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Chemistry of Dihalocyclopropanes XXV. The Influence of Halogen Substituents on the Vinylcyclopropylidene–Cyclopentenylidene Rearrangement

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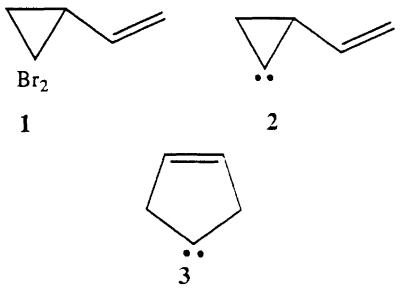
Starting from 2,2-dibromocyclopropanecarbaldehyde and its 1-methyl analogue, some chloro- and bromo-vinyl-substituted derivatives have been prepared, and their reactions with methyllithium studied at 0 and −78°C with emphasis on the formation of cyclopentadienes and allenes. Most reactions produced allenes, monobromides and bicyclopropylidenes. A rearrangement product, *viz.* 1-chloro-4-methylcyclopentadiene, was only encountered from the reaction of (*E*)-1,1-dibromo-2-(2-chloroethenyl)cyclopropane. The electronic effect of a chlorine substituent does not influence significantly the allene to cyclopentadiene ratio, which seems to be governed mainly by steric interactions. Reactions of 1,1-dibromo-2-(2,2-dibromoethenyl)cyclopropane and its 2-methyl analogue furnished the corresponding ethynyl derivatives as sole products; lithium–bromine exchange occurred preferentially at the vinylic carbon.

Reactions of *gem*-dibromocyclopropanes **1** with methyllithium is known to give cyclopentadienes, most probably by way of a vinylcyclopropylidene (**2**) to 3-cyclopentenylidene (**3**) rearrangement.[1] The rearrangement



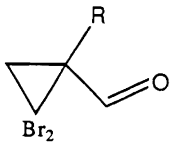
competes with ring opening of the intermediate carbene **2** to vinylallene, and with C–H insertion reactions.[2] It is strongly influenced by steric effects of both alkyl and aryl substituents positioned at either the double bond or the ring.[3] However, the effect of polar substituents on the rearrangement has so far not been studied. Based on calculations, it has been suggested[4] that electron-withdrawing groups on the double bond retard the rearrangement while the opposite should be expected for electron-donating substituents.

We have initiated a study aimed at an understanding of the electronic substituent effect on the rearrangement. In the present paper we report the preparation of some chloro- and bromo-vinyl-substituted dibromocyclopropane derivatives and their reactions with methyllithium.

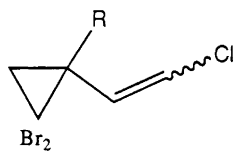
Results and discussion

Treatment of 2,2-dibromocyclopropanecarbaldehyde (**4a**)[5] with the ylide derived from chloromethyltriphenylphosphonium chloride[6] and lithium piperidide in THF, gave a 57% yield of the vinyl chlorides **5a**, as a 65 : 35 ratio of *E*- and *Z*-isomers according to the ^{1}H NMR spectra. The isomers were not obtained pure even after repeated flash chromatography on silica gel, and attempted separation by preparative GLC resulted only in decomposition. A sample enriched in the *E*-isomer was used for further reactions. A similar treatment of the aldehyde **4b**[5] afforded, in 81% yield, a 3 : 2 mixture of *E*- and *Z*-**5b**, and in this case separation into the pure components was readily achieved by flash chromatography on silica gel. In separate experiments, reactions of the aldehydes **4a** and **4b** with carbon tetrachloride and triphenylphosphine[7] afforded the corresponding dichlorovinyl derivatives **6a** and **6b** in 86 and 85% yields, respectively. By the same method, using carbon tetrabromide,[8] the dibromovinyl analogues **7a** and **7b** were obtained pure in 89 and 78% yields, respectively.

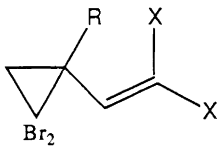
An ether solution of methyllithium was added to the *gem*-dibromocyclopropanes dissolved in ether and kept at either 0 or −78°C. The product composition was, in each case, analysed by capillary GLC. From reactions of the chlorine-containing compounds **5** and **6**, complex product mixtures were obtained in most cases. NMR spectroscopy combined with IR and MS data formed the basis for the structural assignments. When feasible, data



4a: R = H
b: R = Me



5a: R = H
b: R = Me



6a: R = H; X = Cl
b: R = Me; X = Cl

7a: R = H; X = Br
b: R = Me; X = Br

were obtained on samples isolated from the reaction mixtures by flash chromatography or preparative GLC. For analytical purposes the reactions were carried out at 0.05 M concentration of the dibromocyclopropanes. The results are compiled in Table 1. The reproducibility of the data recorded is not quite satisfactory owing mostly to the instability of the compounds causing analytical difficulties. However, we have looked with care for the presence of cyclopentadienes and allenes in the crude reaction mixtures and feel confident that qualitatively the results given in Table 1 represent correctly the general trend of the product distribution.

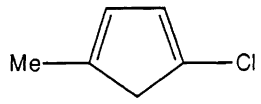
The stereoisomeric mixture of **5a** was also treated with methyllithium and the complex product contained neither cyclopentadienes nor allenes. A cyclopentadiene derivative was formed from the reaction of *E*-**5b** only, but then as major product isolated as a Diels–Alder adduct; addition of *N*-phenylmaleimide to the reaction mixture obtained at −78°C, resulted in a 10 : 1 mixture of the *endo* and *exo* adducts **16** in 43% yield. The adducts

Table 1. Reactions of compounds **5** and **6** with methyllithium.

Cpd.[a]	*T*/°C	Products (%)[b]		
E-**5b**	−78	**8** (68)	*E*-**9** (0)	*E*-**11** (29)	**15a** (3)
E-**5b**	0	**8** (67)	*E*-**9** (12)	*E*-**11** (21)	**15a** (0)
Z-**5b**	−78	*Z*-**9** (36)	*Z*-**11** (47)	**12** (<1)	**15a** (17)
Z-**5b**	0	*Z*-**9** (66)	*Z*-**11** (27)	**12** (7)	**15a** (0)
6a	−78	**10a** (0)	**13a** (11)	**14** (4)	**15b** (85)[c]
6a	0	**10a** (56)	**13a** (5)	**14** (14)	**15b** (25)
6b	−78	**10b** (0)	**13b** (92)	**15c** (7)	
6b	0	**10b** (83)	**13b** (17)	**15** (0)	

[a] 0.05 molar conc. [b] Analysed by GLC. [c] Sole product from reaction at 0.5 molar conc.

correspond to 1-chloro-4-methylcyclopentadiene (**8**), which seems to be the only isomer formed in the reaction. When conducted at 0°C, all the reactions recorded in Table 1 produced allenes. On the other hand, at −78°C only the product from the reaction of **5b** contained an allene, *viz*. (*Z*)-5-chloro-3-methyl-1,2,4-pentatriene (*Z*-**9**).



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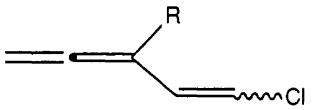

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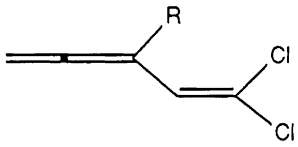
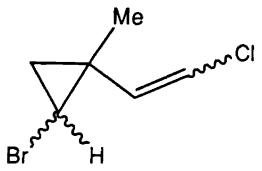
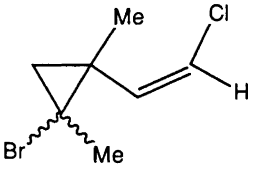


10a: R = H
b: R = Me

The allenes were readily identified from the ^{1}H NMR spectra and by the characteristic IR absorption in the 1950 cm^{-1} region. Reactions of *E*- and *Z*-**5b** produced all the four possible stereoisomeric monobromides **11**, but we were only able to separate them as pairs of isomers using preparative GLC; partial isomerization took place under these conditions. The structures assigned to the monobromides **11** were secured by comparison of GLC retention times and spectra with those of authentic samples, prepared by triphenyltin hydride reduction of the respective dibromide. By analogy the ^{1}H NMR spectrum of the crude reaction product from **5a** indicated the presence of monobromides. The mixture of monobromides **13a**, obtained from the reaction of **6a**, comprised approximately equal amounts of the stereoisomers while from **6b** a 3 : 2 mixture of the monobromides **13b** was formed, with the *cis*-isomer as the predominant component. The proportion of monobromides in the reaction mixtures increases at low temperature, which is as expected. However, the temperature effect can be drastic; when the reaction of **6b** was conducted at −78°C, the product contained 92% of the monobromides **13b**, while only 17% was present at 0°C. It seems that the intermediate organolithium derivative must somehow be stabilized by the chlorovinyl substituent. The configurations were established from the NMR spectra. For *cis*-**13a** the proton geminal to the bromine appeared as a septet centred at δ 2.88 and for *cis*-**13b** this proton gave rise to doublets of doublets at 2.90. For the corresponding *trans*-isomers signals for the same proton were shifted to δ 3.23 and 3.11, respectively. These chemical shifts compare well



11a: *E*
b: *Z*



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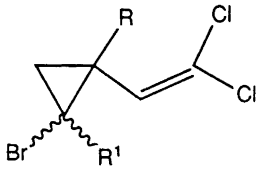
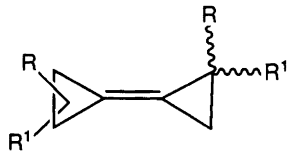


13a: R = R^1 = H
b: R = Me; R^1 = H
14: R = H; R^1 = Me

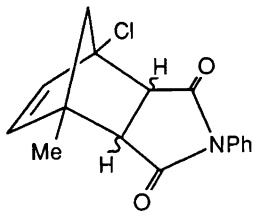
with those of the authentic monobromides **11**, and with literature values reported for similar compounds.[9,10] The methylated monobromides were formed in only small amounts, and in most cases we have assumed their presence in the reaction mixtures by the presence of a singlet in the ^{1}H NMR spectra at about δ 1.80, the chemical shift expected for such methyl protons. The monobromides **14** were actually isolated by preparative GLC as a 2 : 1 mixture of the *trans*- and *cis*-isomers, exhibiting singlets for these methyl protons at δ 1.82 and 1.76, respectively.

Higher-boiling material was produced in variable amounts from all reactions carried out at −78°C, while at 0°C very little was formed. The amounts increased with the concentration of starting material, and the reaction of a 0.5 M solution of **6a** at −78°C gave, as practically the sole product, a non-volatile residue that solidified after being left for several months in the refrigerator. It was shown by TLC to consist of a mixture of compounds, which we were unable to separate. Spectral evidence obtained on the mixture indicated that the product from **6a** consisted of at least two of the four possible isomers with the general bicyclopropylidene framework **15b**, i.e., formally regarded as dimerization products of the intermediate carbene. The mass spectrum of the mixture provided evidence for the dimeric structure, giving rise to the characteristic multiplet of peaks due to the four chlorine atoms in the ionized unfragmented molecule. The signal at δ 114.9 in the ^{13}C NMR spectrum appears to be quite indicative of the quaternary olefinic carbons of the cyclopropylidene moiety.[11] The non-volatile components of the products obtained from the other reactions exhibited similar spectral results, and we therefore conclude that these consist essentially of bicyclopropylidenes of general structure **15** as well. The formation of such compounds from reactions of *gem*-dibromocyclopropanes and alkyllithium is not surprising. In cases where ring opening to allene is for some reason retarded, bicyclopropylidenes are expected to be formed, and have actually been reported as major products.[11]

Contrary to the above results the reaction of the dibromovinyl derivative **7a** with methyllithium at −78°C gave 1,1-dibromo-2-ethynylcyclopropane (**17a**) in 67% isolated yield. A small amount (6%) of dimer was formed as well. Similarly the reaction of **7b** afforded the ethynylcyclopropane derivative **17b** in 69% yield. The spectral properties were in complete agreement with those published.[12]



15a: R = Me; R^1 = CH=CHCl
b: R = H; R^1 = $CH=CCl_2$
c: R = Me; R^1 = $CH=CCl_2$



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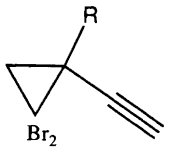

17a: R = H
b: R = Me

The formation of 1-chloro-4-methylcyclopentadiene (**8**) indicates that an electronic effect on the rearrangement must play a minor role; compared with the corresponding non-chlorinated derivative the amount of cyclopentadiene produced is less, but the trend is the same.[1] The

cyclopentadiene **8**, probably thermodynamically the most stable isomer, cannot be a primary product of the intermediate cyclopentenylidene. Its formation requires the carbene to insert (1,2-H shift) exclusively into one of the methylene C–H bonds to form 5-chloro-2-methylcyclopentadiene, that in turn rearranges by a [1,5] hydrogen shift. We have previously encountered selective transformations of cyclopentenylidenes to cyclopentadienes,[3] and it is well documented that 5-substituted cyclopentadienes are prone to undergo [1,5] hydrogen shifts.[13,14] On the other hand, insertion into the methine C–H bond should give rise to 2-chloro-4-methylcyclopentadiene, an unlikely precursor of **8**.

Steric effects on the rearrangement are clearly revealed. Cyclopentadienes were not formed from reactions of the dibromocyclopropanes *Z*-**5** and **6**. Although the steric requirement of the chlorine atom is considerably less than that of a methyl group, it is apparently sufficiently large for the rate of rearrangement to cyclopentadiene to be depressed completely in compounds having a chlorine *cis*-related to the ring. Another interesting observation is the exclusive formation of the acetylenic compounds **17** from reactions of the tetrabromides **7**. The exchange of a vinylic bromine with lithium is apparently faster than that of a cyclopropyl bromine, leading to an intermediate ethylidene that rearranges to the ethynyl derivative. The two-step sequence from readily available dibromocyclopropyl aldehydes may actually turn out to be a convenient route to ethynyl-substituted cyclopropane derivatives.

Experimental

General. GLC analyses were performed on a 30 m capillary column of SP 2100. IR spectra were recorded on a Perkin Elmer 1310 instrument. NMR spectra were obtained on Varian XL-300 and 200 instruments. Capillary melting points were taken on a Büchi SMP-20 apparatus and are uncorrected.

(E)-, (Z)-*1,1-Dibromo-2-(2-chloroethenyl)cyclopropane* (**5a**). Treatment of a suspension of chloromethyltriphenylphosphonium chloride[6] (4.51 g, 13 mmol) in dry ether (9 ml) with lithium piperidide (12 mmol) gave a yellow solution of the ylide. The aldehyde **4a**[5] (2.28 g, 10 mmol) in ether (5 ml) was added and the reaction mixture was stirred at room temp. for 24 h. Work-up gave a 65 : 35 mixture of *Z*- and *E*-**5a** (1.48 g, 57%) as a liquid, after purification by flash chromatography (SiO_2, pentane). As the isomers were inseparable, the spectral data were obtained from the mixture.

Z-**5a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.62 (dd, *J* 7.5 Hz, 1 H), 2.11 (dd, *J* 7.4, 10.4 Hz, 1 H), 2.7–2.8 (m, 1 H), 5.56 (dd, *J* 7.2, 8.5 Hz, 1 H), 6.32 (dd, *J* 0.9, 7.3 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.7, 29.0, 30.2, 121.6 (CH=), 129.6 (=CHCl).

E-**5a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (dd, *J* 7.6 Hz, 1 H), 2.02 (dd, *J* 7.6, 10.3 Hz, 1 H), 2.3–2.4 (m, 1 H), 5.71 dd *J* 8.8, 13.2 Hz, 1 H), 6.26 (dd, *J* 0.7, 13.3 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.3, 29.5, 31.8, 120.9 (CH=), 131.3 (=CHCl).

(E)-, (Z)-*1,1-Dibromo-2-(2-chloroethenyl)-2-methylcyclopropane* (**5b**). Reaction of the aldehyde **4b**[5] with chloromethyltriphenylphosphonium chloride (1.6 molar excess) as described for the preparation of **5a** gave a 3 : 2 mixture of *E*- and *Z*-**5b** as a liquid in 81% yield, b.p. 66–76°C (2 mmHg). The isomers were separated by flash chromatography (SiO_2, pentane).

E-**5b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52 (s, 3 H), 1.67 (d, *J* 7.8 Hz, 1 H), 1.83 (d, *J* 7.8 Hz, 1 H), 6.02 (d, *J* 13.4 Hz, 1 H), 6.15 (d, *J* 13.4 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.2, 30.5, 35.0, 35.9, 120.4 (CH=), 136.2 (=CHCl). IR (film): 1610 (m), 1450 (m), 1430 (m), 935 (s), 840 (s), 695 (s) cm^{-1}.

Z-**5b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52 (s, 3 H), 1.77 (d, *J* 7.8 Hz, 1 H), 1.89 (d, *J* 7.8 Hz, 1 H), 6.05 (d, *J* 7.2 Hz, 1 H), 6.20 (d, *J* 7.2 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.8, 29.0, 36.1, 36.3, 122.5 (CH=), 132.5 (=CHCl). IR (film): 1620 (m), 1450 (m), 1375 (m), 775 (m), 725 (s), 705 (s) cm^{-1}.

1,1-Dibromo-2-(2,2-dichloroethenyl)cyclopropane (**6a**). Reaction of the aldehyde **4a** (3.42 g, 15 mmol) with triphenylphosphine (17.3 g, 66 mmol) and CCl_4 (15 ml) in CH_2Cl_2 (30 ml) for 1 h at 0°C and 2 h gave **6a** (3.86 g, 86%) as a liquid, b.p. 55–56°C (0.5 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.64 (dd, *J* 7.5, 7.6 Hz, 1 H), 2.11 (dd, *J* 7.5, 10.4 Hz, 1 H), 2.54 (ddd, *J* 7.6, 8.4, 10.4 Hz, 1 H), 5.68 (d, *J* 8.4 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.7, 30.2, 30.9, 123.8 (CH=), 127.7 (=CCl_2). IR (film): 1610 (m), 950 (s), 885 (s), 690 (s), 640 (m) cm^{-1}.

1,1-Dibromo-2-(2,2-dichloroethenyl)-2-methylcyclopropane (**6b**). Using the same proportions and conditions as described for **6a**, the aldehyde **4b** gave **6b** (85%) as a liquid, b.p. 58–59°C (0.5 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52 (s, 3 H), 1.75 (d, *J* 7.8 Hz, 1 H), 1.89 (d, *J* 7.8 Hz, 1 H), 6.16 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.5, 30.1, 35.4, 35.8, 125.5 (CH=), 130.6 (=CCl_2). IR (film): 1610 (m), 950 (s), 885 (s), 690 (s), 640 (m) cm^{-1}.

1,1-Dibromo-2-(2,2-dibromoethenyl)cyclopropane (**7a**). Reaction of the aldehyde **4a** (3.42 g, 15 mmol) with triphenylphosphine (17.3 g, 66 mmol) and CBr_4 (10.9 g, 33 mmol) in CH_2Cl_2 (45 ml) at 0°C for 3 h gave **7a** (5.4 g, 89%) as a liquid, after purification by flash chromatography (SiO_2, pentane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.66 (dd, *J* 7.3, 7.8 Hz, 1 H), 2.10 (dd, *J* 7.3, 10.8 Hz, 1 H), 2.46 (ddd, *J* 7.8, 8.3, 10.8 Hz, 1 H), 6.20 (d, *J* 8.3 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.0, 30.0, 33.7, 92.5 (CH=), 136.0 (=CBr_2). IR (film): 1620 (w), 1595 (w), 830 (s), 770 (m), 690 (s) cm^{-1}.

1,1-Dibromo-2-(2,2-dibromoethenyl)-2-methylcyclopropane (**7b**). Using the same proportions and reaction conditions as described for **7a**, the aldehyde **4b** gave **7b** (78%)

as a liquid, after purification by flash chromatography (SiO_2, pentane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52 (s, 3 H), 1.77 (d, *J* 7.8 Hz, 1 H), 1.92 (d, *J* 7.8 Hz, 1 H), 6.74 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.2, 32.6, 34.7, 35.9, 94.3 (CH=), 138.6 (=CBr_2). IR (film): 1590 (w), 860 (m), 820 (m), 805 (s), 700 (s) cm^{-1}.

Reactions of gem*-dibromocyclopropanes with methyllithium. General preparative procedure.* An ether solution of 1.4 M methyllithium (2.1 ml, 3 mmol) was added within 5 min to a stirred solution of the *gem*-dibromocyclopropane derivative (3 mmol) in dry ether (6 ml), kept at −78°C. After 1 h, water (1 ml) was added, and the organic phase analysed. The ether was removed through a small Spaltrohr column, and the residue purified by column chromatography and preparative GLC.

Analytical procedure. The results recorded in Table 1 were obtained essentially as above, but on a 1 mmol scale in dry ether (20 ml), and analysed by capillary GLC (DBI, 30 m).

1-Chloro-4-methyl-1,3-cyclopentadiene (**8**). Treatment of the crude reaction mixture from *E*-**5b** and methyllithium with a THF solution of *N*-phenylmaleimide in the usual way gave the adduct **16** in 43% yield as a 10 : 1 mixture of *endo*- and *exo*-isomers, respectively. As the two isomeric adducts were inseparable, the spectra were obtained from the mixture.

endo-**16**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.62 (s, 3 H), 2.08 (d, *J* 8.5 Hz, 1 H), 2.12 (d, *J* 8.5 Hz, 1 H), 3.22 (d, *J* 7.9 Hz, 1 H), 3.67 (d, *J* 7.9 Hz, 1 H), 6.03 (d, *J* 5.6 Hz, 1 H), 6.28 (d, *J* 5.6 Hz, 1 H), 7.1–7.2 (m, 2 H), 7.3–7.5 (m, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.4, 52.1, 52.9, 54.7, 59.0, 67.3, 126.3, 128.5, 128.9, 131.4, 138.4, 138.7, 173.4, 174.6.

exo-**16**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (s, 3 H), 2.08 (d, *J* 8.5 Hz, 1 H), 2.12 (d, *J* 8.5 Hz, 1 H), 3.25 (d, *J* 8.1 Hz, 1 H), 3.61 (d, *J* 8.1 Hz, 1 H), 6.09 (d, *J* 5.6 Hz, 1 H), 6.24 (d, *J* 5.6 Hz, 1 H), 7.1–7.2 (m, 2 H), 7.3–7.5 (m, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.4, 52.1, 52.9, 54.7, 59.0, 67.3, 126.3, 128.5, 128.9, 131.4, 138.4, 138.7, 173.4, 174.6.

(E)*-5-Chloro-3-methyl-1,2,4-pentatriene* (*E*-**9**). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.71 (t, *J* 3.0 Hz, 3 H), 4.80 (m, *J* 1.3, 3.0, 4.2 Hz, 1 H), 5.81–5.90 (m, 2 H). IR (film): 1935 (s), 1595 (m), 810 (s), 690 (s) cm^{-1}.

(Z)*-5-Chloro-3-methyl-1,2,4-pentatriene* (*Z*-**9**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.96 (t, *J* 3.2 Hz, 3 H), 4.83 (m, *J* 1.4, 1.5, 3.2 Hz, 2 H), 5.91 (dt, *J* 1.5, 8.0 Hz, 1 H), 6.03 (dt, *J* 1.4, 8.0 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.8, 75.3, 95.9, 117.6, 126.8, 211.2. IR (film): 1940 (w), 725 (s) cm^{-1}.

5,5-Dichloro-1,2,4-pentatriene (**10a**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.0 (dd, *J* 1.2, 6.6 Hz, 2 H), 6.0 (dt, *J* 6.6, 10.6 Hz, 1 H), 6.3 (dt, *J* 1.2, 10.6 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 77.3, 89.1, 119.2, 124.1, 212.5. IR (film): 1965 (m), 1940 (s), 1595 (m), 880 (s), 850 (s), 670 (s) cm^{-1}.

5,5-Dichloro-3-methyl-1,2,4-pentatriene (**10b**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88 (t, *J* 3.2 Hz, 3 H), 4.86 (dq, *J* 2.0, 3.2 Hz, 2 H), 6.07 (t, *J* 2.0 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.5, 76.3, 95.6 (CH=), 120.3 (CH_2=), 125.7 (=CCl2), 210.6 (=C=). IR (film: 1935 (m), 1620 (s), 1595 (m), 905 (s), 890 (s), 850 (s) cm^{-1}.

Isomer mixture of bicyclopropylidenes **15b**. Reaction of **6a** at −78°C gave, as the major product, a mixture of isomeric **15b**, obtained as a crystalline solid after several months standing at 5°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (m, 2 H), 1.80 (m, 2 H), 2.50 (m, 2 H), 5.39 (d, 2 H). ^{13}H NMR (75 MHz, $CDCl_3$): δ 12.7, 12.8, 17.8, 18.0, 114.9 (C=C), 119.9 (CH=), 129.9 (=CCl_2). MS (EI): 276, 274, 272, 270, 268 (0.3, *M*), 197 (28), 162 (100), 146 (33), 127 (29), 111 (67), 99 (31), 75 (45).

Preparation of monobromides **11**. *General procedure.* Triphenyltin hydride (176 mg, 0.50 mmol) was added in three portions within 15 min to a vigorously stirred solution of the dibromide *E*- or *Z*-**5b** (82 mg, 0.30 mmol) in methanol (1 ml) kept at 0°C. The stirring was continued until all the starting material was consumed (10 min). The mixture was stirred for another 20 min at the same temperature with oxalic acid dihydrate 38 mg, 0.30 mmol) in order to consume unchanged hydride. Extractive work-up with $CDCl_3$ (1.2 ml) followed by distillation at 0.01 mmHg of all volatile material gave solutions of the monobromides **11** as *cis–trans* mixtures, from which the following spectral data were obtained.

From *E*-**5b** a mixture of *trans*- and *cis*-**11a** was obtained in a ratio of 2 : 3.

trans-*1-Bromo-2-*[(E)*-2-chloroethenyl*]*-2-methylcyclopropane* (*trans*-**11a**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (dd, *J* 5.0, 6.5 Hz, 1 H), 1.27 (dd, *J* 6.5, 8.1 Hz, 1 H), 1.29 (s, 3 H), 2.91 (dd, *J* 5.0, 8.1 Hz, 1 H) 5.52 (d, *J* 13.3 Hz, 1 H), 5.88 (d, *J* 13.3 Hz, 1 H).

cis-*1-Bromo-2-*[(E)*-2-chloroethenyl*]*-2-methylcyclopropane* (*cis*-**11a**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.99 (dd, *J* 4.7, 6.5 Hz, 1 H), 1.15 (s, 3 H), 1.17 (dd, *J* 6.5, 7.5 Hz, 1 H), 2.88 (dd, *J* 4.7, 7.5 Hz, 1 H), 5.87 (d, *J* 13.4 Hz, 1 H), 5.93 (d, *J* 13.4 Hz, 1 H).

From *Z*-**5b** a mixture of *trans*- and *cis*-**11b** was obtained in a ratio of 3 : 2.

trans-*1-Bromo-2-*[(Z)*-2-chloroethenyl*]*-2-methylcyclopropane* (*trans*-**11b**). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.28 (s, 3 H), 3.12 (dd, *J* 4.8, 7.9 Hz, 1 H), 5.81 (d, *J* 7.2 Hz, 1 H), 6.04 (d, *J* 7.2 Hz, 1 H). The cyclopropyl methylene protons could not be distinguished.

cis-*1-Bromo-2-*[(Z)*-2-chloroethenyl*]*-2-methylcyclopropane* (*cis*-**11b**). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.40 (s, 3 H), 2.90 (dd, *J* 4.6, 7.5 Hz, 1 H), 5.95 (d, *J* 7.2 Hz,

1 H), 6.20 (d, *J* 7.2 Hz, 1 H). The cyclopropyl methylene protons could not be distinguished.

1-Bromo-2-(2,2-dichloroethenyl)cyclopropane (**13a**). As the stereoisomers were inseparable, the spectra were obtained from the mixture.

trans-**13a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.8–2.4 (complex abs.), 3.23 (m, 1 H), 5.76 (d, *J* 8.7 Hz, 1 H).

cis-**13a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.8–2.4 (complex abs.), 2.88 (m, 1 H), 5.76 (d, *J* 8.8 Hz, 1 H).

1-Bromo-2-(2,2-dichloroethenyl)-2-methylcyclopropane (**13b**). As the stereoisomers were inseparable, the spectra were obtained from the mixture.

trans-**13b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (dd, *J* 4.9, 6.5 Hz, 1 H), 1.39 (s, 3 H), 1.42 (dd, *J* 6.5, 8.1 Hz, 1 H), 3.11 (dd, *J* 4.9, 8.1 Hz, 1H), 5.97 (s, 1 H).

cis-**13b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (dd, 4.5, 6.7 Hz, 1 H), 1.27 (s, 3 H), 1.39 (dd, 1 H), 2.90 (dd, *J* 4.5, 7.5 Hz, 1 H), 6.08 (s, 1 H).

1-Bromo-2-(2,2-dichloroethenyl)-1,2-dimethylcyclopropane (**14**). As the isomers were inseparable, the spectra were obtained from the mixture.

trans-**14**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.82 (s, 3 H), 5.30 (d, *J* 9.1 Hz, 1 H).

cis-**14**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.76 (s, 3 H), 5.48 (d, *J* 8.6 Hz, 1 H).

1,1-Dibromo-2-ethynylcyclopropane (**17a**). Reaction of **7a** with methyllithium by the general procedure afforded **17a** (67%) as a liquid, b.p. 55°C (8 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.75 (dd, *J* 6.4, 7.3 Hz, 1 H), 2.04 (dd, *J* 7.3, 10.4 Hz, 1 H), 2.25 (s, 1 H), 2.29 (dd, *J* 6.4, 10.3 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 24.2, 30.9, 70.4, 80.8. IR (film): 3300 (s), 2130 (w), 1430 (m), 700 (s) cm^{-1}.

1,1-Dibromo-2-ethynyl-2-methylcyclopropane (**17b**). Reaction of **7b** with methyllithium by the general procedure afforded **17b** (68%) as a liquid, b.p. 54°C (5 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.62 (s, 3 H), 1.66 (d, *J* 7.3 Hz, 1 H), 1.94 (d, *J* 7.3 Hz, 1 H), 2.23 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.5, 23.9, 33.4, 36.6, 69.3, 84.8.

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