A Highly Stereoselective Synthesis of 1-Halo-1-(trimethylsilyl)-2,2-dialkyl Olefins

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Isomerically pure 1-halo-1-(trimethylsilyl)-2,2-dialkyl olefins have the potential for serving as key intermediates in the stereospecific synthesis of tetrasubstituted olefins. Unfortunately, attempts to synthesize these (halovinyl)si-lanes in a highly stereoselective manner have proven to be difficult. In 1977, Sefterth et al.2 reported the synthesis of R₂C=CB₃SiMe₃ compounds, but the procedure is limited to having the 2,2-dialkyl groups the same. In 1978, Snider et al.3 reported the Ni-catalyzed addition of methylMagnesium bromide to silylacetylenes followed by reaction with excess iodine to give a stereoselective synthesis of vinyliodosilanes; however, use of ethylmagnesium bromide did not give similar results. Also in 1978, Eisch et al.4 reported that the carbotitanation of alkynylsilanes may or may not be stereoselective, depending upon the nature of the alkylaluminum chloride used; this work did not attempt to trap the vinylmetallic intermediate with halogens. In 1979, Snider and Karras5 reported the most successful approach; they observed that carbotitanation of alkynylsilanes was highly stereoselective using dialkylaluminum chloride–titancocene dichloride (1:1). Although they were able to cleave the carbon–metal bond with aqueous sodium hydroxide in a highly stereoselective manner to give trisubstituted olefins, when cleavage was attempted with a large excess of iodine considerable loss of stereocchemical control in and yield of the 1-iodo-1-(trimethylsilyl)-2,2-dialkyl olefin product was observed. We describe in this paper a modification of Snider’s approach that allows the synthesis of the 1-halo-1-(trimethylsilyl)-2,2-dialkyl olefins in good yield and a highly stereoselective manner (>95:5 ratio).

Our initial approach to this problem sought to use bromine to cleave the product of carbometalation in analogy to the preparation of 1-bromo-1-(trimethylsilyl)-2-alkyl olefins.6 Thus 1-(trimethylsilyl)-1-hexyne7 was reacted at room temperature with a solution derived from diethylaluminum chloride and titancocene dichloride (1:1) in dichloromethane solvent followed by treatment with bromine in dichloromethane at ~78 °C. Unfortunately, a complex mixture of products was obtained with significant loss of the trimethylsilyl group. Next, cyanogen bromide was used as the electrophile, and it was found that indeed a good yield of cleavage products was obtained. Unfortunately, the products were a mixture of the desired 1-bromo-2-ethyl-1-(trimethylsilyl)-1-hexene (1) and 3-ethyl-2-(trimethylsilyl)-2-hepteninitrile (2) from which a 70% isolated yield of 1 could be obtained by silica gel chromatography. Attempts to determine the E/Z ratio of (bromovinyl)silane 1 directly even on capillary GLC proved unsuccessful. Therefore compound 1 was subjected to halogen–metal exchange with sec-butyllithium at ~78 °C followed by quenching with methanol at ~78 °C to give 2-ethyl-1-(trimethylsilyl)-1-hexene.8 Examination of this trisubstituted olefin by capillary GLC (30–m SE–54) showed 3 to be a 1:1 mixture of E/Z isomers.

The carbometalated intermediate was reacted with N-bromosuccinimide in dichloromethane at ~78 °C in order to eliminate the nitrile side product and lower the temperature at which the cleavage reaction could be carried out. This procedure gave a high yield of the desired 1-bromo-2-ethyl-1-(trimethylsilyl)-1-hexene, which was determined via the trisubstituted olefin to be a 97:3 mix-

(1) For the utility of 1-halo-1-(trimethylsilyl)-2-alkyl olefins in the synthesis of trisubstituted olefins, see: Miller, R. B.; McGarvey, G. J. Org. Chem. 1979, 44, 4623.


(8) It is important to protonate the vinyllithium intermediate at ~78 °C to ensure that isomerization does not take place, see: Zweifel, G.; Murray, R. E.; On, H. F. J. Organomet. Chem. 1981, 24, 35.
ture of E-Z isomers (see Table I). The corresponding 1-chloro and 1-iodo compounds were prepared in a similar manner by using N-chlorosuccinimide and N-iodosuccinimide, respectively.

Thus we have demonstrated that 1-halo-1-(trimethylsilyl)-2,2-dialkyl olefins can be prepared in good yield with high stereoselectivity by carbometalation of alkylnylsilanes with dialkylaluminum chlorides—titanocene dichloride followed by carbon—metal bond cleavage with N-halo-succinimides.

Experimental Section

Boiling points were recorded at gauge pressure and are reported uncorrected. Infrared spectra were obtained on a Beckman IR-8 spectrometer with only selected absorptions being reported. Nuclear magnetic resonance (1H) spectra were obtained on a Varian EM 390 instrument; chemical shifts are reported as δ values downfield relative to the trimethyl absorption of the silicon-containing compound. High-resolution mass spectra were determined by Mr. Kei Miyano on a Varian M-60 mass spectrometer. Analytical GLC was performed on a F & M research chromatograph Model S10 with either a 50-60 SE-30 or 50-60 SE-54 glass capillary column.

Diethylaluminum chloride (Texas Alkyls) was used as a neat liquid and assumed to be 7.6 M. Titanocene dichloride (Alfa Products), the N-halosuccinimides, and dichloromethane (Mal- linckrodt) were used as received. All reactions were stirred magnetically and carried out under an atmosphere of nitrogen in oven-dried (150 °C) glassware.

General Procedure for Preparation of 1-Halo-1-(trimethylsilyl)-2,2-dialkyl Olefins (Table I). In a three-necked, round-bottomed flask that was fitted with two addition funnels, a low-temperature thermometer, a nitrogen adapter, and a magnetic stirring bar was suspended titanocene dichloride (1.1 equiv) in dichloromethane (2 mL/mmol) at room temperature. Addition of diethylaluminum chloride (1.1 equiv) gave a dark-green solution to which was added the alkynylsilane (1 equiv). The resulting red-dark solution was stirred at room temperature for 6 h and then cooled to −78 °C and diluted with dichloromethane (2 mL/mmol of RC=C(SiMe3)) with a dry N-halosuccinimide (2 equiv) was added at a rate so that the temperature remained below −78 °C (2 h for ~60 mmol of RC=C(SiMe3)) and the mixture was stirred at an additional 0.5 h at −78 °C. The resultant red-orange suspension was poured into hexane and washed with an ice cold sodium sulfite–3 N sodium hydroxide mixture. The solids were removed by filtration, and the filtrate was washed with sodium sulfite solution, 3 N hydrochloric acid, and saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. After removal of the solvent the crude product could be purified either by distillation at reduced pressure in the presence of solid potassium carbonate or by chromatography on silica gel.

(a) (E)-1-Bromo-2-ethyl-1-(trimethylsilyl)-1-hexene (4; R = n-Bu, X = Br). Following the general procedure, 1-(trimethylsilyl)-1-hexene (9.5 g, 61.7 mmol) was reacted with N-bromosuccinimide to give 14.6 g (90% distilled yield) of the desired product as a colorless liquid: bp 54–56 °C (0.2 torr); IR (neat) 2960 (s), 2890 (m), 1591 (m), 1455 (s), 1250 (s), 840 (s), 670 (m) cm⁻¹; NMR (CDCl3) δ 0.00 (s, 9 H, (CH3)2Si), 0.70 (m, 6 H, 2 CH2), 1.12 (m, 4 H, CH2), 2.10 (m, 4 H, 2 —CH2=C—); high-resolution mass spectrum,² calc m/e for C11H23°BrSi 262.0753, found 262.0762.

(b) (E)-1-Chloro-2-ethyl-1-(trimethylsilyl)-1-hexene (4; R = n-Bu, X = Cl). Following the general procedure, 1-(trimethylsilyl)-1-hexene (9.924 g, 6.0 mmol) was reacted with N-chlorosuccinimide to give 1.114 g (85% chromatographed yield, eluted from 30 g of silica gel with 100% hexane) of the desired product as a colorless liquid: IR (neat) 2960 (s), 2890 (m), 1595 (m), 1455 (s), 1250 (s), 840 (s) cm⁻¹; NMR (CDCl3) δ 0.00 (s, 9 H, (CH3)2Si), 0.70 (m, 6 H, 2 CH2), 1.12 (m, 4 H, CH2), 2.00 (m, 4 H, 2 —CH2=C—); high-resolution mass spectrum,² calc m/e for C11H23°ClSi 218.1259, found 218.1252.

(c) (E)-2-Ethyl-1-iodo-1-(trimethylsilyl)-1-hexene (4; R = n-Bu, X = I). Following the general procedure, 1-(trimethylsilyl)-1-hexene (0.924 g, 6.0 mmol) was reacted with N-iodosuccinimide to give 1.60 g (86% chromatographed yield, eluted from 30 g of silica gel with 100% hexane) of the desired product as a colorless liquid: IR (neat) 2960 (s), 2890 (m), 1585 (m), 1455 (s), 1250 (s), 840 (s) cm⁻¹; NMR (CDCl3) δ 0.00 (s, 9 H, (CH3)2Si), 0.70 (m, 6 H, 2 CH2), 1.12 (m, 4 H, CH2), 2.5 (m, 4 H, 2 —CH2=C—); high-resolution mass spectrum,² calc m/e for C11H23°I2Si 310.0615, found 310.0637.

(d) (E)-1-Bromo-2-cyclohexyl-1-(trimethylsilyl)-1-butene (4; R = cyclohexyl, X = Br). Following the general procedure, cyclohexyl(trimethylsilyl)lacetylene (7.0 g, 38.9 mmol) was reacted with N-bromosuccinimide to give 8.99 g (80% distilled yield) of the desired product as a colorless liquid: bp 91–92 °C (0.3 torr); IR (neat) 2950 (s), 2880 (m), 1585 (m), 1450 (m), 1250 (s), 885 (s), 845 (s), 760 (m) cm⁻¹; NMR (CDCl3) δ 0.00 (s, 9 H, (CH3)2Si), 0.78 (t, 3 H, J = 7.5 Hz, CH3), 0.81–1.65 (m, 10 H), 1.97 (q, 2 H, J = 7.5 Hz, —CH2=C—), 2.24 (br, 1 H, CH—C); high-resolution mass spectrum,² calc m/e for C15H29°BrSi 288.0910, found 288.0919.

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Registry No. 4 (R = n-Bu, X = Br), 88315-73-5; 4 (R = n-Bu, X = Cl), 88315-74-6; 4 (R = n-Bu, X = I), 88315-75-7; 4 (R = C6H13, X = Br), 88315-76-8; n-BuC≡C(SiMe3), 3844-94-8; C6H13C≡C(SiMe3), 66270-60-8.

(9) All samples on which high-resolution mass spectral data were obtained were shown to be one peak on a 50-m SE-30 glass capillary column.