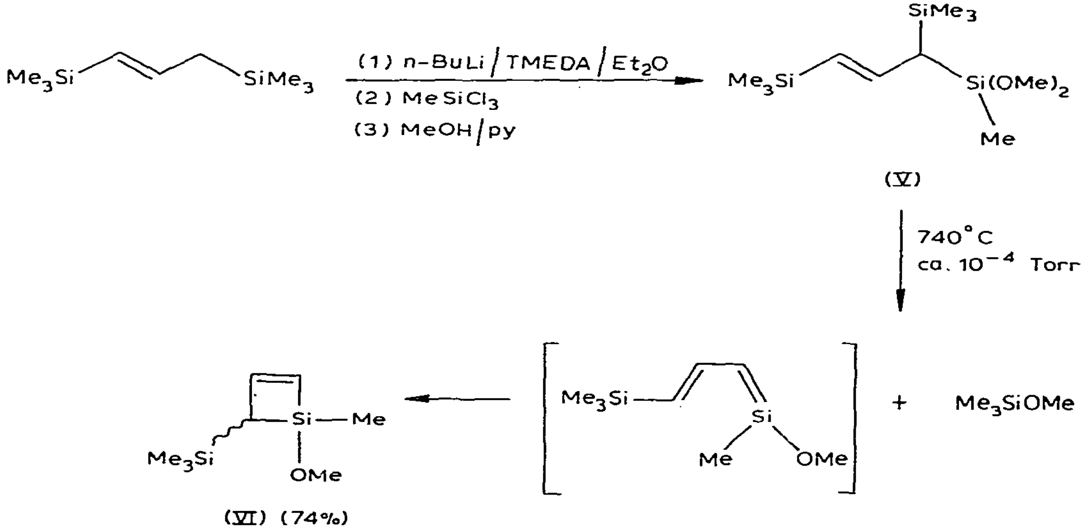
*Flash vacuum pyrolyses were conducted by slowly distilling the neat material through a 30.5 cm (1.6 cm OD) horizontal quartz tube packed with quartz chips. Cooling of the sample flask was employed to ensure slow evaporation.

**Subsequent studies suggest that this is very much a minimum value.

δ (ppm) 0.0 (s, $SiMe_3$, 9H), 0.33 (s, $SiMe_2$, 6H), 1.23 (apparent t actually overlapped d of d, 1H), 6.2 (d of d, *J* 1.5 and 7.5 Hz, *hν* at δ 1.2 collapses to d with *J* 7.5 Hz, 1H), 7.13 (d of d, *J* 1.7 Hz and 7.5 Hz, *hν* at δ 1.2 collapses to d with *J* 7.5 Hz, 1H); calcd. for $C_8H_{18}Si_2$ *m/e* 170.0947, measured *m/e* 170.0947; ν(C=C) 1500 cm^{-1}). We view this reaction as proceeding by β-elimination of trimethylmethoxysilane to produce 1,1-dimethyl-4-trimethylsilyl-1-sila-1,3-butadiene (III) which closes to IV. It should be noted that the essentially identical temperature requirements of this route and the retroene route [2] come as a surprise, as in earlier work [4] we had found the elimination of Me_3SiOMe to proceed at a significantly lower temperature than retroene elimination.

Block [2] has reported the retroene route to silacyclobutenes to fail in the case of diallyldimethoxysilane (no reaction at 710°C), and we too have found methoxy substitution to be incompatible with this method. Thus, we synthesized (Scheme 2) 1,3-bis(trimethylsilyl)-3-dimethoxymethylsilylpropene (V) in 48% yield from an analogous sequence as used for II, with the substitution of methyltrichlorosilane for dimethyldichlorosilane. (V, NMR (CCl_4) δ (ppm) 0.0 (s, $SiMe_3$, 9H), 0.02 (s, $SiMe_3$, 9H), 0.04 (s, SiMe, 3H), 1.3 (d, *J* 10 Hz, Si—*CH*—Si, 1H), 3.4 (s, OMe, 6H), 5.22 (d, *J* 18 Hz, 1H), 5.82 (d of d, *J* 10 and 18 Hz); calcd. for $C_{12}H_{30}Si_3O_2$ *m/e* 290.1554, measured *m/e* 290.1557). FVP of V (740°C, $<10^{-4}$ Torr) afforded, after fractional distillation of the pyrolysate, 3-methyl-3-methoxy-4-trimethylsilyl-3-silacyclobutene (VI) in 74% isolated yield as a colorless liquid. The ^1H NMR spectrum of VI appears quite complex until it is realized that VI is formed as an approximately equal mixture of *cis*- and *trans*-stereoisomers, which we have not yet been successful in separating. (VI, 60 MHz NMR (CCl_4), δ (ppm) 0.0 (s, 2 $SiMe_3$), 0.02 (s, SiMe), 0.25 (s, SiMe), 1.28 (d, Si—*CH*—Si, *J* 2 Hz, *hν* at ca. δ 7 collapses to s), 1.43 (apparent t, actually overlapped d of d, *hν* at δ 7 or δ 5.9 collapses to d, Si—*CH*—Si), 3.33 (s, SiOMe), 3.38 (s, SiOMe), 5.94 (d, Si*CH*=, *J* 7.5 Hz), 5.88 (d of d, Si—*CH*=, *J* 7.5 and 2.5 Hz, *hν* at δ 1.43 collapses to



SCHEME 2

d with J 7.5 Hz), 6.96 (center of apparent to of d which is actually an overlapped pair of d of d at δ 7.01 and δ 6.91, J 6.8 and 2 Hz for the upfield d of d, and J 6.4 and 1.5 Hz for the other, $h\nu$ at δ 1.43 collapses the downfield d of d to a d with J 6.4 Hz, and $h\nu$ at δ 1.28 collapses the upfield d of d to a d with J 6.8 Hz); calcd. for $C_8H_{18}Si_2O$ m/e 186.0896, measured m/e 186.0891 ν(C=C) 1495 cm^{-1}).

Currently we are probing the generality of this method with regard to tolerance of various functionality. Preliminary experiments toward the obvious, ultimate goal of converting VI to silacyclobutadiene have not been promising.

Acknowledgment

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