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Preliminary communication

INTRAMOLECULAR CYCLIZATION OF DIMETHYL(1-PENT-4-ENYL)-SILYLLITHIUM

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Summary

The metal exchange of bis[dimethyl(1-pent-4-enyl)silyl]mercury with lithium is followed by subsequent intramolecular cyclization of the silyllithium reagent formed. The product, 2,2-dimethyl-2-silacyclopentylmethyllithium, forms 1,1,2-trimethyl-1-silacyclopentane upon hydrolysis. A possible mechanism for these reactions is proposed.

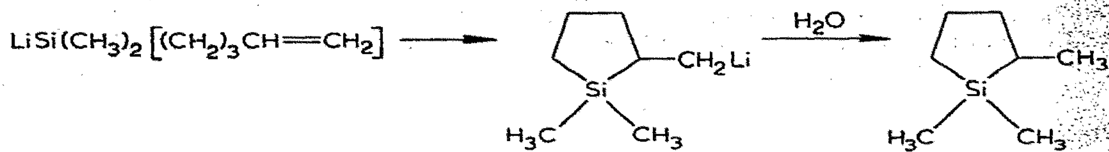
The intramolecular addition of an organolithium compound to an unconjugated carbon—carbon double bond to form a cyclic product occurs readily with 1-hex-5-enyllithium [1, 2] and several other organometallic derivatives [3, 4]. It has been proposed that the cyclization of the organometallic derivative is determined by the polarity of the metal—carbon bond and by the size of the ring that is formed [5]. In the hex-5-enyl case, ring closure occurs during the preparation of the organolithium compound, very likely by the intramolecular addition of the lithium—carbon bond to the terminal C=C bond to produce the cyclic product, cyclopentylmethyllithium. The intermolecular addition of silyllithiums to carbon—carbon multiple bonds is known [6]; however, no intramolecular cyclization has been reported for a silyllithium derivative.

We wish to report the first example of the intramolecular addition of an Si—Li bond to a C=C bond. The reaction provides a new route to cyclic organosilicon compounds. Equations 1 through 4 illustrate the general reactions for the synthesis of 1,1,2-trimethyl-1-silacyclopentane.

$$(CH_3)_2ClSiH + H_2C{=}CH{-}CH_2{-}CH{=}CH_2 \rightarrow [H_2C{=}CH(CH_2)_3](CH_3)_2SiCl \tag{1}$$

$$[H_2C{=}CH(CH_2)_3](CH_3)_2SiCl + Na/Hg \rightarrow Hg\{Si(CH_3)_2[(CH_2)_3CH{=}CH_2]\}_2 \tag{2}$$

$$Hg\{Si(CH_3)_2[(CH_2)_3CH{=}CH_2]\}_2 + Li^0 \rightarrow 2\ LiSi(CH_3)_2[(CH_2)_3CH{=}CH_2] \tag{3}$$



(4)

The procedures for the synthesis of the dimethyl(1-pent-4-enyl)chlorosilane and the organosilylmercurial were similar to those described by Kobrakov [7] and Eaborn [8], respectively. Bis[dimethyl(1-pent-4-enyl)silyl]mercury, the first reported silylmercury compound containing an olefinic double bond, was prepared from dimethyl(1-pent-4-enyl)chlorosilane and sodium amalgam (1/1 molar ratio of SiCl to Na). This mixture was placed in a sealed tube and agitated at room temperature for two weeks. The solution turned from colorless to green-yellow; completion of the reaction was assumed when no further apparent change in intensity was observed. After separation of the by-products and solvent, a viscous, nonvolatile, air-sensitive, yellow liquid was obtained in 60% yield*. (Found: C, 37.19; H, 6.85; Hg, 43.99. $C_{14}H_{30}Si_2Hg$ calcd.: C, 36.95; H, 6.60; Hg, 44.12%.) The mercurial was identified by its NMR spectrum which was characterized by a silylmethyl proton resonance at δ 0.25 ppm and $^3J(^{199}HgSiC^1H_3)$ 41.5 Hz. The mass spectrum of bis[dimethyl(1-pent-4-enyl)silyl]mercury showed the parent molecular ion, $C_{14}H_{30}HgSi_2^+$, *m/e* 456 based on ^{202}Hg isotope. The organosilyllithium compound was prepared by the method of Schaaf and Oliver [9]. Bis[dimethyl(1-pent-4-enyl)silyl]mercury and an excess of lithium metal were vigorously stirred for 48 hours in cyclopentane. An NMR spectrum of the reaction solution showed the absence of olefinic bonds and mercury—silicon bonds. Hydrolysis of the reaction solution resulted in the formation of a colorless liquid. The gas chromatogram of the hydrolysis mixture, on a 30% SE-30 column, indicated the presence of one component. This product, obtained in quantitative yield, was identified as 1,1,2-trimethyl-1-silacyclopentane, n_D^{25} 1.4386, lit. [7], 1.4380. Three sharp resonances were observed in the NMR spectrum of a benzene solution of this compound and have been assigned to the two methyl groups on the silicon, δ 0.083 and 0.120 ppm and the methyl group attached to the carbon, δ 1.07 ppm. A thin film infrared spectrum showed absorptions compatible with the assigned structure: 1144s, 1092s, 1036m, 1010m, 843s, lit. [11] (for 1,1-dimethylsilacyclopentane) 1151, 1075, 1030, 1021, 870. The 70 eV mass spectrum showed a parent molecular ion, $C_6H_{16}Si$, *m/e* 128 and is characteristic of 1,1-dimethylsilacyclopentane derivatives as reported by Chernyak et al. [10] who found that the peak of maximum intensity corresponds to a fragment in which an ethylene fragment with a mass of 28 has been eliminated from the ring. In the present case, the mass spectrum is characterized by a parent molecular ion with mass 128 and with subsequent loss of mass 28 to yield the maximum intensity peak (equation 6).

The reactions, which appear to proceed readily at room temperature, may be depicted as an internal addition across the double bond with the transition

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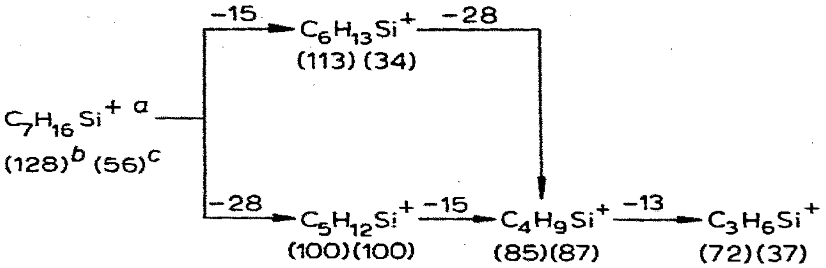
*In our work on the synthesis of this and other silylmercurials the yields vary widely with different preparations despite using identical conditions.



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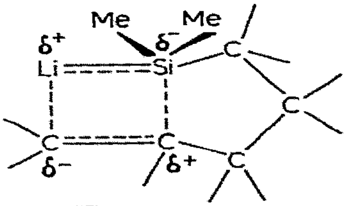
^{a} = parent molecular ion
^{b} =(m/e value)
^{c} = relative abundance (%)



(I)

state indicated in I. The dimethyl(1-pent-4-enyl)silyllithium could not be isolated under the reaction conditions used. It also is noteworthy that the silyllithium cyclization proceeds with greater facility than that of analogous 1-hex-5-enyllithium derivative [2]. This new reaction appears to provide an interesting and readily available procedure for the formation of five-membered silacycloalkanes which is potentially significant for synthetic purposes. Such routes to other silacycloalkane ring systems are now under investigation.

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References

1 V.N. Drozd, Yu.A. Ustynyuk, M.A. Tsel'eva and L.B. Dimitriev, Zh. Obshch. Khim., 38 (1968) 2114.
2 T. Dolzine, J. St. Denis and J.P. Oliver, J. Amer. Chem. Soc., 94 (1972) 8260.
3 G. Zweifel, G.M. Clark and R. Lynd, Chem. Commun., (1971) 1593.
4 J. St. Denis, T.W. Dolzine and J.P. Oliver, submitted for publication.
5 G. Hata and A. Miyaki, J. Org. Chem., 28 (1963) 3237.
6 D.D. Davis and C.E. Gray, Organometal. Chem. Rev., A, 6 (1970) 283.
7 K.I. Kobrabov, T.I. Chernysheva and N.S. Nametkin, Dokl. Akad. Nauk. SSSR, 198 (1971) 1340.
8 C. Eaborn, R.A. Jackson and R.W. Walsingham, J. Chem. Soc. C, (1967) 2188.
9 T.F. Schaaf and J.P. Oliver, J. Amer. Chem. Soc., 91 (1969) 4327.
10 N.Ya. Chernyak, R.A. Khmel'nilskii, T.V. D'yakova and V.M. Vdovin, Zh. Obshch. Khim., 36 (1966) 89.
11 N.S. Nametkin, U.D. Oppengein, U.I. Zav'Yalov, K.S. Pushchevaya and V.M. Vdovin, Izv. Akad. Nauk., SSSR, Ser. Khim., (1965) 1547.