Luz.[15] They report activation parameters of 10.2, 10.1, and 10.15 kca/mol for $\Delta G^{\ddagger}_{298}$, 10.9, 11.5, and 10.3 kcal/mol for $\Delta H^{\ddagger}$, and 2.8, 4.6, and 0.5 eu for $\Delta S^{\ddagger}$, respectively.

The observed phase dependence is compatible with a negative activation volume. The partial derivative of $\Delta G^{\ddagger}$, the free energy of activation, with respect to pressure, equals the activation volume, $\Delta H^{\ddagger}$, for the process. The internal pressure of an ideal gas is zero, and of liquid CS_2 at 298 K, it is 3714 atm.[16] Using these values and a $\Delta(\Delta G^{\ddagger})$ of 370 cal, a $\Delta V^{\ddagger}$ value of ~−4 cm^3/mol is obtained. Recently, variable-pressure and -temperature NMR studies of cyclohexane in several solvents have revealed that interconversion rates increase with increasing pressure. The pressure dependence observed over a pressure range 1–5000 bar yields activation volumes, $\Delta H^{\ddagger}$'s, ranging from −5.0 cm^3/mol for an acetone solution to −1.5 cm^3/mol for a $C_6D_{11}CD_3$ solution.[17] These results are qualitatively consistent with the slower gas-phase inversion rates reported in the present study.

Registry No. Cyclohexane, 110-82-7; sulfur hexafluoride, 2551-62-4.

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Hydroalumination of 1-(Trimethylsilyl)-1,3-diynes. Syntheses of Stereodefined Enynes and Dienes

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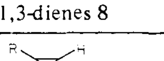
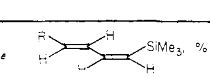
The conjugated enyne moiety is incorporated in a number of natural products.[1] Also, it can be readily converted in a stereospecific manner into the corresponding diene system.[2] Thus, it is not surprising that considerable effort has been expended in seeking stereoselective methods for syntheses of conjugated enynes.[3]

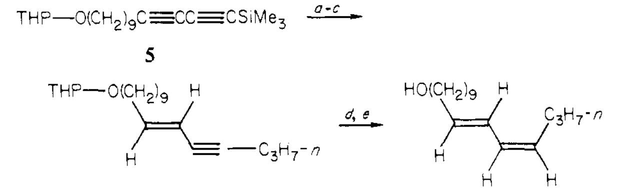
We have previously shown that symmetrically substituted 1,3-diynes react with lithium diisobutylmethylaluminum hydride in diglyme solvent to produce, after hydrolysis of the intermediate (*Z*)-enynylalanates, the corresponding *trans*-enynes.[4] Unfortunately, this *trans*-enyne synthesis cannot be employed for the preparation of unsymmetrical enynes since the reducing agent does not discriminate in its addition between the triple bonds of unsymmetrically alkyl-substituted conjugated diynes.[4] Hence, we have searched for a readily accessible 1,3-diyne system in which the triple bonds exhibit appreciably different reactivities toward nucleophilic and electrophilic reducing agents and contain a functionality capable of being elaborated into various derivatives. We now report that 1-(trimethylsilyl)-1,3-diynes **1**[5] fulfill this requirement.

Table I. Yields of 1-(Trimethylsilyl)-3-en-1-ynes **4** and 1-(Trimethylsilyl)-1,3-dienes **8**

$RC\equiv C—C\equiv CSiMe_3$ **1**	 %^{a,c,e} **4**	 %^{b,c,e} **8**
a, R = *n*-C_6H_{13}	95 (99)	97 (99)
b, R = Cy	93 (98)	96 (98)
c, R = *t*-Bu	90 (95)	91 (95)
d, R = Me_3Si	91 (96)^d	93 (96)^f

[a] Derived from hydroalumination of **1** with Li[AlH(*i*-Bu)$_2$-*n*-Bu] followed by protonolysis. [b] Derived from hydroalumination of **4** with *i*-Bu_2AlH followed by protonolysis. [c] Isolated yields (Kugelrohr distillations). Isomeric purities are in parentheses. [d] The reaction was carried out at 25 °C for 18 h. [e] The IR, ^{1}H NMR, and mass spectral data of the compounds were consistent with the assigned structures. [f] Reference 16.

Scheme I

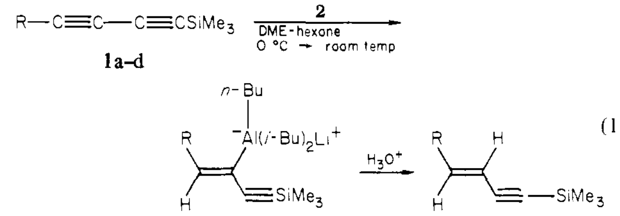


5

6

[a] Li[AlH(*i*-Bu)$_2$-*n*-Bu]/DME–hexane/25 °C/1 h; 3 N HCl. [b] KF·2H_2O/DMF/25 °C.[7] [c] *n*-BuLi/hexane–diglyme/−78 → 25 °C; *n*-C_3H_7Br/25 → 80 °C/18 h.[9] [d] Disiamylborane/THF/0 °C/3 h; AcOH/60 °C/5 h, H_2O_2–NaOH/30 → 50 °C.[10] [e] CH_3OH–3 N HCl (trace).

Addition of 1-(trimethylsilyl)-1,3-decadiyne (**1a**) to lithium diisobutyl-*n*-butylaluminum hydride (**2**, Li[AlH(*i*-Bu)$_2$-*n*-Bu]) furnished, as evidenced by ^{1}H NMR analysis, the enynylalanate **3a** (eq 1). The regioselective formation of **3** points to a strong electron-withdrawing effect of the (trimethylsilyl)ethynyl moiety upon the alkyl-substituted triple bond, thus making it more susceptible to attack by the nucleophilic reducing agent **2**. This activating effect of the (trimethylsilyl)ethynyl group is further evidenced by the observation that treatment of an equimolar mixture of **1a** and 4,6-decadiyne with **2** (1 equiv) resulted in the nearly exclusive hydroalumination of the silyldiyne **1a**. The *Z* stereochemistry of the enynylalanate **3a** follows from its conversion to 1-(trimethylsilyl)-*trans*-3-decen-1-yne (**4a**) upon protonolysis. As shown in Table I, trans hydroalumination of 1-(trimethylsilyl)-1,3-diynes **1** followed by protonolysis represents a high-yield method for synthesis of a variety of 1-(trimethylsilyl)-*trans*-3-en-1-ynes **4**.[6]



(1)

1a–d

3a–d **4a–d**

a, R = *n*-hexyl; **b**, R = cyclohexyl; **c**, R = *tert*-butyl; **d**, R = trimethylsilyl

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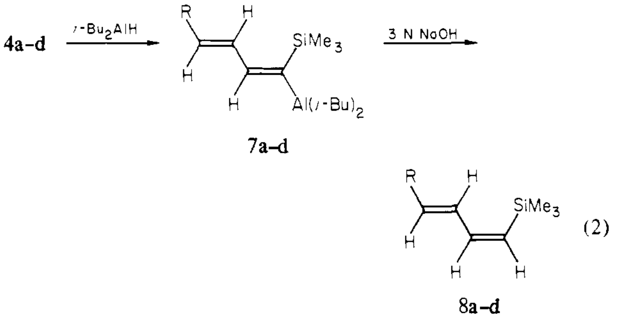
0002-7863/83/1505-1383$01.50/0

From a practical point of view, it is important to note that the now readily available 1-(trimethylsilyl)-*trans*-3-en-1-ynes **4** contain the easily manipulable (trimethysilyl)ethynyl group and hence are themselves of considerable value as synthetic intermediates. Thus, treatment of crude 1-(trimethylsilyl)-*trans*-3-decen-1-yne (**4a**) with $KF\cdot 2H_2O$ in DMF[7] resulted in quantitative desilylation to afford the terminal enyne, *trans*-3-decen-1-yne, in 93% yield on the basis of the silyldiyne precursor **1a**. This novel methodology has been successfully applied to the synthesis of the insect pheromone Bombykol **6**[8] in an 81% yield based on **5**[5] (Scheme I).

Another attractive synthetic use of the 1-(trimethylsilyl)-*trans*-3-en-1-ynes **4** was their reduction to the corresponding trimethylsilylated butadienes **8**, which are valuable substrates for cycloaddition reactions.[11] Thus, treatment of **4** with diisobutylaluminum hydride produced the dienylalanes **7**.[12] Hydrolysis of **7**[14] afforded the 1-(trimethylsilyl)-(1*Z*,3*E*)-dienes **8** (eq 2) in high yields (Table I).



To establish the regiochemistry for hydroalumination of **4a**, the dienylalane **7a** was treated at 0 °C with deuterium oxide. Examination of the resultant deuterated dienylsilane by ^1H NMR revealed that at least 95% of one deuterium was incorporated at the C-1 carbon. Therefore, the hydroalumination of **4a** with diisobutylaluminum hydride must involve a cis addition of the Al-H bond to the (trimethylsilyl)ethynyl group with aluminum being attached nearly exclusively at the silicon-bearing carbon.[15]

Typical procedures for the preparation of **4a** and **8a** are as follows. To a solution of diisobutylaluminum hydride (1.0 mL, 5.5 mmol) in DME (7 mL) was added at 0 °C a 2.4 **M** solution of *n*-butyllithium (2.3 mL, 5.5 mmol) in hexane. The mixture was stirred at 0 °C for 15 min, treated with **1a**[5] (1.0 g, 5.5 mmol), stirred at 0 °C for 15 min, then warmed to room temperature, and stirred for an additional hour. The resultant solution was slowly poured into stirred, ice-cold 3 N HCl (10 mL). After extraction with hexane, the combined organic phases were washed successively with 3 N HCl, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl and dried over $MgSO_4$. Distillation (Kugelrohr) yielded 0.99 g (95%) of **4a**: bp 95 °C (2 torr); $n^{25}{}_D$ 1.4681.

1-(Trimethylsilyl)-*trans*-3-decen-1-yne (**4a**) was reduced as follows. To a solution of **4a** (0.42 g, 2.0 mmol) in ether (2 mL) at 25 °C was added neat diisobutylaluminum hydride (0.4 mL, 2.2 mmol). The mixture was heated at 40 °C for 4 h, then cooled to room temperature, and slowly poured into stirred, ice-cold 3 N NaOH (10 mL). After extraction with hexane, the combined organic phases were successively washed with 3 N NaOH and saturated aqueous NaCl and then were dried ($MgSO_4$). Distillation (Kugelrohr) afforded 0.41 g (97%) of **8a**: bp 65 °C (0.01 torr); $n^{25}{}_D$ 1.4667.

Acknowledgment. We thank the National Science Foundation for support of this investigation.

Supplementary Material Available: Data supporting the purity and assignment of the products **4**, **6**, and **8** (3 pages). Ordering information is given on any current masthead page.

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An Unprecedented Bis(carbyne) Cluster Rearrangement Involving Simultaneous Coupling and Decoupling of Carbyne Fragments: A New Homogeneous Model for C-C Bond Forming and Bond Breaking on Surfaces

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Carbyne complexes are of considerable current interest because of their intrinsic novelty[1] and their potential as homogeneous analogues of surface carbynes, postulated to occur as crucial intermediates in hydrocarbon rearrangements[2] and synthesis via the reduction of carbon monoxide (Fischer-Tropsch synthesis).[3] Carbyne-carbyne coupling[4a] could constitute an alternative to the currently accepted mechanisms of carbon chain buildup in these

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