Preparation of 2-chlorobuta-1,3-dienes by dichlorocyclopropanation of allylsilanes followed by desilylation

Michiharu Mitani,* Yosinori Kobayashi and Kikuhiko Koyama
Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380, Japan

Allylsilanes react with dichlorocarbene to form dichlorocyclopropanes which, in turn, afford 2-chlorobuta-1,3-dienes when treated with cesium fluoride in DMF under reflux. The *Z* stereochemistry of the products differs from that of the starting allylsilanes. Lengthy reaction times were necessary to induce desilylation because of the lack of steric congestion in the intermediate silylmethyl-substituted cyclopropanes. 5-Methyl-7-trimethylsilylhepta-1,5-diene was cyclopropanated regioselectively at the inner ene function in spite of unfavourable steric congestion, possibly as a result of the electron-donating effect of the allylic silyl group induced by the σ-π conjugation.

Allylsilanes when subjected to Lewis acid-induced regio-controlled electrophilic attack by carbonyl compounds, conjugated enones, acyl halides, acetals, epoxides and alkyl halides, undergo a shift of the double bond together with loss of the silyl group.[1] Similar reactions of allylsilanes with carbenes, however, have been little explored although they are known to occur with silyl enol ethers,[2] ketene silyl acetals,[3] vinylsilanes[4] and silylbutadienes.[5] In our work, we found that allylsilanes reacted with dichlorocarbene to afford dichlorocyclopropanes which, in turn, formed 2-chlorobuta-1,3-dienes through desilylative ring-opening. Although conjugated diene systems have usually been prepared by the induction of 1,2- or 1,4-elimination in allylic derivatives,[6] such procedures often suffer from poor regioselectivity. Because of this, new methods including palladium-catalysed cross-coupling of vinyl metal compounds with vinyl halides[7] have been recently developed to improve the regioselectivity. Our reaction regioselectively provides 2-chloro-1,3-dienes, and thus complements previous methods for the preparation of conjugated dienes.

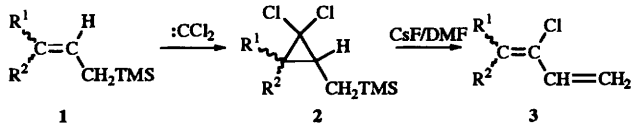
Results and discussion

The reaction of 1-trimethylnon-2-ene **1a** with dichlorocarbene, generated from CCl_4, $TiCl_4$ and $LiAlH_4$,[8] afforded a quantitative yield of the dichlorocyclopropanation product **2a**. Treatment of this with tetrabutylammonium fluoride in THF in an attempt to effect desilylation[9] failed, both at room temperature and under reflux. Treatment of **2a** with cesium fluoride in DMF at an elevated temperature, however, did result in desilylation, and formation of 3-chlorodeca-1,3-diene **3a** (58% at 120 °C, 72% under reflux). Potassium *tert*-butoxide in DMF also effected a similar desilylation although the yield of **3a** was slightly less (52% at 120 °C). GLC analysis showed that the product was a single stereoisomer, the stereochemistry of which may be assigned as *Z*, on the basis of a comparison of the observed chemical shift for 4-H (δ 5.66 ppm) with the calculated chemical shift (δ = 5.65 and 5.70 ppm for *Z* and *E* isomers, respectively).[10] Wittig reaction of β-silylethylidene-phosphorane with heptanal,[11] gave **1a** as a stereoisomeric mixture (*E*/*Z* = 6.1) similar to that from previous work.[12] Thus, the stereochemistry of **3a** differs from that of the starting substrate and the reason for this is unclear at present.

A variety of allylsilanes was subjected to dichlorocyclopropanation followed by desilylation with cesium fluoride in DMF under reflux, the optimum conditions for the formation of **3a**, and the results for these reactions are shown in Table 1.

The 3-chloro-4-methylbuta-1,3-dienes **3b–d** from 3-methyl-1-trimethylsilylalk-2-enes **1b–d**, obtained as stereoisomeric mixtures (GC–MS), were shown to contain more of the *Z* isomers by integration of ^1H NMR 4-Me signals (Table 1). Those at the upper and lower fields may be assigned as the *Z*- and *E*-forms, respectively, by inference from the calculated

Table 1 Preparation of 3-chloro-1,3-dienes from allylsilanes



1 2 3

1	R^1	R^2	*E*/*Z*	Cyclopropanation method[a]	Desilylation time (min)	3 Yield (%)[b]	3 *Z*/*E*
a	$CH_3(CH_2)_5$	H	6.1/1	A	180	72	1/0
b	$CH_3(CH_2)_5$	CH_3	0.9/1	B	20	65	1.3/1
c	$(CH_3)_2CH(CH_2)_2$	CH_3	1/1	B	20	74	1.5/1
d	$CH_2{=}CH(CH_2)_2$	CH_3	0.9/1	B	20	33	1.9/1
e	Ph	H	6.5/1	B	20	33	1/0
f	$-(CH_2)_5-$			A	20	61	
g	H	H		B	900	*c*	

[a] A; $TiCl_4$, $LiAlH_4$, CCl_4, B; CCl_3CO_2Et, NaOMe. See also Experimental section. [b] Based on compound **1**. [c] The formation of **3g** was ascertained by GC–MS, although the compound was not isolable owing to its high volatility.

chemical shift of 4-H of **3a**. As with **3a**, the stereochemistry of **3b–d** differs from that of the starting allylsilanes **1b–d**. The reaction of a mixture of *cis*- and *trans*-1-phenyl-3-trimethylsilylprop-1-ene **1e** afforded 2-chloro-1-phenylbuta-1,3-diene **3e** as a single stereoisomer, the configuration of which is believed to be *Z* on the basis of the stereoselective formation of (*Z*)-**3a** from a stereoisomeric mixture of **1a**.

The times required for the desilylation of compounds **2** deserve comment. Thus, while desilylation of **2a** required 3 h, the cyclopropanes **2b–f** from the branched or phenylated allylsilanes **1b–f** were completely desilylated after only 20 min. In contrast, 15 h was needed for the desilylation of the cyclopropane derivative **2g** from the parent allylsilane **1g** to afford 2-chlorobuta-1,3-diene as the sole volatile product, which, although not isolated owing to its high volatility, was identified by GC–MS. Desilylation is more readily effected since the cyclopropane derivative is more sterically crowded. This result, which is apparently in contradiction to the steric ease of the attack of a fluoride ion on the silyl group, may be explained in terms of strain release by the desilylative ring-opening.

Finally, it is noteworthy that **1d**, which contains two different types of ene function, underwent regioselective dichlorocyclopropanation at the inner ene function in spite of unfavourable steric congestion; this is possibly a result of the electron-donating effect of the allylic silyl group by σ-π conjugation.[13]

Experimental

IR spectra were recorded on a Horiba FT-210 spectrometer. ^{1}H (60 MHz) and ^{13}C (15 MHz) NMR spectra were recorded with a JEOL FX60 spectrometer for $CDCl_3/CCl_4$ solutions; the chemical shifts (δ) are expressed in ppm relative to tetramethylsilane as internal standard and the coupling constants (J) are given in Hz. Mass spectra were obtained at 70 eV using a Hitachi M-80B instrument. Column chromatography was performed on silica gel with a Yamazen MPLC instrument.

DMF was distilled from CaH_2. CsF supplied by Nacarai Tesque was used without further purification. Allylsilanes **1a–d**, **f** were prepared by the Wittig reaction of 2-silylethylidenephosphorane with heptanal or the corresponding ketones according to the method by Fleming and Paterson,[11] and **1e** was obtained by the magnesium-promoted reaction of cinnamyl chloride with chlorotrimethylsilane following the method of Slutsky and Kwart.[14]

Dichlorocyclopropanation of the allylsilanes 1a–f

Method A. Under a nitrogen atmosphere, $TiCl_4$ (2.85 g, 15 mmol) was added with stirring to THF (20 cm^3) at a rate that allowed the temperature to remain < 5 °C. A solution of $LiAlH_4$ (0.57 g, 15 mmol) in THF (13 cm^3) was then added to the reaction mixture at a rate that allowed the temperature to remain < 15 °C, after which the dark-brown mixture was allowed to warm to 19 °C over a period of 40 min. The flask was cooled again in a salt–ice bath. When the temperature had fallen to 0 °C, compound **1** (5 mmol) and then CCl_4 (2.15 g, 15 mmol) in THF (8 cm^3) were added in this order at a rate that allowed the temperature to remain at 0 °C. After being stirred at 0 °C for 30 min, the reaction mixture was poured into cold 6.7% hydrochloric acid in water (100 cm^3). The upper organic layer was separated from the aqueous layer and the latter was extracted with dichloromethane. The combined organic layers were washed with 10% aqueous sodium carbonate, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was subjected to treatment with cesium fluoride (*vide infra*).

Method B. Ethyl trichloroacetate (3.20 g, 16.7 mmol) was added in one portion to a stirred mixture of compound **1** (5 mmol) and sodium methoxide (0.82 g, 15.2 mmol) in pentane (15 cm^3) at 0 °C, and stirring was continued at this temperature for 6 h. After being stirred at room temperature for 15 h, the mixture was filtered and the precipitate was washed with pentane. The combined filtrate and washings were evaporated under reduced pressure and the residue was treated with cesium fluoride (*vide infra*).

Preparation of 2-chloro-1,3-dienes 3

A DMF (15 cm^3) solution of CsF (1.5 g, 10 mmol) was added to the reaction residue containing **2** from either Method A or B, and the resulting mixture was refluxed and stirred. After compound **2** had been consumed (GLC), the reaction mixture was poured into water (100 cm^3) and extracted with ether. The extract was dried, concentrated under reduced pressure, and then purified by column chromatography.

3-Chlorodeca-1,3-diene 3a. The title compound (0.619 g, 72%) was isolated as a colourless oil using benzene as eluent; ν/cm^{-1} 3103, 3010, 1639 and 1606; δ_H 6.29 (1 H, dd, *J* 17.1, 10.2, 2-H), 5.66 (1 H, t, *J* 7.7, 4-H), 5.42 (1 H, d, *J* 17.1, 1-H), 5.02 (1 H, d, *J* 10.2, 1-H), 2.57–2.20 (2 H, m, 5-H), 1.71–1.17 (8 H, m, 6–9-H) and 0.94 (3 H, t, *J* 6.0, 10-H); δ_C 134.3, 131.0, 115.0, 31.5, 28.8, 28.7, 28.4, 22.4 and 13.9; *m*/*z* 174 [M (^{37}Cl)$^+$, 31%], 172 (M$^+$, 95), 137 (30), 88 (94) and 55 (100) (Found: M$^+$, 172.1025. $C_{10}H_{17}Cl$ requires *M*, 172.1018).

3-Chloro-4-methyldeca-1,3-diene 3b. The title compound (0.605 g, 65%) was isolated as a colourless oil using benzene as eluent; ν/cm^{-1} 3099, 3030, 1628 and 1610; δ_H 6.64 (1 H, dd, *J* 17.1, 10.2, 2-H), 5.46 (1 H, d, *J* 17.1, 1-H), 5.03 (1 H, d, *J* 10.2, 1-H), 2.36 (2 H, t, *J* 6.0, C-5), 2.03 (3 × 7/16 H, s, 4-Me), 1.97 (3 × 9/16 H, s, 4-Me), 1.74–1.17 (8 H, m, 6–9-H) and 0.93 (3 H, t, *J* 6.0, 10-H); δ_C 130.1, 129.6, 115.6, 115.4, 36.6, 36.4, 31.5, 28.9, 28.3, 27.0, 22.3, 22.5 and 14.0; *m*/*z* 188 [M (^{37}Cl)$^+$, 33%], 186 (M$^+$, 95), 151 (19) and 102 (100) (Found M$^+$, 186.1166. $C_{11}H_{19}Cl$ requires *M*, 186.1173).

3-Chloro-4,7-dimethylocta-1,3-diene 3c. The title compound (0.636 g, 74%) was isolated as a colourless oil using light petroleum; ν/cm^{-1} 3103, 3025, 1633 and 1605; δ_H 6.64 (1 H, dd, *J* 17.1, 10.2, 2-H), 5.45 (1 H, d, *J* 17.1, 1-H), 5.02 (1 H, d, *J* 10.2, 1-H), 2.33 (2 H, t, *J* 6.0, 5-H), 2.03 (3 × 2/5 H, s, 4-H), 1.97 (3 × 3/5 H, s, 4-H), 1.80–1.24 (3 H, m, 6-H, 7-H) and 0.97 (6 H, d, *J* 6.0, 7-Me, 8-H); δ_C 130.1, 129.5, 115.5, 115.4, 37.3, 36.0, 34.4, 32.2, 28.0, 27.9 and 22.4; *m*/*z* 174 [M (^{37}Cl)$^+$, 34%], 172 (M$^+$, 95), 137 (44), 116 (100) and 102 (64) (Found: M$^+$, 172.1027. $C_{10}H_{17}Cl$ requires *M*, 172.1018).

3-Chloro-4-methylocta-1,3,7-triene 3d. The title compound (0.257 g, 33%) was isolated as a colourless oil using light petroleum; ν/cm^{-1} 3101, 3078, 3026, 1637 and 1595; δ_H 6.65 (1 H, dd, *J* 17.1, 10.2, 2-H), 6.09–5.38 (1 H, m, 7-H), 5.49 (1 H, d, *J* 17.1, 1-H), 5.35–4.80 (3 H, m, 1-H, 8-H), 2.57–2.17 (4 H, m, 5-H, 6-H), 2.06 (3 × 3.5/10 H, s, 4-Me) and 2.00 (3 × 6.5/10 H, s, 4-Me); δ_C 137.3, 136.8, 130.0, 129.5, 115.9, 115.7, 115.2, 114.8, 35.8, 33.7, 32.3, 31.1 and 21.0; *m*/*z* 158 [M (^{37}Cl)$^+$, 25%], 156 (M$^+$, 65), 121 (72), 115 (90) and 79 (100) (Found: M$^+$, 156.0705. $C_9H_{13}Cl$ requires *M*, 156.0705).

2-Chloro-1-phenylbuta-1,3-diene 3e. The title compound (0.271 g, 33%) was isolated as a colourless oil using benzene as eluent; ν/cm^{-1} 3101, 3080, 3059, 3028, 1620, 1585 and 1493; δ_H 7.26 (5 H, s, Ph), 6.81 (1 H, s, 1-H), 6.75 (1 H, dd, *J* 17.1, 10.2, 3-H), 5.70 (1 H, d, *J* 17.1, 4-H) and 5.26 (1 H, d, *J* 10.2, 4-H); δ_C 130.1, 130.0, 128.8, 128.1, 127.4 and 119.6; *m*/*z* 166 [M (^{37}Cl)$^+$, 15%], 164 (M$^+$, 45), 129 (100) and 77 (55) (Found: M$^+$, 164.0389. $C_{10}H_9Cl$ requires *M*, 164.0392).

(1-Chloroprop-2-enylidene)cyclohexane 3f. The title compound (0.476 g, 61%) was isolated as a colourless oil using light petroleum; ν/cm^{-1} 3101, 3028, 1626 and 1593; δ_H 6.74 (1 H, dd, *J* 17.1, 10.2, 2-H), 5.51 (1 H, d, *J* 17.1, 3-H), 5.02 (1 H, d, *J* 10.2, 3-H), 2.75–2.40 (4 H, m, CH_2C=C) and 1.90–1.58 [6 H, m, $(CH_2)_3$]; δ_C 129.3, 116.1, 32.5, 30.8, 27.6, 27.1 and 26.4; *m*/*z*

158 [M (^{37}Cl)$^+$, 32%], 156 (M^+, 100) and 121 (75) (Found: M^+, 156.0689. $C_9H_{13}Cl$ requires *M*, 156.0705).

References

1 I. Fleming, J. Dunoguès and R. Smithers, *Org. React. (N.Y.)*, 1989, **37**, 57.
2 (*a*) M. Mitani and Y. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 284; (*b*) P. Amice, L. Blanco and J. M. Conia, *Synthesis*, 1976, 196.
3 (*a*) G. Rousseau and N. Slougui, *J. Am. Chem. Soc.*, 1984, **106**, 7283; (*b*) N. Slougui, G. Rousseau and J. M. Conia, *Synthesis*, 1982, 58.
4 M. G. Banwell, M. Corbett, J. Gulbis, M. F. Mackay and M. E. Reum, *J. Chem. Soc., Perkin Trans. 1*, 1993, 945.
5 W.-W. Weng and T.-Y. Luh, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2687.
6 H. von Brachtel and U. Bahr, in Houben-Weil, *Methoden der Organische Chemie*, ed. E. Muller, George Thieme Verlag, Stuttgart, 1970; Band 5/1C, p. 1.
7 E. Negishi, *Acc. Chem. Res.*, 1982, **15**, 340.
8 W. R. Dolbier and C. R. Burkholder, *J. Org. Chem.*, 1990, **55**, 589.
9 For example see: (*a*) A. Hosomi, A. Shirahata and H. Sakurai, *Tetrahedron Lett.*, 1978, 3043; (*b*) D. T. W. Chu, J. E. Hengeveld and L. David, *Tetrahedron Lett.*, 1983, **24**, 139.
10 C. Pascual, J. Meier and W. Simon, *Helv. Chim. Acta*, 1966, **49**, 164.
11 I. Fleming and I. Paterson, *Synthesis*, 1979, 446.
12 D. Seyferth, K. R. Wursthorn and R. E. Mammarella, *J. Org. Chem.*, 1977, **42**, 1977.
13 S. G. Wierschke, J. Chandrasekhar and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1985, **107**, 1496.
14 J. Slutsky and H. Kwart, *J. Am. Chem. Soc.*, 1973, **95**, 8678.

Paper 4/06351A
Received 18*th October* 1994
Accepted 6*th December* 1994