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Stereoselective Syntheses of Substituted Enynes, Dienes, and Alkenes via Stannylation of 1-Trimethylsilyl 1,3-Diynes

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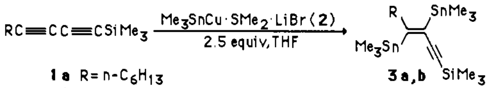
Abstract: Treatment of 1-trimethylsilyl 1,3-diynes with 2.5 equiv of (trimethylstannyl)copper in tetrahydrofuran solvent leads chemo- and stereoselectively to the corresponding (*E*)-1-(trimethylsilyl)-3,4-bis(trimethylstannyl)-3-alken-1-ynes. These bis(stannyl) enynes undergo stepwise transmetalation with methyllithium to furnish the corresponding enynyllithium reagents. Further elaboration of these via a sequence of alkylation and protonation reactions provides a novel and powerful method for the preparation of stereodefined tri- and tetrasubstituted enynes containing the easily manipulable (trimethylsilyl)ethynyl moiety. Thus, hydroalumination of the silyl-substituted enynes followed by protonolysis furnishes the corresponding 1-(trimethylsilyl)-1,3-butadienes, whereas hydroboration–oxidation affords tetrasubstituted olefins containing the carboxyl group.

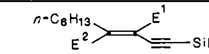
Recently we have shown that 1-trimethylsilyl 1,3-diynes undergo regio- and chemoselective trans hydroalumination at the alkyl-substituted triple bond when treated with lithium diisobutyl-*n*-butylaluminum hydride.[1] The observation that the presence of the trimethylsilyl moiety imparts appreciably different reactivities to the triple bonds of 1-trimethylsilyl 1,3-diynes **1** led us to explore the feasibility of simultaneously and stereoselectively introducing onto the alkyl-substituted triple bond two metal centers[2] that would exhibit different reactivities toward electrophilic reagents. Specifically, we were interested in the utilization of such bis-metallic compounds as intermediates for the preparation of substituted enynes of predictable stereochemistry.

We initially investigated the reaction of diyne **1**[3] with various stannyllithium reagents. Although the stannyllithiation reaction proceeded with chemo- and regioselective trans addition of the Sn–Li bond to the alkyl-substituted triple bond of **1**, it was accompanied by appreciable metalation at the propargylic positions of 1-trimethylsilyl 1,3-diynes containing primary or secondary alkyl substituents.[4] In search of a way to bypass the metalation side reaction, we investigated the behavior of stannylcopper reagents toward **1**. These had been reported to add to the triple bonds of acetylenes.[5,6] We now disclose that treatment of silyl diynes **1** with 2.5 equiv of the (trimethylstannyl)copper reagent **2** in THF at −50 °C converts them chemo- and stereoselectively into the corresponding *trans*-bis(trimethylstannyl) enynes **3** in high yields. These can be selectively elaborated into stereodefined trisubstituted enynes, tetrasubstituted enynes, and, via further reaction of these, the corresponding dienes or alkenes.



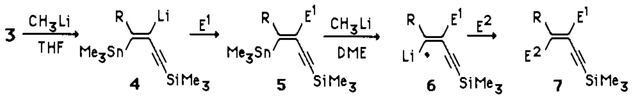
The formation of **3** can be envisioned to proceed via an initial, chemoselective addition of the stannylcopper reagent **2** to the more electrophilic alkyl-substituted triple bond, followed by exchange of the copper by tin. The observed *trans* addition of the two trimethylstannyl groups to the triple bond has its counterpart in the bis(stannylation) of acetylenic esters and amides reported by Piers and co-workers.[5] In this connection it should be noted that addition of hexamethyldistannane to 1-alkynes in the presence of tetrakis(triphenylphosphine)palladium affords the corresponding *cis*-1,2-bis(trimethylstannyl)-1-alkenes.[7]

Table I. Yields of Substituted Enynes Derived from 1-(Trimethylsilyl)-1,3-decadiyne

	electrophile				
	E^1	E^2	E^1	E^2	yield,[a–c] %
7a	CH_3I	CH_3OH	CH_3	H	94
7b	C_2H_5I	CH_3OH	C_2H_5	H	87
7c	n-C_4H_9I	CH_3OH	n-C_4H_9	H	92
7d	C_3H_5Br	CH_3OH	C_3H_5	H	93
7e	CH_3OH	CH_3I	H	CH_3	92
7f	CH_3I	CH_3I	CH_3	CH_3	90
7g	n-C_4H_9I	CH_3I	n-C_4H_9	CH_3	88
7h	CH_3I	n-C_4H_9I[d]	CH_3	n-C_4H_9	81

[a] Isolated yields. [b] GLC analysis on an SE-54 glass capillary J&W column revealed that the enynes were all at least 97% isomerically pure. [c] The IR, ^1H NMR, and mass spectral data of the enynes obtained were consistent with the assigned structures. [d] Since the alkylation of the lithiated enyne **6** was sluggish with *n*-butyl iodide, the transmetalation and alkylation reactions were carried out in diglyme solvent.

An attractive feature of the bis(trimethylstannyl) enynes **3** is that they possess two carbon–metal bonds, which, based on electronic considerations, should be amenable to stepwise conversion into the corresponding vinyllithium reagents. Thus, addition of 1 equiv of methyllithium to a solution of **3** in THF at −78 °C results in the selective transmetalation of the trimethylstannyl moiety at C-3 to produce the enynyllithium **4**. To establish the stereochemistry of **4**, the organolithium compound was converted to the monostannyl enyne **5** (E^1 = H) by treatment with methanol at −78 °C. The ^1H NMR spectrum of **5** (R = n-C_6H_{13}; E^1 = H) exhibited *J* values for the ^{117}Sn–H and the ^{119}Sn–H coupling of 115 and 120 Hz, respectively, which are typical of *trans*-vinylstannanes. By contrast, reported *J* values for *cis*-vinylstannanes are 60–70 Hz.[5,8,9] Thus, provided that the tin–lithium exchange of **3** proceeded with retention of configuration, a characteristic of exchange reactions of simple vinylic tin compounds with alkyllithiums,[10] the bis(trimethylstannyl) enyne



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[2] For a recent summary on the preparation and utilization of bimetallic reagents, see: Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3562.

[3] Miller, J. A.; Zweifel, G. *Synthesis* **1983**, 128.

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[5] Piers, E.; Chong, J. M.; Morton, H. E. *Tetrahedron Lett.* **1981**, *22*, 4905. Piers, E.; Chong, J. M. *J. Org. Chem.* **1982**, *47*, 1602. Piers, E.; Chong, J. M.; Keay, B. *Tetrahedron Lett.* **1985**, *26*, 6265. Piers, E.; Skerlj, R. T. *J. Chem Soc., Chem. Commun.* **1986**, 626.

[6] Westmijze, H.; Ruitenberg, K.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1982**, *23*, 2797.

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[8] Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* **1967**, *9*, 285. Also see ref 4.

[9] Further confirmatory evidence for the structure of 4 was obtained by its conversion into the known (*E*)-1-(trimethylsilyl)-3-decen-1-yne (R = n-C_6H_{13}; E^1 = E^2 = H)[1] by a sequence of alkylation–transmetalation–alkylation reactions.

[10] Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1962**, *84*, 361. Seyferth, D.; Vaughan, L. G. *J. Am. Chem. Soc.* **1964**, *86*, 883.

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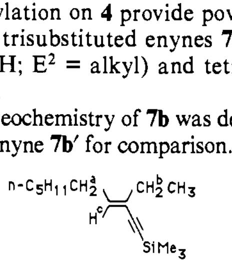
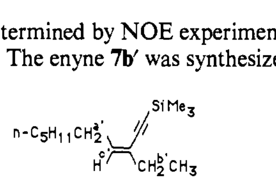
3 must have the *trans* configuration. The organolithium intermediates **4** also react readily with primary alkyl iodides and with allyl bromide to furnish the corresponding alkyl-substituted enynes **5** (E^1 = alkyl).

Attempts to transmetalate the trimethylstannyl group in **5** (E^1 = H, alkyl) with various alkyllithiums in THF solvent revealed that the reaction did not proceed to completion.[11] However, by replacing the THF with dimethoxyethane (DME) or diglyme and using methyllithium, one can achieve quantitative exchange of tin by lithium to furnish the enynyllithium **6**. As shown in Table I, the sequences of alkylation–transmetalation–protonation, protonation–transmetalation–alkylation, or alkylation–transmetalation–alkylation on **4** provide powerful tools for one-pot preparations of trisubstituted enynes **7a-d** (E^1 = alkyl; E^2 = H) and **7e** (E^1 = H; E^2 = alkyl) and tetrasubstituted enynes **7f–h**, respectively.

The stereochemistry of **7b** was determined by NOE experiments using the enyne **7b′** for comparison. The enyne **7b′** was synthesized

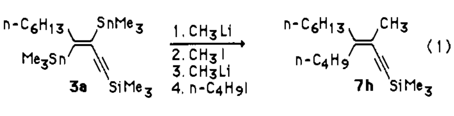


7b

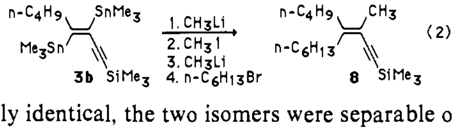


7b′

by a Peterson olefination reaction involving 1,3-bis(trimethylsilyl)-3-lithio-1-pentyne and heptanal in the presence of $MgBr_2$.[13] The assignment of the *E* stereochemistry to **7b** was based on the absence of a nuclear Overhauser effect (NOE) between the allylic protons H^b and the vinylic proton H^c in the 360-MHz NMR spectrum. On the other hand, there was a 1.2% NOE observed for the allylic protons $H^{b'}$ and the vinylic proton $H^{c'}$ in the spectrum of **7b′**. Both enynes **7b** and **7b′** exhibited a 1% NOE between the allylic protons on H^a and $H^{a'}$ and the vinylic protons H^c and $H^{c'}$, respectively. The structures of the other trisubstituted enynes shown in Table I are based on these assignments. In the case of the tetrasubstituted enynes **7g** and **7h**, both isomers were available (eq 1 and 2). Although the ^{1}H NMR spectra of these enynes were nearly identical, the two isomers were separable on a glass capillary column (SE-54, 30 m). It is important to note that the corresponding isomeric trisubstituted enynes containing an alkyl group at C-4 as well as the corresponding tetrasubstituted enynes are also accessible by proper choice of the alkyl-substituted 1,3-diynes and alkylating agents as exemplified in eq 1 and 2. Unfortunately, difficulties were encountered in extending the synthesis of substituted enynes to 1-trimethylsilyl 1,3-diynes containing secondary alkyl substituents. Although the bis(stannyl) enynes were obtained in high yields, transmetalation of the tin by lithium at C-4 did not proceed to completion. Ways to obviate this problem are currently under investigation.

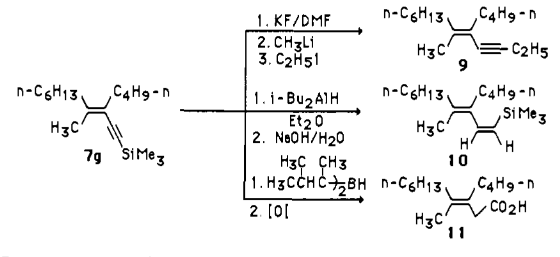


(1)



(2)

An attractive feature of the enynes derived by the present methodology is that they contain the easily manipulable (trimethylsilyl)ethynyl group and hence are themselves of considerable value as synthetic intermediates for further transformations. Thus, replacement of the trimethylsilyl moiety in **7g** by an alkyl group provides the substituted enyne **9**, whereas chemoselective hydroalumination–protonation of the triple bond[1] furnishes the diene **10**. Finally, hydroboration–oxidation[14] of the same enyne affords the corresponding tetrasubstituted olefin **11**.



In summary, the application in various orders of a sequence of transmetalation–alkylation–protonation reactions to 1-trimethylsilyl 1,3-diyne derived *trans*-bis(trimethylstannyl) enynes **3** provides a novel and valuable approach for the preparation of a variety of stereodefined tri- and tetrasubstituted enynes. These may be further elaborated by reactions at the (trimethylsilyl)ethynyl moiety into substituted dienes or tri- and tetrasubstituted alkenes that may be difficult to obtain by current methodologies.

Experimental Section

Ether, tetrahydrofuran, 1,2-dimethoxyethane (DME), and diglyme were distilled from sodium and benzophenone immediately prior to use. All glassware, syringes, and needles were oven-dried at 150 °C for 6 h, assembled hot, and cooled under a stream of nitrogen before use. All reactions involving these reagents were stirred magnetically and conducted under an atmosphere of argon or nitrogen. The boiling points reported for the compounds are Kugelrohr pot temperatures.

Procedures. *Note: To ensure high yields and high isomeric purities of the compounds described below, it is essential that the reagents be added precisely in the stoichiometric amounts indicated.* **(*E*)-1-(Trimethylsilyl)-3,4-bis(trimethylstannyl)-3-decen-1-yne (3a).** Into a dry 250-mL, three-necked flask equipped with a nitrogen inlet, a gas outlet tube with a stopcock connected to a mercury bubbler, a thermometer, and a magnetic stirring bar and maintained under a positive pressure of nitrogen was placed by means of a double-ended needle 93 mL of a 0.56 M solution of (trimethylstannyl)lithium in THF.[15] To the cooled solution (−50 °C, aqueous $CaCl_2$–dry ice bath)[16] was added $CuBr{\cdot}SMe_2$ (10.7 g, 52 mmol, Aldrich). The resultant deep red solution was stirred for 30 min and then treated at −50 °C with 1-(trimethylsilyl)-1,3-decadiyne (**1a**) (4.12 g, 20 mmol).[3] The mixture was stirred for 30 min, gradually warmed to 0 °C, stirred for an additional 3 h, diluted with ether (60 mL), and filtered through Celite. To the filtrate was added saturated aqueous NH_4Cl (100 mL), the layers formed were separated, and the aqueous phase was extracted with *n*-pentane. The combined extracts were washed with brine, dried ($MgSO_4$), filtered, concentrated, and distilled (Kugelrohr) to give 9.2 g (86%) of **3a**. Alternatively, the bis(stannyl) enynes may be purified by flash chromatography on silica gel using *n*-hexane as eluant.[17] **3a**: bp 121–123 °C (10^{-3} mmHg), $n^{25}{}_D$ 1.5192; IR (neat) 3000, 2955, 2880, 2110, 1450, 1150, 850, 770, 690 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.10 (s, 9 H, $SiMe_3$), 0.15 (s, 9 H, $SnMe_3$), 0.17 (s, 9 H, $SnMe_3$), 0.70 (t, J = 7.5 Hz, 3 H, CH_3), 1.0–1.4 (brm, 8 H, CH_2), 2.1–2.4 (brt, J = 7.5 Hz, 2 H, $CH_2C{=}C$). The *trans* relationship of the Me_3Sn groups in **3** follows from its conversion into the known (*E*)-1-(trimethylsilyl)-3-decen-1-yne[1] via transmetalation with methyllithium followed by protonation of the intermediate alkenyllithiums.

(*E*)-1-(Trimethylsilyl)-3-methyl-3-decen-1-yne (7a). To a well-stirred solution of the bis(stannyl) enyne **3a** (1.60 g, 3.0 mmol) in THF (6 mL) contained in a 25-mL flask and maintained at −78 °C under a static pressure of nitrogen was added dropwise a 1.30 M solution of methyllithium (3.3 mmol, low halide) in ether. The mixture was stirred at −78 °C for 1 h and the resultant lithiated enyne **4** was treated with methyl iodide (0.42 g, 3.0 mmol). The reaction mixture was stirred for an additional 1 h at −78 °C, warmed to room temperature, and stirred for 2 h. The solvents were removed under reduced pressure (1 mmHg) and the residue obtained was diluted with DME (6 mL). *It is important that these operations are carried out with exclusion of air.* To the resultant solution was added at −78 °C a 1.30 M solution of methyllithium (3.3 mmol, low halide) in ether. After 1 h of stirring at −78 °C, the resultant vinyllithium intermediate was protonated at −78 °C with methanol (1 mL). The mixture was warmed to room temperature and diluted with

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(11) Vinyltin–lithium exchange reactions are equilibrium processes and depend on the nature of the vinylic tin and lithium reagents as well as the solvents used in the transmetalations.[12]

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(17) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

brine (20 mL), and the layers formed were separated. The aqueous phase was extracted with *n*-pentane (3 × 5 mL) and concentrated. Distillation (Kugelrohr) afforded 0.63 g (94%) of **7a**: bp 110–112 °C (1 mmHg); $n^{25}{}_D$ 1.4686; IR (neat) 2959, 2928, 2856, 2145, 1659, 1559, 1468, 1377, 1250, 1186, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.15 (s, 9 H, $SiMe_3$), 0.85 (t, J = 7.0 Hz, 3 H, CH_3), 1.10–1.55 (m, 8 H, CH_2), 1.75 (s, 3 H, C=CCH_3), 1.9–2.2 (m, 2 H, C=CCH_2), 5.8 (tq, J = 7.7, 1.5 Hz, 1 H, C=CH; high-resolution MS, m/z 222.1800 (calcd for $C_{14}H_{26}Si$, 222.1804). GLC examination (120 °C) revealed that the compound was 98% isomerically pure.

(*E*)-1-(Trimethylsilyl)-3-ethyl-3-decen-1-yne (7b). Following the procedure for the preparation of **7a**, alkylation of the vinyllithium intermediate **4** derived from the enyne **3a** (1.60 g, 3.0 mmol) with ethyl iodide (0.47 g, 3.0 mmol) followed by transmetalation–protonation afforded 0.61 g (87%) of **7b**: bp 108–112 °C (10^{-3} mmHg; Kugelrohr); $n^{22}{}_D$ 1.4667; IR (neat) 2950, 2910, 2840, 2135, 1670, 1455, 1240, 840, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.15 (s, 9 H, $SiMe_3$), 0.8–0.9 (t, J = 7.5 Hz, 3 H, CH_3), 1.0 (t, J = 7.5 Hz, 3 H, C=CCCH_3), 1.1–1.4 (m, 8 H, CH_2), 1.9–2.2 (m, 4 H, C=CCH_2), 5.75 (t, J = 7.5 Hz, 1 H, C=CH); high-resolution MS, m/z 236.1961 (calcd for $C_{15}H_{28}Si$, 236.1963). GLC analysis (150 °C) showed that the compound was at least 98% isomerically pure.

(*E*)-1-(Trimethylsilyl)-3-*n*-butyl-3-decen-1-yne (7c). Following the procedure for the preparation of **7a**, alkylation of the vinyllithium intermediate **4** derived from the enyne **3a** (1.6 g, 3.0 mmol) with *n*-butyl iodide (0.55 g, 3.0 mmol) followed by transmetalation–protonation furnished 0.73 g (92%) of **7c**: bp 107–110 °C (1 mmHg, Kugelrohr); $n^{23}{}_D$ 1.4683; IR (neat) 2959, 2926, 2858, 2137, 1579, 1468, 1379, 1250, 1186, 843 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.15 (s, 9 H, $SiMe_3$), 0.75–1.0 (m, 6 H, CH_3), 1.1–1.6 (br m, 12 H, CH_2), 1.9–2.3 (m, 2 H, C=CCH_2), 5.75 (t, J = 7.2 Hz, 1 H, C=CH); high-resolution MS m/z 264.2256 (calcd for $C_{17}H_{32}Si$, 264.2275). GLC examination (150 °C) showed that the compound was at least 98% isomerically pure.

(*E*)-1-(Trimethylsilyl)-3-(3-propenyl)-3-decen-1-yne (7d). Following the procedure for the preparation of **7a**, alkylation of the vinyllithium intermediate **4** derived from the enyne **3a** (1.6 g, 3.0 mmol) with allyl bromide (0.40 g, 3.3 mmol) followed by transmetalation–protonation yielded 0.46 g (93%) of **7d**: bp 73–75 °C (0.01 mmHg; Kugelrohr); $n^{23}{}_D$ 1.4738; IR (neat) 2959, 2928, 2858, 2143, 1659, 1641, 1468, 1250, 1082, 910, 843 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.10 (s, 9 H, $SiMe_3$), 0.90 (t, J = 7.5, 3 H, CH_3), 1.1–1.5 (m, 8 H, CH_2), 1.9–2.2 (t, J = 7.5 Hz, 2 H, C=CCH_2), 2.80 (d, J = 6.75 Hz, 2 H, C=CCH_2C=C), 4.90 (d, J = 1.8 Hz, 1 H, C=CH), 5.05 (dd, J = 5.4, 1.8 Hz, 1 H, C=CH), 5.5–6.0 (m, 1 H, HC=CC≡CSi), 5.85 (t, J = 5.4 Hz, 1 H, C=CCH=C); high-resolution MS, m/z 248.1958 (calcd for $C_{16}H_{28}Si$, 248.1961). GLC examination (150 °C) showed that the compound was at least 98% isomerically pure.

(*E*)-1-(Trimethylsilyl)-4-methyl-3-decen-1-yne (7e). In an oven-dried, nitrogen-flushed 25-mL flask was placed a solution of **3a** (1.60 g 3.0 mmol) in THF (6 mL). To this solution was added dropwise at −78 °C a 1.27 M solution of methyllithium (3.0 mmol, low halide) in ether. The solution was stirred for 1 h at −78 °C, treated with 3 mL of a 1 M solution of methanol in THF, stirred for an additional 1 h at −78 °C, and gradually warmed to room temperature. The volatiles were removed under reduced pressure (1 mmHg, 15 min) and the resiude obtained was diluted with DME (6 mL). These operations were carried out with the exclusion of air. To the resultant mixture was added at −78 °C a 1.27 M solution of methyllithium (3.3 mmol, low halide) in ether. After 1 h of stirring at −78 °C, the resultant vinyllithium **6** (E^1 = H) was treated with methyl iodide (0.47 g, 3.3 mmol). The mixture was stirred for 1 h, warmed to room temperature, and stirred for an additional 2 h. The mixture was then diluted with brine (20 mL), the layers formed were separated, and the aqueous layer was extracted with *n*-pentane (3 × 5 mL). The combined organic extracts were washed with brine (20 mL) and dried ($MgSO_4$). The solvents were removed and the residue obtained was distilled (Kugelrohr) to afford 0.61 g (92%) of **7e**: bp 92–93 °C (1 mmHg); $n^{22}{}_D$ 1.4714; IR (neat) 2959, 2930, 2859, 2133, 1626, 1460, 1381, 1250, 1196, 843, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.15 (s, 9 H, $SiMe_3$), 0.8–1.0 (t, J = 7.5 Hz, 3 H, CCH_3), 1.15–1.55 (m, 8 H, CH_2), 1.90 (s, 3 H, C=CCH_3), 1.95–2.15 (t, J = 7.5 Hz, 3 H, CH_2C=C), 5.25–5.30 (m, 1 H, C=CH); high-resolution MS, m/z 222.1804 (calcd for $C_{14}H_{26}Si$, 222.1800). GLC examination (150 °C) revealed that the compound was at least 98% pure.

(*E*)-1-(Trimethylsilyl)-3,4-dimethyl-3-decen-1-yne (7f). To a solution of **3a** (1.60 g, 3.0 mmol) in THF (6 mL) contained in a 25-mL flask and maintained under a static pressure of nitrogen was added dropwise at −78 °C a 1.26 M solution of methyllithium (3.0 mmol, low halide) in ether. The mixture was stirred at −78 °C for 1 h, treated with methyl iodide (0.42 g, 3.0 mmol), stirred for an additional 1 h, and then warmed to room temperature and stirred for 2 h. The volatiles were removed under reduced pressure (1 mmHg) and the residue obtained was diluted with DME (6 mL). These operations were carried out with exclusion of air. To the resultant solution was added at −78 °C a 1.26 M solution of methyllithium (3.3 mmol, low halide) in ether. After 1 h of stirring at −78 °C, the vinyllithium intermediate **6** (E^1 = CH_3) was treated with methyl iodide (0.47 g, 3.3 mmol). The mixture was stirred at −78 °C for 1 h, warmed to room temperature, stirred at this temperature for 2 h, and then quenched with brine (20 mL). The phases were separated, and the aqueous phase was extracted with *n*-pentane (3 × 5 mL). The combined organic extracts were washed with brine (10 mL), dried ($MgSO_4$), and concentrated. Distillation (Kugelrohr) yielded 0.64 g (90%) of **7f**; bp 102–104 (1 mmHg); $n^{25}{}_D$ 1.4700; IR (neat) 2959, 2928, 2130, 1626, 1466, 1374, 1250, 1111, 910, 840, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.15 (s, 9 H, $SiMe_3$), 0.7–1.0 (t, J = 7.5 Hz, 3 H, CH_3), 1.1–1.5 (br m, 8 H, CH_2), 1.75 (t, J = 2.3 Hz, 3 H, RC=CCH_3), 1.85 (t, J = 2.3 Hz, 3 H, RCH_3C=C), 2.15 (t, J = 7.2 Hz, 2 H, CH_2C=C); high-resolution MS, m/z 236.1948 (calcd for $C_{15}H_{28}Si$, 236.1961). GLC analysis (150 °C) showed that the compound was at least 98% isomerically pure.

(*E*)-1-(Trimethylsilyl)-3-*n*-butyl-4-methyl-3-decen-1-yne (7g). Following the procedure for the preparation of **7f**, sequential treatment of **3a** (3.0 mmol) with methyllithium (3.0 mmol), *n*-butyl iodide (0.55 g, 3.0 mmol), methyllithium (3.3 mmol), and methyl iodide (0.47 g, 3.3 mmol) yielded 0.73 g (88%) of **7g**: bp 121–123 °C (1 mmHg; Kugelrohr); $n^{22}{}_D$ 1.4718; IR (neat) 2960, 2930, 2860, 2135, 1455, 1380, 1240, 840, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.15 (s, 9 H, $SiMe_3$), 0.8–1.0 (m, 6 H, CH_3), 1.1–1.6 (br m, 12 H, CH_2), 1.85 (s, 3 H, C=CCH_3), 2.0 (t, J = 7.2 Hz, 4 H, C=CCH_2). Anal. Calcd for $C_{18}H_{34}Si$: C, 77.63; H, 12.36. Found: C, 77.36; H, 12.26. GLC analysis (150 °C) revealed that the compound was at least 98% isomerically pure.

(*E*)-1-(Trimethylsilyl)-4-*n*-butyl-3-methyl-3-decen-1-yne (7h). Following the procedure for the preparation of **7f**, the enyne **3a** (2.13 g, 4.0 mmol) was converted to the stannyl enyne **5** (E^1 = CH_3). The volatiles were removed under reduced pressure (1 mmHg) and the residue obtained was diluted with diglyme (8 mL). These operations were carried out with exclusion of air. To the enyne **5** was added at −78 °C a 1.32 M solution of methyllithium (4.4 mmol, low halide) in ether. After 1 h of stirring at −78 °C, the vinyllithium intermediate **6** was treated with *n*-butyl iodide (0.81 g, 4.4 mmol). The reaction mixture was stirred at −78 °C for 1 h, warmed to room temperature, stirred for 2 h, and quenched with brine (20 mL). Workup and distillation (Kugelrohr) furnished 0.95 g (86%) of **7h**: bp 108–111 °C (0.2 mmHg); $n^{28}{}_D$ 1.4687; IR (neat) 2940, 2920, 2830, 2130, 1450, 1240, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.10 (s, 9 H, $SiMe_3$), 0.8–1.0 (t, J = 7.5 Hz, 6 H, CH_3), 1.1–1.5 (br m, 12 H, CH_2), 1.75 (s, 3 H, C=CCH_3), 2.05 (t, J = 7.7 Hz, 4 H, C=CCH_2); high-resolution MS, m/z 278.2417 (calcd for $C_{18}H_{34}Si$, 278.2431). GLC analysis (150 °C) showed that the compound was at least 98% isomerically pure.

(*Z*)-1-(Trimethylsilyl)-4-*n*-butyl-3-methyl-3-decen-1-yne (8). Following the procedure for the preparation of **7h**, 1-(trimethylsilyl)-3,4-bis(trimethylstannyl)-3-octen-1-yne (**3b**) (3.0 mmol) was converted to the stannyl enyne **5** (E^1 = CH_3). The volatiles were removed under reduced pressure (1 mmHg) and the residue obtained was diluted with diglyme (6 mL). These operations were carried out with exclusion of air. To the enyne **5** was added at −78 °C a 1.32 M solution of methyllithium (3.3 mmol, low halide) in ether. After stirring 1 h at −78 °C, the vinyllithium intermediate **6** was treated with *n*-hexyl bromide (0.54 g, 3.3 mmol). The reaction mixture was stirred at −78 °C for 1 h, warmed to room temperature, stirred for 2 h, and quenched with brine (20 mL). Workup and distillation (Kugelrohr) afforded 0.72 g (86%) of (*Z*)-1-(trimethylsilyl)-3-methyl-4-*n*-butyl-3-decen-1-yne (**8**): bp 102–104 °C (0.3 mmHg); $n^{22}{}_D$ 1.4720; IR (neat) 2940, 2915, 2850, 2135, 1460, 1245, 840, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.10 (s, 9 H, $SiMe_3$), 0.75–0.95 (t, J = 7.5 Hz, 3 H, CH_3), 0.90 (t, J = 7.5 Hz, 3 H, CH_3), 1.1–1.5 (br m, 12 H, CH_2), 1.75 (s, 3 H, C=CCH_3), 2.05 (t, J = 7.5 Hz, 2 H, C_3H_2C=C), 2.35 (t, J = 7.5 Hz, 2 H, C_5CH_2C=C); high-resolution MS, m/z 278.2443 (calcd for $C_{18}H_{34}Si$, 278.2431). GLC analysis (150 °C) indicated the compound was at least 97% pure.

(*E*)-3-*n*-Butyl-4-methyl-5-dodecen-3-yne (9). To a slurry of potassium fluoride dihydrate (0.28 g, 3.0 mmol) in *N,N*-dimethylformamide (3 mL) at 25 °C was added (*E*)-1-(trimethylsilyl)-3-methyl-4-*n*-butyl-3-decen-1-yne (0.41 g, 1.5 mmol). The slurry was stirred at 25 °C for 3 h and then poured into a separatory funnel containing 10 mL of a mixture of 3 N HCl and ice. The layers were separated and the aqueous phase was extracted with pentane (3 × 10 mL). The combined extracts were washed successively with 3 N HCl (2 × 10 mL), saturated aqueous $NaHCO_3$, and brine and dried ($MgSO_4$). The volatiles were removed (1 mmHg) and the residue obtained was dissolved in diglyme (1.5 mL). To the resulting solution was added at −78 °C a 1.78 M solution of methyllithium (1.6 mmol) in ether. The resultant solution was stirred at −78 °C for 1 h, treated with ethyl iodide (0.49 g, 3.0 mmol), stirred for 15 min, warmed to room temperature, and stirred for an additional 5 h. The reaction mixture was poured into a separatory funnel containing 10 mL of cold 3 N HCl. The layers formed were separated and the aqueous phase was extracted with pentane (3 × 10 mL). The combined organic extracts were successively washed with 3 N HCl (2 × 10 mL), saturated aqueous $NaHCO_3$, and brine. The organic phase was dried ($MgSO_4$), filtered, and concentrated. Distillation (Kugelrohr) yielded 0.28 g (78%) of **9**: bp 99–102 °C (1 mmHg); $n^{22}{}_D$ 1.4709; IR (neat) 2950, 2920, 2850, 1455, 1173, 1113, 1060 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, J = 7.5 Hz, 3 H, CH_3), 0.91 (t, J = 7.5 Hz, 3 H, CH_3), 1.18 (t, J = 7.5 Hz, 3 H, $C{\equiv}CCCH_3$), 1.2–1.4 (m, 12 H, CH_2), 1.77 (s, 3 H, $C{=}CCH_3$), 2.05 (t, J = 7.5 Hz, 2 H, $C{=}CCH_2$), 2.28 (t, J = 7.5 Hz, 2 H, $C{=}CCH_2$), 2.35 (q, J = 7.5 Hz, 2 H, $C{\equiv}CCH_2$); high-resolution MS, m/z 234.2369 (calcd for $C_{17}H_{30}$, 234.2349). GLC analysis (DB-1 glass capillary column, 30 m) revealed that the compound was at least 96% isomerically pure.

(1*Z*,3*E*)-1-(Trimethylsilyl)-3-*n*-butyl-4-methyl-1,3-decadiene (10). Into a 25-mL three-necked flask maintained under a static pressure of nitrogen was placed 0.56 g (2.0 mmol) of **7g** in ether (2 mL). To the well-stirred solution was added dropwise at 25 °C diisobutylaluminum hydride (neat, 0.41 mL, 2.2 mmol). The solution was stirred for 15 min and then heated at 40 °C for 4 h. After cooling to room temperature, the reaction mixture was hydrolyzed by slowly pouring it into ice-cold 3 N NaOH. The layers were separated and the aqueous phase was extracted with pentane (3 × 15 mL). The combined organic extracts were washed successively with 3 N NaOH and brine (2 × 10 mL) and dried ($MgSO_4$). The solvents were removed and the residue obtained was distilled (Kugelrohr) to furnish 0.38 g (90%) of **10**: bp 78–80 °C (0.05 mmHg); $n^{22}{}_D$ 1.4622; IR (neat) 2950, 2935, 2850, 2135, 1455, 1240, 840, 755 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.10 (s, 9 H, $SiMe_3$), 0.8–1.0 (m, 6 H, CH_3), 1.1–1.5 (br m, 12 H, CH_2), 1.75 (s, 3 H, $C{=}CCH_3$), 2.05 (t, J = 7.5 Hz, 2 H, $C_3CH_2C{=}C$), 2.35 (t, J = 7.5 Hz, 2 H, $C_5CH_2C{=}C$), 5.35 (d, J = 14.4 Hz, 1 H, $C{=}CCHC{=}CSi$), 5.35 (t, J = 7.5 Hz, 1 H, $RCH{=}C$), 6.65 (d, J = 14.4 Hz, 1 H, $C{=}CHSi$); high-resolution MS, m/z 280.2576 (calcd for $C_{18}H_{36}Si$, 280.2588). GLC analysis (150 °C) indicated that the compound was at least 97% isomerically pure.

(*E*)-3-*n*-Butyl-4-methyl-3-decenoic Acid (11). To a 1.90 M solution of $BH_3{\cdot}SMe_2$ (2.2 mmol) in THF maintained under a positive pressure of nitrogen was added at −15 °C ($CaCl_2$–dry ice bath) 2-methyl-2-butene (0.31 g, 4.4 mmol). The disiamylborane formed was stirred at 0 °C for 2 h, cooled to −15 °C, and added dropwise to the enyne **7g** (0.56 g, 2.0 mmol) in THF (2 mL) maintained at −15 °C. The solution was stirred for an additional 30 min at −15 °C, warmed to room temperature, and stirred for 1 h. The reaction mixture was diluted with methanol (2 mL), treated with 3.8 mL of a 3 N aqueous solution of NaOH, and oxidized by dropwise addition of 1.5 mL of 30% H_2O_2 while the temperature was maintained below 50 °C during the addition. The mixture was treated at 0 °C with 20 mL of 6 N HCl. The layers formed were separated and the aqueous phase was extracted with ether (3 × 5 mL). The combined organic extracts were washed with brine and dried ($MgSO_4$). The solvents were removed and the residue obtained was distilled (Kugelrohr) to afford 0.43 g (90%) of **11**: bp 105–115 °C (10^{-3} mmHg); $n^{24}{}_D$ 1.4620; IR (neat) 3600–2400, 3200, 2950, 2860, 1700, 1460, 1405, 1255, 1150, 950, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.75–1.00 (m, 6 H, CH_3), 1.05–1.65 (br m, 12 H, CH_2), 1.65 (s, 3 H, $CH_3C{=}C$), 1.80–2.25 (m, 4 H, $CH_2C{=}C$), 3.0 (s, 2 H, $CH_2C{=}O$), 10.95–11.20 (s, 1 H, COOH). Esterification of the acid with diazomethane furnished the methyl ester **12** in 80% yield: bp 83–85 °C (10^{-3} mmHg); $n^{22}{}_D$ 1.4551; IR (neat) 2950, 2930, 2855, 1730, 1455, 1155, 1015 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.86–0.91 (m, 6 H, CH_3), 1.27–1.32 (m, 12 H, CH_2), 1.65 (s, 3 H, $C{=}CCH_3$), 1.93–2.09 (m, 4 H, $C{=}CCH_2$), 3.04 (s, 2 H, $CH_2C{=}O$), 3.65 (s, 3 H, OCH_3); high-resolution MS, m/z 254.2262 (calcd for $C_{16}H_{30}O_2$, 254.2243). GLC analysis (DB-1701 glass capillary column, 15 m, 150 °C) showed that the compound was at least 95% isomerically pure.

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Charge-Transfer Complexes as Potential Organic Ferromagnets

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Abstract: One proposal for the synthesis of an organic ferromagnetic material has been investigated. Two new derivatives of hexaazatritetralin have been prepared carrying electron-withdrawing substituents on nitrogen. These form crystalline one-to-one charge-transfer complexes with tris(dicyanomethylene)cyclopropane. The physical and chemical data for these systems indicate that one of them exists as the cation radical/anion radical complex in the solid, but the other has additional partial second charge transfer. Although the dications of the electron donors have triplet spin multiplicity and the charge-transfer solid appears to fulfill the requirements of our model for ferromagnetism, the charge-transfer solids show antiferromagnetic, not ferromagnetic, ordering.

There has been much recent interest in the design of organic materials with special properties, such as electrical conductivity. Ferromagnetism is another very useful physical property that has not yet clearly been detected in any purely organic compound, although two groups have reported organic materials with small, irreproducible ferromagnetic components.[1,2] Several groups are currently trying to prepare ferromagnetic organic materials, using several very different proposals.[1-5]

Ferromagnetism is the result of a high-spin solid state, with many electrons aligned parallel. Proposals for the construction of ferromagnetic interactions in organic compounds have been around for many years. The first proposal of which we are aware for the production of intermolecular ferromagnetic interactions in organic solids was published by McConnell in 1963.[6] His idea has been investigated experimentally by several groups.[7] In 1968, Mataga proposed a method for preparing macroscopic ferromagnets based on intramolecular ferromagnetic interactions in large molecules.[8] The high-spin polycarbene molecules of

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