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Dihexylmagnesium Promoted Carboalumination of Silylacetylenes

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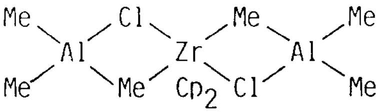
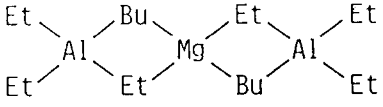
Abstract: The bimetallic species, $^{n}Bu_2Mg{\cdot}2Et_3Al$ has been found to be effective for the carboalumination of silylacetylenes.

Carbometalation of terminal acetylenes with Me_3Al is catalyzed by transition-metal compounds such as Cp_2TiCl_2 or Cp_2ZrCl_2 and finds extensive applications in olefin synthesis.[1] The successful reaction is ascribed to such bimetallic species 1 as derived from Cp_2ZrCl_2 and $2Me_3Al$.[2] The compound, $^{n}Bu_2Mg{\cdot}2Et_3Al$ (2),[3] carrying a similarly bridged structure has been found to be effective for the carboalumination of silylacetylenes.[4]



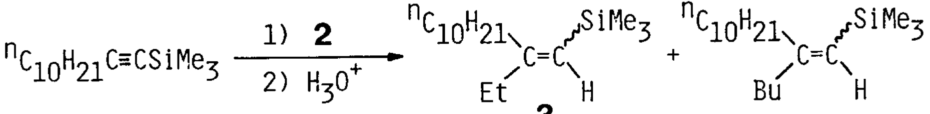
1



2

Treatment of 1-trimethylsilyl-1-dodecyne with **2** in chlorobenzene-heptane (1:10) at 60°C for 3 h followed by the addition of water gave stereoisomeric mixtures (E/Z = 1/1) of ethylated vinylsilane (**3**)[5] and butylated one in a 5:1 ratio in 80% combined yield (Scheme 1). The accompanying β elimination followed by hydroalumination or hydromagnesation occurs to a minor extent, if any, as the expected by-product, 1-trimethylsilyl-1-dodecene, has been detected in less than 3% yield. The use of the reagent prepared from $^{n}Hex_2Mg$ and Et_3Al ($^{n}Hex_2Mg/Et_3Al$ = 1:5) instead of the compound **2** improved the yield of ethylated product, as only a trace of the hexylated one was detected (<3%). In the absence of $^{n}Hex_2Mg$, 1-trimethylsilyl-2-ethyl-1-dodecene (**3**) was obtained in ca 50% yield[4a] after prolonged heating at 60°C for 10 h. Moreover, the compound **3** was contaminated by 1-

Scheme 1



3

5 : 1

trimethylsilyl-1-dodecene (10% yield) and an unidentified olefinic compound (ca 10% yield) which could not be separated from **3** by silica gel column chromatography. The coexistence of $^{n}Hex_2Mg$ is thus essential for carbometalation reaction to be of preparative value.

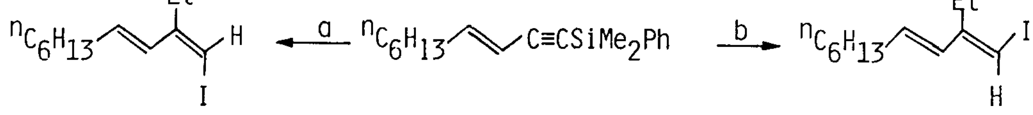
As summarized in Table 1, carboalumination of simple silylated acetylenes such as 1-trimethylsilyl-1-dodecyne proceeded in a regiospecific but nonstereoselective manner. In contrast, however, substrates carrying unsaturated groups in conjugation of the triple bond gave high or exclusive trans selectivities, as it turned out. A typical procedure is as follows.

A hexane solution of triethylaluminum (1.0 M, 3.0 ml, 3.0 mmol) was added to a heptane solution of $^{n}Hex_2Mg$ (0.6 mmol) at 0°C and the mixture was stirred for 10 min at 0°C. Then a solution of (E)-1-dimethylphenylsilyl-3-decen-1-yne (0.27 g, 1.0 mmol) in hexane-chlorobenzene (2.0 ml, 5:1) was added and the resulting mixture was heated at 60°C for 2 h. Workup (Et_2O, 1N HCl) followed by chromatography on a silica gel column gave (E,E)-1,3-diene **4** (R^1 = $C_6H_{13}CH{=}CH-$, R^2 = Et, X = $SiMe_2Ph$) in 95% yield as an oil[6]: bp 125-130°C (bath temp, 1 Torr); IR (neat) 2900, 2830, 1560, 1465, 1245, 1110, 965, 840, 725, 698 cm^{-1}; ^1H-NMR ($CDCl_3$) δ0.43 (s, 6H), 0.88-1.13 (m, 6H), 1.15-1.58 (m, 8H), 2.25 (m, 4H), 5.50 (s, 1H), 5.71 (dt, *J* = 15.8 and 6.8 Hz, 1H), 6.02 (d, *J* = 15.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ135.5, 133.8, 131.0, 130.9, 128.7, 127.7, 125.5, 32.9, 31.8, 29.8, 29.4, 25.5, 22.6, 14.5, 13.1, 0.0. The stereochemistry of the product was identified by the comparison with the sample prepared independently by the reported procedure.[7] It is worth noting that the steric integrity of the original double bond is preserved during the reaction pathway. Thus, (Z)-1-trimethylsilyl-3-decen-1-yne provided only (E,Z) isomer (Table 1, run 10).

The intermediary alkenyl metal species could be transformed further in a next step. Iodinolysis followed by protodesilylation[8] gave (Z,E)-1-iodo-2-ethyl-1,3-decadiene in 85% overall yield. Another (E,E) isomer was prepared in 70% yield via ethyl metalation-hydrolysis-iododesilylation[9] (Scheme 2).[10]

As shown in Scheme 3, a silylacetylene was treated, in the presence of $^{n}Hex_2Mg$, with an alkenylaluminum derived from another silylacetylene via hydroalumination.[11,12] Thus were obtained diene mixtures of **6** and **7**.[13] Treatment of the mixture of **6b** and **7b** with $^{n}Bu_4NF$ in DMSO[8] gave a mixture of

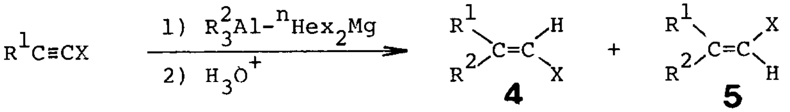
Scheme 2

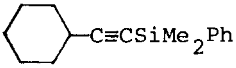
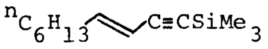
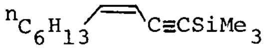
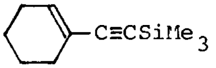


a: 1) Et_3Al-$^{n}Hex_2Mg$, I_2 2) $^{n}Bu_4NF$

b: 1) Et_3Al-$^{n}Hex_2Mg$, H_2O 2) I_2

Table 1. Carbometalation of alkynylsilanes catalyzed by $^{n}Hex_2Mg$[a]



Run	Alkynylsilane	Aluminum Reagent	Product Y (%)	Ratio of **4/5**
1	$^nC_6H_{13}C\equiv CSiMe_3$	Et_3Al	85	50/50
2		$^nPr_3Al$	92	50/50
3	$^nC_6H_{13}C\equiv CSiMe_2Ph$	Et_3Al	80	50/50[b]
4		$^nBu_3Al$	85	50/50[c]
5		Et_3Al	87	60/40
6	$PhC\equiv CSiMe_3$	Et_3Al	65	99/1
7		$^nPr_3Al$	67	95/5
8		Et_3Al	90	95/5
9		$^nPr_3Al$	92	95/5
10		Et_3Al	76	99/1
11		$^nPr_3Al$	72	95/5
12		Et_3Al	87	95/5

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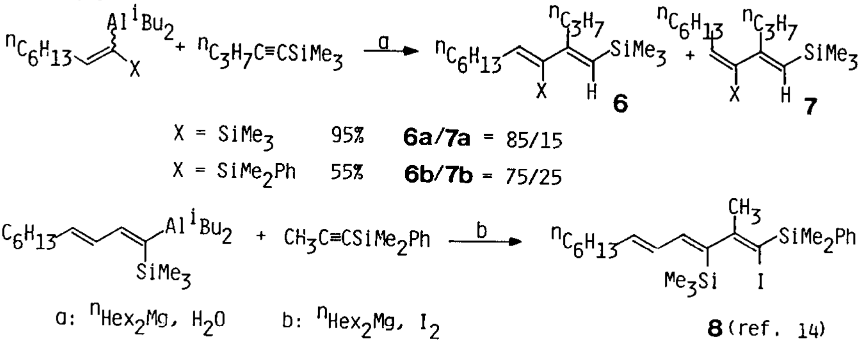
[a] Three mol of R_3Al, 0.6 mol of $^nHex_2Mg$, and 1.0 mol of acetylene substrate were employed. The reactions were performed at 60°C in hexane-chlorobenzene (10:1). [b] See, ref. 5 [c] The product was a mixture of butylated vinylsilane and hexylated one (4:1).

(E,E) and (E,Z)-1-trimethylsilyl-2-propyl-1,3-decadiene, both isomers being identical with those prepared above (Table 1, run 9 and 11). The addition proceeded completely in cis fashion. The new method was applied to the stereoselective synthesis of trienyl iodide (Scheme 3).

Scheme 3



X = SiMe$_3$ 95% **6a/7a** = 85/15

X = SiMe$_2$Ph 55% **6b/7b** = 75/25

a: $^nHex_2Mg$, H_2O b: $^nHex_2Mg$, I_2

References and Notes

1. Van Horn, D. E.; Negishi, E. *J. Am. Chem. Soc.* **1978**, *100*, 2252-2254. Okukado, N.; Negishi, E. *Tetrahedron Lett.* **1978**, 2357-2360. Fung,S.; Siddall,J. B. *J. Am. Chem. Soc.* **1980**, *102*, 6580-6581. Schiavelli, M. D.; Plunkett, J. J.; Thompson, D. W. *J. Org. Chem.* **1981**, *46*, 807-808.
2. Negishi, E. *Pure & Appl. Chem.* **1981**, *53*, 2333-2356.
3. MAGALA® 0.5E is a trade mark of Texas Alkyls Inc. for 0.5:1 di-n-butylmagnesium:triethylaluminum complex whose molecular weight has been determined to be 370 by cryoscopic measurement. We thank Toyo Stauffer Chemical Company for gifts of $^{n}Bu_2Mg{\cdot}2Et_3Al$ and $^{n}Hex_2Mg$.
4. The reaction of silylacetylenes with $RAlCl_2$-Cp_2TiCl_2 has been reported: (a) Eisch, J. J.; Manfre, R. J.; Komar, D. A. *J. Organomet. Chem.* **1978**, *159*, C13-C19. (b) Van Horn, D. E.; Valente, L. F.; Idacavage, M. J.; Negishi, E. *ibid*, **1978**, *156*, C20-C24. Stereochemical results with our new method was completely different from those with Eisch's procedure. Moreover, any trace of allenic silanes which have been obtained with Negishi's method was not detected in our procedure. For Ni(0) catalyzed carbometalation with Grignard reagent, see Snider, B. B.; Karras, M.; Conn, R. S. E. *J. Am. Chem. Soc.* **1978**, *100*, 4624-4625.
5. **3**(E/Z = 1/1 mixture): Bp 105-110°C (bath temp, 1 Torr); IR (neat) 2900, 2825, 1600, 1460, 1422, 1245, 1110, 835, 722, 695 cm^{-1}; NMR ($CDCl_3$) δ0.35 (s, 6H), 0.90 (m, 3H), 1.05 (t, *J* = 7.0 Hz, 3H), 1.13-1.55 (m, 8H), 2.10 (m, 4H), 5.35 (s, 1H), 7.30-7.65 (m, 5H); MS m/z (%) 274 (3), 259 (14), 204 (16), 148 (18), 135 (100), 105 (6). Found: C, 78.61; H, 11.16%. Calcd for $C_{18}H_{30}Si$: C, 78.75; H, 11.01%.
6. Glpc analysis (Silicone OV-17 3% on Uniport HP, 2m, 140°C) showed that the compound was contaminated by (E,Z) isomer (<5%).
7. Matsushita, H.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 2882-2884. Carbometalation of (E)-3-decen-1-yne with Et_3Al-Cp_2ZrCl_2 followed by the addition of I_2 to give a mixture of (E,E)-1-iodo-2-ethyl-1,3-decadiene and its regio isomer, (E,E)-4-iodo-3,5-dodecadiene in 4:1 ratio. The former was transformed into (E,E)-1,3-diene **4** (R^1 = $C_6H_{13}CH$=CH-, R^2 = Et, X = $SiMe_2Ph$) on treatment with $^{n}BuLi$ and $Me_2PhSiCl$.
8. Oda, H.; Sato, M.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 2877-2880.
9. Chan, T. H.; Lau, P. W. K.; Mychajlowskij, W. *Tetrahedron Lett.* **1977**, 3317-3320.
10. Similarly, (Z,Z) and (E,Z) isomers were prepared from (Z)-1-dimethylphenylsilyl-3-decen-1-yne.
11. Uchida, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2215-2217. Eisch, J. J.; Damasevitz, G. A. *ibid*. **41**, 2214-2215.
12. The reaction of alkenylaluminum derived from 1-dodecyne and $^{i}Bu_2AlH$ provided the corresponding diene, but the yield was only 35% due to the instability of the alkenylaluminum reagent.
13. The formation of **7** was attributed to the isomerization[11] of the primary cis adduct generated by hydroalumination of silylacetylene.
14. The compound **8** was isolated as a single product. No isomeric products were detected. **8**: IR (neat) 2900, 2830, 1575, 1460, 1420, 1245, 1110, 965, 840, 695 cm^{-1}; ^1H-NMR ($CDCl_3$, 200 MHz) δ0.28 (s, 6H), 0.93-1.45 (m, 8H), 2.06 (s, 3H), 2.28 (t *J* = 6.8 Hz, 2H), 5.47 (dt, *J* = 14.4 and 6.8 Hz, 1H), 5.88 (d, *J* = 11.7 Hz, 1H), 6.05 (dd, *J* = 14.4 and 11.7 Hz, 1H), 7.13-7.55 (m, 5H); ^{13}C-NMR ($CDCl_3$, 23 MHz) δ-0.92, 0.0, 14.1, 22.7, 23.8, 29.2, 31.7, 31.8, 35.8, 127.8, 127.9, 128.8, 133.8, 133.9, 136.1, 136.6, 139.4.

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