Preparation of (*Z*)-1,2-dichloroalkenes from terminal alkynes

Ningzhang Zhou, Qiang Wang, Alan J. Lough, and Hongbin Yan

Abstract: (*Z*)-1,2-Dihaloalkenes are thermodynamically disfavoured of the two stereoisomers. This paper reports the synthesis of some (*Z*)-1,2-dichloroalkene analogues from mucochloric acid. A more versatile approach involved the chloroboration of terminal alkynes to yield corresponding (*Z*)-chloroboronic acid as a first step. Treatment of the organoboronic acid with potassium hydrogen difluoride followed by tetrabutylammonium trichloride gave (*Z*)-1,2-dichloroalkenes in moderate to good yields in a stereospecific manner.

Key words: cis-dichloroalkene, chloroboration, chlorodeboronation, NOE, terminal alkyne.

Résumé : Dans les séries de 1,2-dihalogénoalcènes, les isomères (*Z*)- sont thermodynamiquement défavorisés. Dans ce travail, on a réalisé la synthèse de quelques analogues de (*Z*)-1,2-dichloroalcènes à partir de l'acide mucochlorique. Une approche encore plus versatile implique une première étape de chloroboration d'alcynes terminaux qui conduit à l'acide (*Z*)-chloroboronique correspondant. Le traitement de l'acide organoboronique avec du difluorure de potassium et d'hydrogène, suivi d'une réaction avec du trichlorure de tétrabutylammonium fournit les (*Z*)-1,2-dichloroalcènes d'une manière stéréospécifique, avec des rendements allant de modérés à bons.

Mots-clés : cis-dichloroalcène, chloroboration, chlorodéboronation, effet Overhauser nucléaire (EN), alcyne terminal.

[Traduit par la Rédaction]

Introduction

1,2-Dihaloalkenes are useful precursors in organic synthesis, particularly in the carbon–carbon bond-forming reactions.[1] Of the two stereoisomers, (Z)-isomers have found applications in reactions such as the Bergman cyclization.[2] In this respect, challenges remain in the preparation of 1,2-(*Z*)-dihaloalkenes as the (E)-isomers are thermodynamically favoured and are formed predominantly in direct electrophilic halogenation of alkynes.[3–5] A few methods have been reported for the stereoselective synthesis of 1,2-dihaloalkenes,[6–9] including a recent report on the synthesis of (*Z*)-dibromoalkenes by a bromodeboronation sequence of potassium bromoalkenyl – trifluoroborates;[10] however, as far as we are concerned, the only known reliable stereospecific approach to (*Z*)-1,2-dichloroalkene derivatives is the use of mucochloric acid (**1**) as the starting material.[11] We now report a chlorodeboronation methodology that is applicable to the synthesis of (*Z*)-1,2-dichloroalkenes.

Results and discussion

Synthesis of (*Z*)-1,2-dichloroalkenes from mucochloric acid

As mentioned previously, the only known stereospecific method for the preparation of (*Z*)-1,2-dichloroalkenes utilized mucochloric acid (**1**) as starting material. Upon treatment with sodium hydroxide, 2,3-(*Z*)-dichloropropenoic acid (**2**) was obtained. This latter compound can be transformed into corresponding alcohol **3**, allyl chloride **4**, anhydride **5**, or ester **6** (Scheme 1). However, this process is rather limited in scope, requiring complex transformations to access higher carbon derivatives.

Stereoselectivity of bromodeboronation reaction from potassium bromoalkenyl – trifluoroborates

It was recently shown[10] that (*Z*)-1,2-dibromoalkenes can be prepared in a stereospecific manner from a sequence of transformations using terminal alkynes as starting materials. This approach (Scheme 2) begins with the addition of boron tribromide across the triple bond to give (*Z*)-bromovinylboron dibromide (**8**).[12] Upon hydrolysis, bromovinylboronic acid (**9**) was obtained, which was subsequently transformed into corresponding potassium trifluoroborate (**10**) by treatment with potassium hydrogen difluoride.[10,12] Final bromodeboronation with tetrabutylammonium tribromide gave (*Z*)-1,2-dibromoalkenes (**11**) with retention of stereochemistry.[10]

With a model compound ((*Z*)-3,4-dibromobutenyl *p*-tosylate, **12**), we were able to confirm the stereochemistry with crystal

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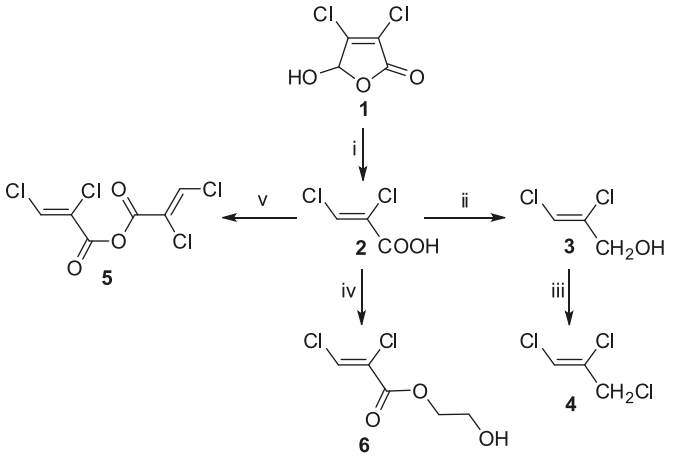
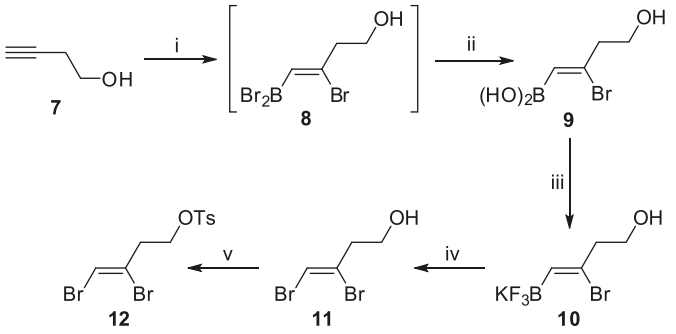
Scheme 1. Reagents and conditions: (*i*) aq NaOH and then aq HCl; (*ii*) $LiAlH_4$, Et_2O; (*iii*) $SOCl_2$, C_5H_5N, CH_2Cl_2; (*iv*) $HOCH_2CH_2OH$, DCC; (*v*) DCC, Et_2O.



Scheme 2. Reagents and conditions: (*i*) BBr_3, CH_2Cl_2; (*ii*) aq $NaHCO_3$; (*iii*) KHF_2, CH_3OH, H_2O; (*iv*) $Bu_4N^+Br_3^-$, aq THF; (*v*) TsCl, C_5H_5N.



structure (Fig. 1), where the two bromines are clearly in a Z-configuration.

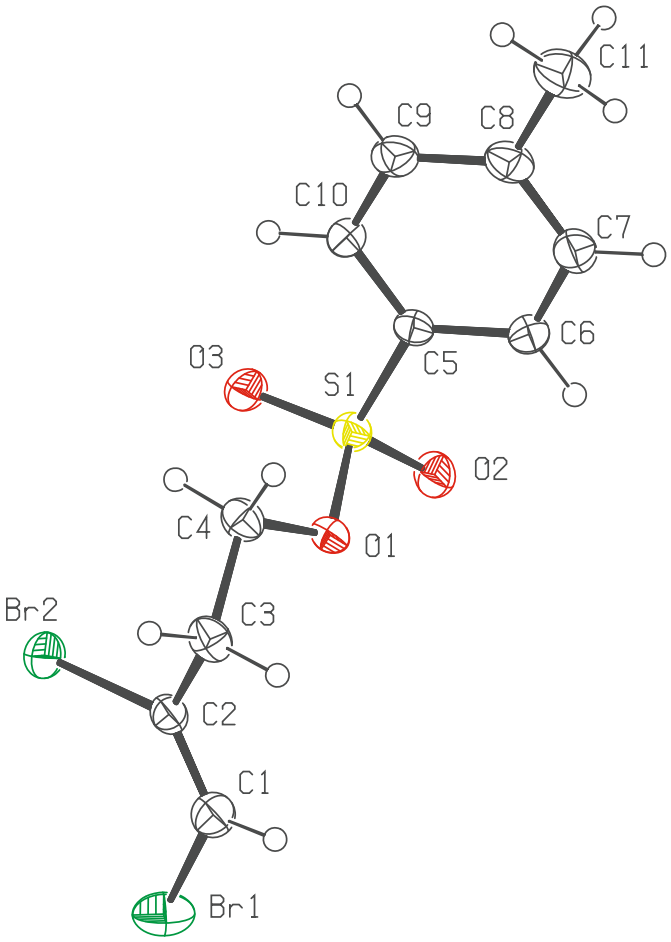
The chemistry described in this section extends its scope to both aliphatic and aromatic alkynes and therefore represents a versatile approach for the access of (*Z*)-1,2-dibromoalkenes.

Preparation of (*Z*)-1,2-dichloroalkenes from terminal alkynes

In our search for suitable 1,2-dihaloalkenes as Sonogashira reaction precursors, a versatile approach for the synthesis of (*Z*)-1,2-dichloroalkenes was required. It occurred to us that it is highly likely that a strategy similar to the bromodeboronation sequence described previously would provide access to the desired (*Z*)-1,2-dichloroalkenes. Indeed, it was reported previously that treatment of phenylacetylene with boron trichloride gave corresponding (2-chloro-2-phenylvinyl)dichloroborane.[14] To our satisfaction, this approach gave (*Z*)-1,2-dichloroalkenes from terminal alkynes in moderate to good yields and in a stereospecific manner (Scheme 3).

The transformations began with the treatment of terminal alkynes with boron trichloride, followed by hydrolysis to give corresponding chlorovinylboronic acid (**15**). Upon formation of the corresponding potassium trifluoroborate (**16**), chlorodeboronation was effected using tetrabutylammonium

Fig. 1. The molecular structure of (*Z*)-3,4-dibromobutenyl *p*-tosylate (**12**) with 30% probability displacement ellipsoids (prepared with PLATON).[13]



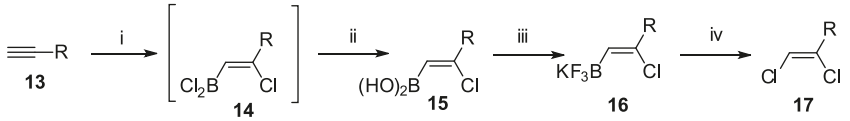
trichloride. This latter reagent is not commercially available, however, it can be readily prepared as a stable solid by bubbling chlorine gas into a solution of tetrabutylammonium chloride in dichloromethane.[15,16] The results for chlorodeboronation of some substrates are shown in Table 1. It is noted that some of the lower yields shown in Table 1 were most likely due to the relatively low boiling points of the products.

To illustrate the stereochemistry of the transformations, 3,4-(*E*)-dichlorobutenol (**18**) was prepared using a literature procedure.[3] Thus, treatment of 3-alkynol with copper(II) chloride and lithium chloride (Scheme 4) gave **18** almost as the sole product.

The two stereoisomers **17a** and **18** displayed different ^1H NMR chemical shifts (Fig. 2*a*), and in NOE experiments, the clear NOE signal present in **17a**, which is absent in **18**, clearly confirmed the (Z)-configuration.

The utility of this method can be extended to the preparation of 1,2-(*Z*)-bromochloro (or chlorobromo) alkenes from 1,2-terminal alkynes. As exemplified in Scheme 5, treatment of 4-bromo-1-butyne (**19**) with either BCl_3 or BBr_3 followed by hydrolysis gives the corresponding (*Z*)-2-chloro-4-bromo-1-butenylboronic acid (**15e**) or (*Z*)-2-bromo-4-bromo-1-butenylboronic acid (**20**). Transformation of these two organoboronic acids into the corresponding potassium trifluoroborates

Scheme 3. Reagents and conditions: (*i*) BCl_3, CH_2Cl_2; (*ii*) H_2O; (*iii*) KHF_2, CH_3OH, H_2O; (*iv*) $Bu_4N^+Cl_3^-$, aq THF.

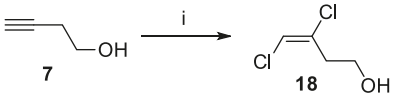


a) R = -CH_2CH_2OH; **b)** R = -Ph; **c)** R = -CH_2OH;
d) R = -$(CH_2)_5CH_3$; **e)** R = -CH_2CH_2Br

Table 1. Chlorodeboronation **16** → **17**.

Entry (product)	R	Yield (%)
1 (**17a**)	–CH_2CH_2OH	51
2 (**17b**)	–Ph	84
3 (**17c**)	–CH_2OH	45
4 (**17d**)	–$(CH_2)_5CH_3$	77
5 (**17e**)	–CH_2CH_2Br	62

Scheme 4. Reagents and conditions: (*i*) $CuCl_2$, LiCl, CH_3CN.



16e and **21**, respectively, was readily effected by treatment with potassium hydrogen difluoride. Subsequent bromo- (or chloro-) deboronation gave 1,2-(*Z*)-bromochloro (or chlorobromo) alkenes **23** and **22**, respectively. It is anticipated that these 1,2-(*Z*)-dihaloalkenes could find synthetic utilities in sequential coupling reactions because of the different reactivity between vinyl chlorides and bromides. This aspect of the application is being explored in our laboratory to access the enediyne moieties with different substituents on 1,2-alkenes.

Conclusion

In conclusion, tetrabutylammonium trichloride-based chlorodeboronation of potassium bromoalkenyl trifluoroborates represents an efficient approach to the synthesis of (*Z*)-1,2-dichloroalkenes from terminal alkynes. This method provides access to these thermodynamically less stable alkenes as important synthetic intermediates.

Experimental details

^{1}H NMR spectra were measured at 300 and 600 MHz with Bruker AV300 and AV600 spectrometers, respectively; tetramethylsilane was used as an internal standard; *J* values are given in Hz. ^{13}C NMR spectra were measured at 75.5 or 150.9 MHz with the same spectrometers. Chemical shifts are given in ppm. Low- and high-resolution mass spectra were obtained with a Kratos Concept 1S high-resolution mass spectrometer using electron impact or fast atom bombardment sources interfaced with a DART 32 bit acquisition system through a Sun Sparcstation 10 and Mach 3 software. Desican 230–400 mesh silica gel 60 was used for flash column chromatography. Chemicals were purchased from Sigma-Aldrich or TCI America and used without further purification unless stated otherwise. Dichloromethane, diethyl ether, and tetrahydrofuran were purified by a Pure-Solv solvent purification system (Innovative Technology), and stored over activated 4 Å molecular sieves.

Experimental procedures for the synthesis of **17a** and corresponding intermediates are described in the following. Synthetic procedures for **17b–17d** and corresponding intermediates can be found in the Supplementary data.

(*Z*)-2-Chloro-4-hydroxy-1-butenylboronic acid (15a)

To a solution of boron trichloride in dichloromethane (1 mol/L, 8.0 mL, 8.0 mmol) was added dropwise a solution of 3-butyn-1-ol (0.48 g, 6.85 mmol) in dry dichloromethane (10 mL) at 0 °C under nitrogen. After the reaction mixture was stirred for 20 h at room temperature, the products were transferred via cannulation to a stirred mixture of diethyl ether and water (20 mL, 1:1 *v*/*v*) at 0 °C. The resulting mixture was stirred for 4 h at room temperature and then concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel. The appropriate fractions, which were eluted with dichloromethane, were pooled and concentrated under reduced pressure to yield the title compound as a colourless oil (0.48 g, 47%). δ_H (D_2O): 2.47 (2 H, t, J = 5.8 Hz), 3.63 (2 H, t, J = 5.9 Hz), 5.49 (s, 1H). δ_C (D_2O): 43.9, 58.5, 120.6 (br), 145.6.

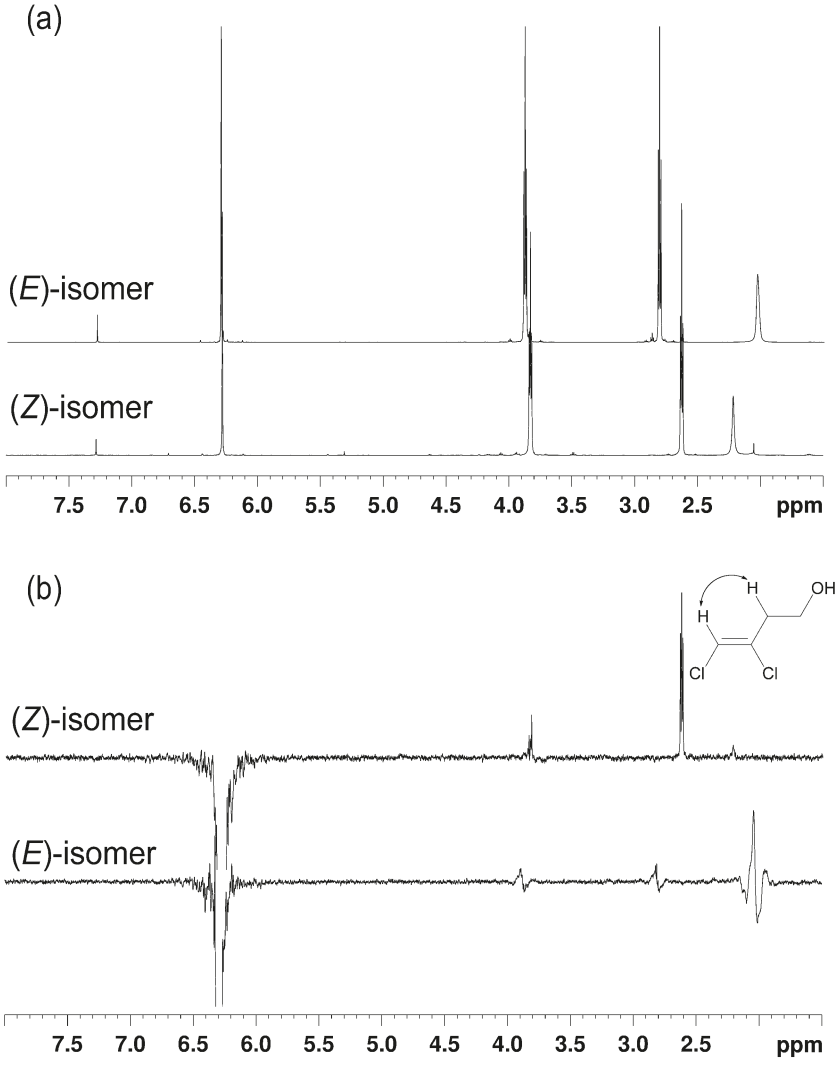
Potassium (*Z*)-2-chloro-4-hydroxy-1-butenyl trifluoroborate (16a)

To a solution of the organoboronic acid **15a** (0.31 g, 2.06 mmol) in methanol (8 mL) was added dropwise a solution of potassium hydrogen difluoride (0.80 g, 10.2 mmol) in water (8 mL) at 0 °C. After the reaction mixture was stirred at room temperature for 3 h, the products were concentrated to dryness under reduced pressure. The resulting solid was extracted with acetone (5 × 30 mL), aided by sonication. The acetone extracts were combined and evaporated at room temperature under reduced pressure to give the title compound as a light brown solid (0.31 g, 1.44 mmol, 71%). δ_H (D_2O): 2.48 (2 H, t, J = 6.1 Hz), 3.69 (2 H, t, J = 6.1 Hz), 5.44 (1 H, q, J = 4.5 Hz). δ_C (D_2O): 44.1, 59.0, 129.0 (br), 138.7 (q).

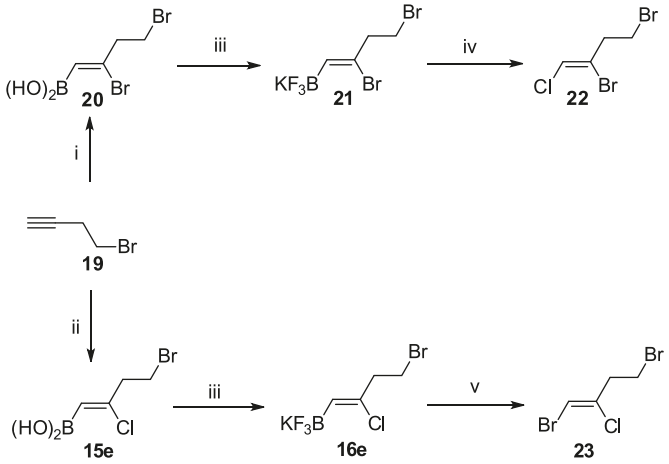
(*Z*)-3,4-Dichloro-3-buten-1-ol (17a)

To a solution of potassium trifluoroborate **16a** (0.20 g, 0.94 mmol) in aqueous tetrahydrofuran (12 mL, 1:1 *v*/*v*) was added tetrabutylammonium trichloride (0.68 g, 1.95 mmol) at room temperature. After the mixture was stirred for 3 h, the products were diluted with water (20 mL) and extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel. Evaporation of the combined fractions, which

Fig. 2. NMR spectra of the (Z)- and (E)-stereoisomers **17a** and **18**. (*a*) ^{1}H NMR spectra of **17a** and **18**. (*b*) NOE of **17a** and **18**.



Scheme 5. Reagents and conditions: (*i*) (*a*) BBr_3, CH_2Cl_2; (*b*) H_2O; (*ii*) (*a*) BCl_3, CH_2Cl_2; (*b*) H_2O; (*iii*) KHF_2, CH_3OH, H_2O; (*iv*) $Bu_4N^+Cl_3^-$, aq THF; (*v*) $Bu_4N^+Br_3^-$, aq THF.



were eluted with hexanes – ethyl acetate (9:1 *v*/*v*), gave the title compound as a colourless oil (68 mg, 51%). δ_H ($CDCl_3$): 2.18 (1 H, s), 2.62 (2 H, t, J = 5.8 Hz), 3.83 (2 H, t, J = 5.9 Hz), 6.28 (s, 1H). δ_C ($CDCl_3$): 40.7, 59.2, 115.7, 133.8. HR-MS (EI) calcd for $C_4H_6Cl_2O$: 139.97957; found: 139.97914.

(*Z*)-2,3-Dichloropropenoic acid (**2**)

To a cooled (ice water bath) solution of sodium hydroxide in distilled water (24.00 g NaOH in 120 mL water, 0.600 mol) was added mucochloric acid (40.00 g, 0.237 mol) in small portions to maintain a light yellow mixture. The resulting clear yellow solution was heated at 50 °C for 2 h. Upon cooling (ice water bath), concentrated hydrochloric acid (37%, 40 mL) was added slowly under stirring. After the reaction mixture was stirred for 1 h at 0 °C, the solid that formed was collected by filtration, followed by washing with small portions of ice-cold water (2 × 30 mL). The pale yellow solid was dissolved in diethyl ether (50 mL) and dried ($MgSO_4$). Evaporation of solvents under reduced pressure gave the title compound as a yellow oil that solidified upon standing as a creamy solid (23.3 g, 70%). δ_H ($CDCl_3$): 7.83 (1 H, s), 10.57 (1 H, s). δ_C ($CDCl_3$): 126.8, 135.4, 166.3. HR-MS (EI) calcd for $C_3H_2O_2Cl_2$: 139.94318; found: 139.94348.

Reduction of (*Z*)-2,3-dichloropropenoic acid (2) to (*Z*)-1,2-dichloro-3-hydroxy-1-propene (17c or **3**)

To a cooled (ice water bath) suspension of lithium aluminum hydride (0.84 g, 95% purity, 21 mmol) in dry diethyl ether (20 mL) was added dropwise a solution of (*Z*)-2,3-dichloropropenoic acid (**2**, 3.00 g, 21.3 mmol) in dry diethyl ether (20 mL). After stirring, first at 0 °C for 20 min and then at room temperature for 2 h, the reaction mixture was cooled (ice water bath), followed by sequential addition of methanol (0.5 mL) and water (20 mL). When the evolution of hydrogen gas ceased, dilute hydrochloric acid (approximately 3 N) was added to acidify the mixture until all precipitate dissolved. The layers were separated and the aqueous layer was back-extracted with diethyl ether (50 mL). The combined organic layers were washed with brine (2 × 20 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was distilled to give (*Z*)-1,2-dichloro-3-hydroxy-1-propene as a colourless oil (1.62 g, 45–48 °C/2 mm Hg (1 mm Hg = 133.3224 Pa), 61%). The NMR spectra were identical to those of **17c**.

(*Z*)-1,2,3-Trichloro-propene (4)

To a cooled (ice water bath) solution of (*Z*)-1,2-dichloro-3-hydroxy-1-propene (**3**, 3.00 g, 23.6 mmol) in dry dichloromethane (12 mL) and dry pyridine (2.7 mL) was added dropwise thionyl chloride (2.4 mL, 33 mmol). After the reaction mixture was stirred, first at 0 °C for 20 min and then at room temperature for 2 h, nitrogen gas was bubbled into the reaction mixture. The products were then evaporated under reduced pressure, and the residue was extracted with diethyl ether (3 × 50 mL). The combined ether layers were concentrated under reduced pressure. The residue was purified by column chromatography on silica gel. The appropriate fractions, which were eluted with hexanes–dichloromethane (3:2 *v*/*v*), were evaporated under reduced pressure to give the title compound as a colourless oil (1.30 g, 38%). δ_H ($CDCl_3$): 4.67 (2 H, s), 6.64 (1 H, s). δ_C ($CDCl_3$): 63.5, 120.9, 130.7. HR-MS (EI) calcd for $C_3H_3Cl_3$: 143.93003; found: 143.92975.

(*Z*)-3,4-Dibromo-3-buten-1-tosylate (12)

To a cold (ice water bath) solution of (*Z*)-3,4-dibromo-3-buten-1-ol (**11**,[10] 0.20 g, 0.87 mmol) in dry pyridine (3.5 mL) was added *p*-tosyl chloride (0.33 g, 1.73 mmol). After 24 h, the products were concentrated under reduced pressure, and the residue was taken up in dichloromethane (20 mL) and washed successively with water (20 mL) and brine (20 mL), and dried ($MgSO_4$). Evaporation of solvents gave a yellow oil that was purified by column chromatography on silica gel. The appropriate fractions, which were eluted with petroleum ether – ethyl acetate (9:1 *v*/*v*), were combined and evaporated under reduced pressure to give the title compound as a colourless oil that solidified upon standing (0.15 g, 45%). δ_H ($CDCl_3$): 2.47 (3 H, s), 2.84 (2 H, dt, J = 1.1 and 6.0 Hz), 4.21 (2 H, t, J = 6.0 Hz), 6.69 (1 H, t, J = 1.1 Hz), 7.27 (2 H, d, J = 8.0 Hz), 7.78 (2 H, d, J = 8.0 Hz). δ_C ($CDCl_3$): 21.7, 40.5, 66.6, 109.6, 127.2, 128.0, 130.0, 132.7, 145.1. HR-MS (EI) calcd for $C_{11}H_{12}O_3Br_2S$: 383.88547; found: 383.88595.

Single crystal growth: Single crystals of the tosylate **12** were obtained by slow evaporation of a solution of **12** in hexanes.

X-ray diffraction experiment

Data were collected on a Nonius Kappa-CCD diffractometer using monochromated Mo Kα radiation and were measured using a combination of ϕ scans and ω scans with κ offsets, to fill the Ewald sphere. The data were processed using the Denzo-SMN package.[17] Absorption corrections were carried out using SORTAV.[18] The structure was solved and refined using SHELXTL V6.1[19] for full-matrix least-squares refinement that was based on F^2. All H atoms were included in the calculated positions and allowed to refine in riding-motion approximation with U_{iso} tied to the carrier atom.

Supplementary data

Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/v2012-041. CCDC 859121 contains the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/request (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 33603; or e-mail: depost@ccdc.cam.ac.uk.

Conclusion

In conclusion, an approach for the synthesis of the thermodynamically disfavoured (*Z*)-1,2-dichloroalkenes was developed. Chloroboration of terminal alkynes gives corresponding (*Z*)-chloroboronic acids, which are readily transformed into potassium trifluoro organoborate. Subsequent chlorodeboronation gives (*Z*)-1,2-dichloroalkenes in a stereospecific manner.

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