dissolving in CCl_4 (5 mL) and heating at reflux for 1 h to produce **5** in quantitative yield from **3**.

Registry No. **1**, 88343-77-5; **2**, 88343-78-6; **5**, 88343-82-2; **6**, 88343-84-4; **8**, 88390-10-7; (*E*)-2-butenyl acetoacetate, 82259-92-5; 3,7-dimethylocta-1,6-dien-3-yl acetoacetate, 25456-03-5; (*E*)-1-phenyl-2-butenyl acetoacetate, 88343-79-7; 4,4-dimethylpent-1-en-3-ol, 88357-95-3; geranyl acetoacetate, 10032-00-5; (*E*)-1-(trimethylsilyl)-3-penten-2-ol, 80993-48-2; 3-methyl-1-(trimethylsilyl)-3-buten-2-ol, 80399-29-7; (*E*)-2-buten-1-ol, 504-61-0; 4,4-dimethyl-1-penten-3-ol, 24580-44-7; 3,8-dimethyl-1,7-nonadien-3-ol, 88343-80-0; (*E*)-2,8-dimethyl-2,7-nonadien-1-ol, 88343-81-1; diketene, 674-82-8; (E)-4-[(trimethylsilyl)methyl]-5-hepten-2-one, 88343-83-3; 5-methyl-4-[(trimethylsilyl)methyl]-5-hexen-2-one, 88343-85-5; 4-methyl-5-hexen-2-one, 61675-14-7; (*E*)-6,10-dimethyl-5,9-undecadien-2-one, 3796-70-1; (*Z*)-6,10-dimethyl-5,9-undecadien-2-one, 3879-26-3; (*E*)-4-methyl-6-phenyl-5-hexen-2-one, 88343-86-6; (*E*)-4-phenyl-5-hepten-2-one, 88343-87-7; (*E*)-7,7-dimethyl-5-octen-2-one, 61478-31-7; 4-(dimethylamino)pyridine, 1122-58-3; 4,8-dimethylnona-1,7-dien-3-yl acetoacetate, 88343-88-8; (*E*)-2,8-dimethylnona-2,7-dien-2-yl acetoacetate, 88343-89-9.

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

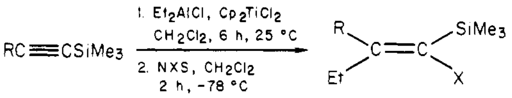
R. Bryan Miller* and Mohammed I. Al-Hassan

Department of Chemistry, University of California, Davis, California 95616

Received July 6, 1983

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.[1] Unfortunately, attempts to synthesize these (halovinyl)silanes in a highly stereoselective manner have proven to be difficult. In 1977, Seyferth et al.[2] reported the synthesis of $R_2C{=}CBrSiMe_3$ 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 vinyl metallic intermediate with halogens. In 1979, Snider and Karras[5] reported the most successful approach; they observed that carbotitanation of alkynylsilanes was highly stereoselective using dialkylaluminum chloride–titanocene 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 stereochemical 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).

Table I

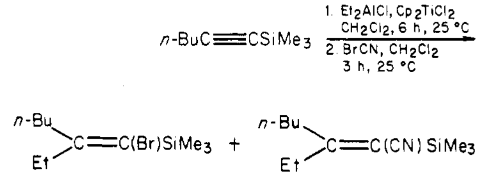


4

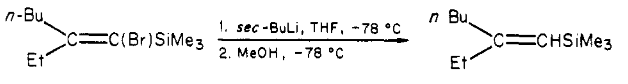
R	X	% yield of 4[a]	*E*:*Z*[b]
n-Bu	Br	90	97:3
n-Bu	Cl	85	
n-Bu	I	86	99:1
C_6H_{11}	Br	80	95:5

[a] Isolated yields. [b] Determined by capillary GLC on the corresponding trisubstituted olefin.

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.[1,6] Thus 1-(trimethylsilyl)-1-hexyne[7] was reacted at room temperature with a solution derived from diethylaluminum chloride and titanocene 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-heptenenitrile (**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 **3**.[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.



3:1 2



3

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.

(2) Seyferth, D.; Lefferts, J. L.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1977**, *142*, 39.

(3) Snider, B. B.; Karras, M.; Conn, R. S. E. *J. Am. Chem. Soc.* **1978**, *100*, 4624. Snider, B. B.; Conn, R. S. E.; Karras, M. *Tetrahedron Lett.* **1979**, 1679.

(4) Eisch, J. J.; Manfre, R. J.; Komar, D. A. *J. Organomet. Chem.* **1978**, *159*, C13.

(5) Snider, B. B.; Karras, M. *J. Organomet. Chem.* **1979**, *179*, C37.

(6) Zweifel, G.; Lewis, W. *J. Org. Chem.* **1978**, *43*, 2739.

(7) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1978**, *43*, 2739.

(8) It is important to protonate the vinyllithium intermediate at -78 °C to insure that isomerization does not take place, see: Zweifel, G.; Murray, R. E.; On, H. P. *J. Org. Chem.* **1981**, *46*, 1292.

0022-3263/84/1949-0725$01.50/0

J. Org. Chem. 1984, 49, 726-728

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 alkynylsilanes with dialkylaluminum chlorides–titanocene dichloride followed by carbon–metal bond cleavage with *N*-halosuccinimides.

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 (^{1}H) 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 810 with either a 50-m SE-30 or 50-m 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 (Mallinckrodt) 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 dark-red solution was stirred at room temperature for 6 h and then cooled to −78 °C and diluted with dichloromethane (2 mL/mmol of $RC{\equiv}CSiMe_3$). Dry *N*-halosuccinimide (2 equiv) was added at a rate so that the temperature remained below −78 °C (2 h for ~60 mmol of $RC{\equiv}CSiMe_3$) and the mixture was stirred 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 anhdrous sodium sulfate. After removal of the solvent the crude product could be purified either by distillation at reduced pressure in the presence of solid sodium 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-hexyne (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 (CCl$_4$) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.70 (m, 6 H, 2 CH$_3$), 1.12 (m, 4 H, CH$_2$), 2.10 (m, 4 H, 2 $-CH_2C{=}C$); high-resolution mass spectrum,[9] calcd *m*/*e* for $C_{11}H_{23}{}^{79}BrSi$ 262.0753, found 262.0782.

(b) (*E*)-1-Chloro-2-ethyl-1-(trimethylsilyl)-1-hexene (4; R = *n*-Bu, X = Cl). Following the general procedure, 1-(trimethylsilyl)-1-hexyne (0.924 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 (CCl$_4$) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.70 (m, 6 H, 2 CH$_3$), 1.12 (m, 4 H, CH$_2$), 2.00 (m, 4 H, 2 $-CH_2C{=}C$); high-resolution mass spectrum,[9] calcd *m*/*e* for $C_{11}H_{23}{}^{35}ClSi$ 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-hexyne (0.924 g, 6 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 (CCl$_4$) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.70 (m, 6 H, 2 CH$_3$), 1.12 (m, 4 H, CH$_2$), 2.5 (m, 4 H, 2 $-CH_2C{=}C$); high-resolution mass spectrum,[9] calcd *m*/*e* for $C_{11}H_{23}ISi$ 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)acetylene[7] (7.00 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 (CCl$_4$) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.78 (t, 3 H, J = 7.5 Hz, CH$_3$), 0.81–1.65 (m, 10 H), 1.97 (q, 2 H, J = 7.5 Hz, $-CH_2C{=}C$), 2.24 (br, 1 H, $CHC{=}C$); high-resolution mass spectrum,[9] calcd *m*/*e* for $C_{13}H_{25}{}^{79}BrSi$ 288.0910, found 288.0919.

Acknowledgment. We thank the Committee on Research, University of California, Davis, for partial support of this work.

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 = C_6H_{11}, X = Br), 88315-76-8; *n*-$BuC{\equiv}CSiMe_3$, 3844-94-8; $C_6H_{11}C{\equiv}CSiMe_3$, 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.

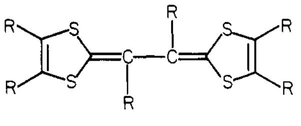
Novel Oxidative Rearrangement of *o*-Xylene-α,α'-diylidenebis(4,5-dicarbomethoxy-1,3-dithiole)

M. V. Lakshmikantham,* Michael P. Cava, and
Patrick J. Carroll

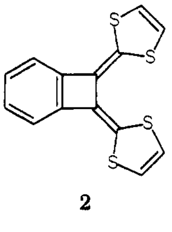
*Chemistry Department, University of Pennsylvania,
Philadelphia, Pennsylvania 19104*

Received August 8, 1983

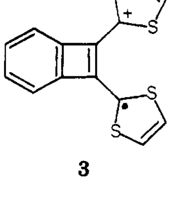
The synthesis and properties of tetrathiafulvalenes have been the subject of much study during the past decade due to the ability of many of these compounds to undergo one-electron oxidation to stable cation radicals which can form the cationic portion of crystalline salts of considerable electrical conductivity.[1,2]



1



2



3

---

[1] Narita, M., Pittman, C. U., Jr. *Synthesis*, **1976**, 489.
[2] Engler, E. M. CHEMTECH **1976**, 274.

0022-3263/84/1949-0726$01.50/0