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REGIOSPECIFICITY IN THE NUCLEOPHILIC RING OPENING REACTIONS OF gem-DICHLOROCYCLOPROPYLCARBINYL CATIONS

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Abstract: gem-Dichlorocyclopropylcarbinyl cations, generated under acidic conditions from the corresponding alcohol or alkene, undergo ring opening by nucleophilic attack exclusively at the halogenated carbon when the alternative electrophilic ring carbon is unsubstituted. In one case, a novel trifluoroacetoxydichloromethyl function has been produced and characterized as a masked carboxylic acid chloride.

In marked contrast to the reported reaction[1] of 1 with excess aqueous HBr to give 2 and 3, treatment of the tertiary alcohol 4 with HBr produces a complex array of products none of which is analogous to 2 or 3. While it is not surprising that cyclobutanes are absent,[2] the presence of 6 is noteworthy since it represents a reversal in the regiochemistry of nucleophilic attack on the cyclopropane ring. By varying the reaction parameters (Table 1), it is possible to change rather dramatically the composition of the product mixture and thus determine the origins of some of its components.

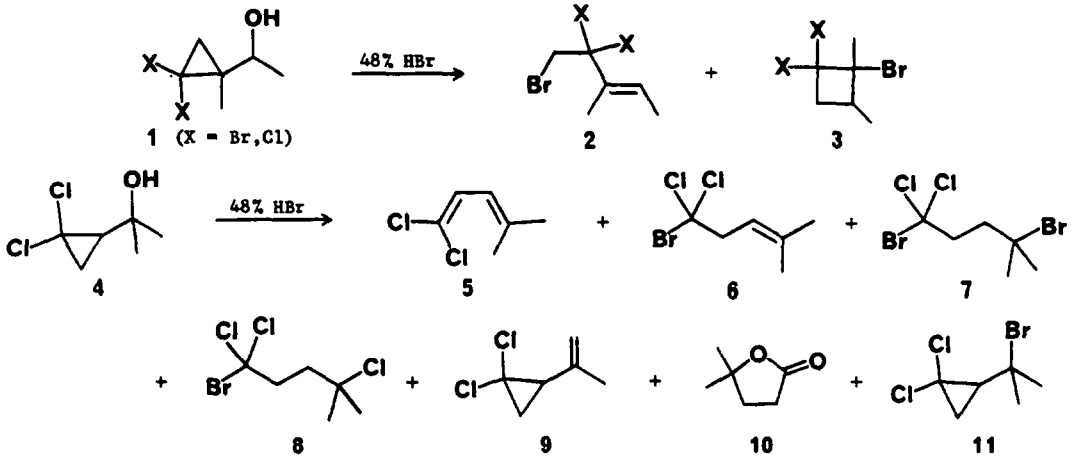


Table 1. Composition of the product mixture from reaction of 4 with 48% aqueous HBr

Run	Conditions	Moles of HBr / Moles of 4	Composition (mole %) 5	6	7	8	9	10	Recov.4	Yield[a]
1	95° C/90 min	6.3	4.9	13.8	70.3	8.8	-	2.2	-	69.2%
2	95° C/20 min	6.0	7.5	33.9	49.9	4.6	-	4.1	-	83.9%
3	80° C/ 5 min	3.0	5.7	55.3[b]	18.9	1.3	11.3	7.5	-	81.0%
4	85° C/20 min	2.0	5.8	52.5	21.0	3.5	9.9	7.3	-	85.4%
5	85° C/ 5 min	1.0	4.4	51.9[b]	7.4	-	20.8	5.9	9.6	79.2%

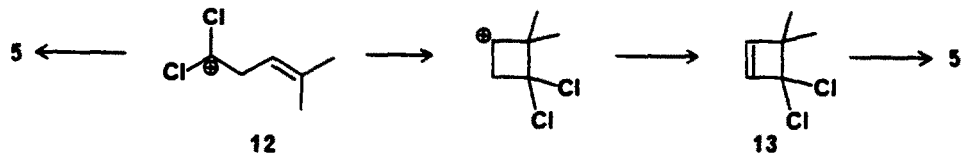
[a] Calculated on the basis of the distilled mass and the theoretical yield estimated from the product distribution.
[b] Represents 6 + 11, since 11 cannot be separated cleanly from 6 by preparative vpc.

Clearly, 6 and 9 are primary products. The cyclopropylcarbinyl cation generated from 4 can lose H^+ to give 9 or react with bromide at the halogenated ring carbon to give 6. A third primary product, 11, is also observed but has not been separated cleanly from 6 by preparative vpc. However, 11 can be identified easily by comparison of spectral data obtained from a mixture of 6 and 11 with that of pure 11 prepared by the reaction of 4 with PBr_3. As expected,

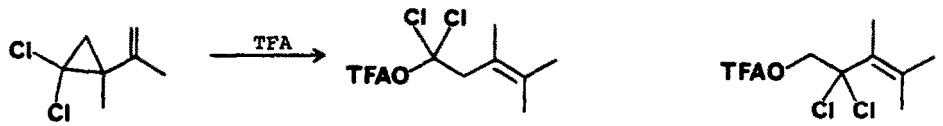
both **9** and **11** are labile and lie below detectable concentrations when reaction times are increased. The olefin **6** is identified and differentiated readily from 5-bromo-4,4-dichloro-2-methyl-2-pentene by its proton NMR spectrum, particularly the broadened doublet for the methylene group at 3.46 ppm δ. The structure of **9** is established by comparison of spectral data with an authentic sample produced as the minor product (4%) of the reaction of isoprene with dichlorocarbene.

Two tetrahalides, **7** and **8**, are present in varying amounts depending on conditions. Compound **7**, the result of HBr addition to **6**, is the major product of the reaction when a large excess of HBr is used. However, the production of **8** is probably related to the formation of **10** in that chloride ion must be generated in the process. Thus, **8** comes from the reaction of **6** with HCl generated *in situ*. Both **7** and **8** appear to be end products; *i.e.*, neither is a precursor to **5** or **10** under the conditions of these reactions. Treatment of a mixture of **7** and **8** with HBr using the conditions of Run 2 (Table 1) results in no change and a quantitative recovery of the starting material.[3]

At least one source of the lactone **10** is the hydrolysis of **6** and subsequent cyclization of the unsaturated acid. The reaction of **6** with HBr in an independent experiment using the conditions indicated for Run 2 (Table 1) gives **7**, **8**, and **10**. The same unsaturated acid can also arise from nucleophilic attack by water at the chlorinated carbon of the original cyclopropylcarbinyl cation intermediate or **12**. The origin of diene **5** is speculative at this point. Loss of H^+ from the homoallylic cation **12** can give **5** directly, but the intervention of



cyclobutene **13** cannot be ruled out[4] by existing evidence. Attempts to dehydrate **4** by heating with catalytic 85% H_3PO_4 give mostly polymers and low yields of volatile material containing three products-**5**, **10**, and 5,5,5-trichloro-2-methyl-2-pentene.

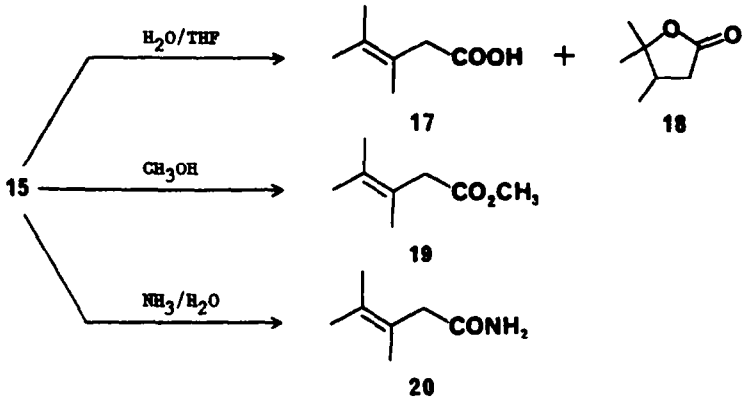


14 **15** **16**

In a second example of the same regiospecific ring opening, the olefin **14** is converted in high yield to **15** by treatment with trifluoroacetic acid (TFA). This reaction proceeds smoothly at room temperature and is relatively free of secondary products since there is only one viable nucleophile in solution. The only mentionable by-products are the trace esters resulting from addition of TFA to the double bond of **15**.

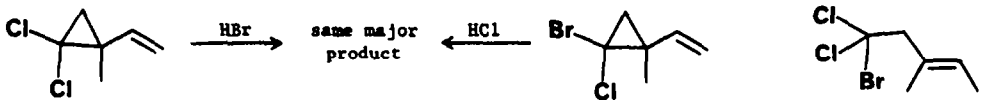
The structure of **15** is established from spectral data and its reactions. The high intensity (89.7%) of the $C_5H_{11}^+$ peak ($M-Cl_2COTFA$) is consistent with the expected mass spectral fragmentation pattern of **15**; and the absence of the $(M-Cl)^+$ peak for an allylic chloride[5] tends to rule out **16**. The methylene hydrogens of **15** appear as a slightly broadened singlet exhibiting no definitive homoallylic coupling with the methyls, but the chemical shift (3.42 ppm δ) is much higher field than that to be expected for the methylene group of **16**. The heretofore unreported trifluoroacetoxydichloromethyl functional group behaves as a masked carboxylic acid chloride.

Hydrolysis of 15 in pure water gives the acid 17 and a small amount of lactone 18. The latter is absent when aqueous bicarbonate (and subsequent neutralization) is used. Methanolysis and ammonolysis give 19 and 20 respectively.



It is clear from the reactions of 4 and 14 that ring opening occurs by nucleophilic attack at the halogenated carbon of the intermediate ion when the alternative electrophilic ring carbon is unsubstituted. With respect to 1, the only structural difference which might alter the electronic nature of the intermediate is that both 4 and 14 lead to a tertiary rather than a secondary cyclopropylcarbinyl cation. While this may affect the relative stabilities of the various ions, it is not obvious that such a factor would lead to regiochemical reversal in the ring opening step. Indeed, solvolysis of the tosylate from 1 (X = Br) in buffered aqueous acetone gives as one of several products 3-methyl-3-pentenoic acid, a compound whose formation has been described previously[6] as the result of nucleophilic attack by water on the brominated carbon of the intermediate ion.

Although the reaction of 1 (X = Cl) has not been repeated in these laboratories, treatment of 1-methyl-1-vinyl-2,2-dichlorocyclopropane (21) with 48% HBr under the conditions described[1] for 1 was investigated. This experiment reproduced both the product distribution and the spectral data reported in the literature for 2 and 3. However, the absence of discernible allylic coupling of the methylene protons to the vinyl proton in the olefinic product of these reactions does not necessarily relegate 22 from consideration as the correct structure.[7] In fact, the chemical shift for the methylene protons of 6 is almost identical to that for the methylene protons of the compound cited as 2 (X = Cl). The mass spectrum of the product



21 23 22

reported as 2 (X = Br)[strong $(M-CBr_3)^+$, 100% and a much weaker $(M-Br)^+$][1] exhibits a fragmentation pattern very similar to that of 6 [strong $(M-CCl_2Br)^+$, 100% and a weak $(M-Br)^+$] .

In another experiment, paralleling the one described above for olefin 21, the bromochlorocarbene adduct 23 of isoprene was heated for 2 hours at 100° C with conc. HCl. The result was not totally satisfying in that the reaction gave at least 5 products and proceeded to to only 40% completion. However, the major product was identical to the olefinic compound from reaction of 21 with HBr. These data suggest that the structure 2 may be in error and call for a reinvestigation of the reaction of 1 with HBr.

Experimental Section

General Methods. All reactions were carried out under a nitrogen atmosphere. ^1H NMR spectra were recorded with a Varian EM390 spectrometer using $CDCl_3$ solutions with Me_4Si as an internal standard. ^{13}C NMR spectra were recorded with a JEOL FX-60 spectrometer using $CDCl_3$ solutions with Me_4Si as an internal standard. IR spectra were recorded with a Beckman IR 4250 by using a thin film of the neat liquid between NaCl plates or KBr pellets for solid samples. Mass spectra were obtained from a Finnegan 1020 OWA instrument using gc injection through a 6' x 1/8" id column packed with 10% SE-30 on 60/80 WAWDCS and an ionization energy of 70 eV. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Combustion analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN.

2,2-Dichlorocyclopropanecarboxylic Acid. Triallyl orthoformate was prepared according to the procedure of Robinson.[8] A solution of 11.7 g (63.5 mmol) of triallyl orthoformate and 0.1 g of benzyltriethylammonium chloride in 40 mL of chloroform was added all at once to a mechanically stirred solution (previously degassed with N_2) of 100 g of NaOH in 100 mL of water at 0° C. The mixture was allowed to stir at 0°C under N_2 for 4 h and an additional 10 h at room temperature. Water (80 mL) and pentane (100 mL) were added to the flask with stirring, and the resulting mixture was transferred to a separatory funnel. The organic layer was separated and the aqueous layer was extracted with 50 mL of pentane. The organic layers were combined, washed with 25 mL of brine, and dried over $MgSO_4$. Removal of the solvent in vacuo afforded 22.0 g of brown oil. NMR analysis indicated a mixture of orthoformates containing an average of 2.3 cyclopropane moieties per molecule. Ten mL of this mixture was added dropwise to 90 mL of conc. HNO_3 (magnetic stirring) which had been pre-warmed to 65° C. The temperature of the reaction mixture was maintained at 65-70° C by controlling the rate of addition and occasionally the use of an ice bath. After complete addition, the solution was stirred at 65° C for 3 h, then cooled to room temperature, and diluted with 150 mL of H_2O. The product was extracted with CH_2Cl_2 (2 x 30 mL; and the extracts were combined, dried over $MgSO_4$, and concentrated by rotary evaporation. The residual yellow oil crystallized on standing. Recrystallization of the crude semisolid from cyclohexane gave 3.7 g of pure acid, mp 76-77° C (lit.[9] mp 75-76° C).

Alcohol 4. To a solution of 16.0 g (103 mmol) of 2,2-dichlorocyclopropanecarboxylic acid in 30 mL of CCl_4 was added 22.6 g (108 mmol) of PCl_5 in small portions over 30 min at room temperature. The resulting solution was heated at reflux for 1 h and then cooled to room temperature. Solvent was removed by rotary evaporation, and the residue was distilled to give 15.2 g (85%) of acid chloride, bp 89-92° C/62 mm (lit.[10] bp 58° C/15 mm). A solution of 14.0 g (80 mmol) of the acid chloride to 200 mL of ether was cooled to 0° C and 62 mL (180 mmol) of 2.9 M CH_3MgCl in THF was added dropwise (magnetic stirring). The reaction mixture was allowed to stir overnight at room temperature and was then quenched at 0° C by cautious addition of 100 mL of water followed by 50 ML of 1 M HCl. The organic layer was separated, washed with 50 mL of brine, and dried over $MgSO_4$. Solvent was removed by rotary evaporation, and the brown residual oil was distilled to give 9.6 g (71%) of pure 4, bp 27-28° C/0.5 mm: ^1H NMR δ 1.32 (s,3H) and 1.55 (s,3H) [diastereotopic CH_3's] , 1.57-1.80 (m,3H, ring H's), 1.84 (s,1H,OH); ^{13}C NMR δ22.5, 28.9, 29.8, 39.6, 59.7, 68.9; IR 3450, 1370, 1219, 1183, 1124, 1046, 956, 930, 843, and 750 cm^{-1}. Anal. Calcd for $C_6H_{10}Cl_2O$: C, 42.63%; H, 5.96%. Found: C, 42.82%; H, 5.67%.

Reaction of 4 with HBr: Representative Procedure. A mixture of 2.0 g (11.8 mmol) of 4 and 4.0 g (23.7 mmol) of 48% HBr under N_2 in a 50-mL flask was immersed into a water bath pre-heated to 85° C and allowed to stir at that temperature for 20 min. The water bath was removed and 30 mL of ice/water was added to the flask. Products were extracted with ether (3 x 15 mL) an dried over $MgSO_4$. Removal of solvent by rotary evaporation afforded 2.31 g of pale yellow oil. See Table 1 for the specific conditions of other experiments.

Volatile components were removed from the crude by vacuum line transfer at 30° C/0.2 mm and separated by preparative vpc using a 16' x 1/4" column packed with 20% Carbowax 20M on 45/60 Chromosorb WAW at 170° C (He flow: 30 mL/min). These products, characterized below, are listed in their order of emergence from the column.

9: ^1H NMR δ1.92 (br s,3H), 4.81 (br s,1H), 5.07 (m,1H); ^{13}C NMR δ22.8, 25.1, 37.0, 60.0, 114.1, 139.6; vpc retention time and spectral data identical to the minor product from the reaction of isoprene with dichlorocarbene.

5: ^1H NMR δ1.77 (br s,3H), 1.85 (br s,3H), 5.98 (d of multiplets, J=10.9,1H), 6.62 (d,J=10.9,1H); ^{13}C NMR δ18.9, 26.2, 118.9, 119.6, 125.5, 139.9; MS consistent with that reported by Szabo et al.[5]

10: ^{13}C NMR δ27.7, 29.3, 34.6, 84.5, 176.9; ^1H NMR and IR absorptions consistent with those reported by Meyers.[11]

11: Obtained in an enriched mixture with 6 and identified by comparison of spectral data for the mixture with that of 11 synthesized as described below.

6: ^1H NMR δ1.72 (br s,3H), 1.82 (br s,3H), 3.46 (br d,J=7.2,2H), 5.43 (t of multiplets,J=7.2,1H); ^{13}C NMR δ18.6, 26.0, 55.1, 82.7, 117.7, 138.8; MS: m/e 236, 234, 232, 230 (M^+, 0.6, 4.7, 10.6, 6.7%); 155, 153, 151 (M^+-Br, 6.7, 27.2, 30.9%); 136, 134 (M^+-$C_2H_2Cl_2$, 29.9, 30.5%); 69 (M^+-$CBrCl_2$, 100%). Anal. Calcd for $C_6H_9BrCl_2$: C, 31.07%; H, 3.91%. Found: C, 30.90%; H, 3.78%.

The solid material remaining after removal of volatiles was recrystallized from hexane at -20° C to give a white crystalline product, mp 53.0-53.5° C, which appeared to be a eutectic mixture of **7** and **8** in a ratio of 87.5 mole % of **7** to 12.5 mole % of **8**. Anal. Calcd. for a mixture of $C_6H_{10}Br_2Cl_2$ (87.5 mole %) and $C_6H_{10}BrCl_3$ (12.5 mole %): C, 23.45%; H, 3.28%. Found: C, 23.62%; H, 3.25%. Pure **7** could not be obtained by repeated recrystallizations of this mixture. Structural assignments were based on the dehydrohalogenation experiment described below, consistent spectral data, and a comparison with the spectral data of 1,1,1,4-tetrachloro-4-methylpentane (from reaction of **4** with HCl under the conditions of Run 1).

7: ^{1}H NMR δ1.83 (s,6H), 2.12-2.36 and 2.92-3.20 (AA'BB' pattern,4H); ^{13}C NMR δ34.4, 44.3, 53.9, 63.9, 81.4.

8: ^{1}H NMR δ1.63 (s) with other signals obscured by **7**; ^{13}C NMR δ32.6, 42.9, 52.7, 68.1, 81.6.

Bromide **11**. Phosphorus tribromide (0.30 g, 1.1 mmol) was added to 0.35 g (2.1 mmol) of **4** at 0° C under N_2. After 1 h at 0° C, the reaction mixture was diluted with 2 mL of $CHCl_3$ and decanted from a small amount of brown oil which separated. The solution was washed with 1 mL of 10% $NaHCO_3$, dried over Na_2SO_4, and concentrated by rotary evaporation. Distillation of the residual liquid gave 0.32 g (66%) of **11**, bp 35-36° C/0.25 mm, contaminated with 2% of the isomer **6**. ^{1}H NMR δ1.87 (s) and 1.97 (s) [diastereotopic CH_3's] , 1.50-2.50 (ABC pattern, ring protons, 3H); ^{13}C NMR δ25.7, 32.6, 33.0, 43.3, 60.0, 62.1.

Dehydrohalogenation of **7** and **8**. A solution of 1.10 g (3.6 mmol) of a mixture of 87.5 mole % of **7** and 12.5 mole % of **8** in 5 mL of ether was cooled to 0° C and 1.30 g (8.5 mmol) of 1,8-diazabicyclo[5.4.0]undec-7ene (DBU) was added. The solution was stirred for 21 h at room temperature during which a dark brown semisolid separated. The reaction mixture was diluted with 10 mL of ether, washed once with 10 mL of water and once with 10 mL of 5% HBr, and dried over $MgSO_4$. Removal of the solvent *in vacuo* and bulb-to-bulb transfer of the residual liquid at 25° C/0.1 mm gave 0.50 g (93%) of pure **5**.

2,2-Dichloro-1-methyl-1-isopropenylcyclopropane **14**. A solution of 16.4 g (0.20 mol) of 2,3-dimethyl-1,3-butadiene, 28.7 g (0.24 mol) of $CHCl_3$, and 300 mg of benzyltriethylammonium chloride was added all at once to 60 mL of degassed 50% NaOH at 0° C under N_2. The mixture was mechanically stirred for 3 h at 0° C and then for 17 h at room temperature. Water (100 mL) was added and the product was extracted with petroleum ether (3 x 20 mL). Extracts were combined, dried over $MgSO_4$, and concentrated by rotary evaporation. Distillation of the residual oil gave 24.5 g (74%) of pure **14**, bp 69-70° C/32 mm (lit.[12] 52.5° C/21 mm).

Trifluoroacetate **15**. A solution of 3.3 g (0.02 mol) of **14** and 2.3 g (0.02 mol) of trifluoroacetic acid was allowed to stand at room temperature under N_2 for 48 h. NMR analysis of an aliquot indicated a 90% conversion.[13] Distillation of the reaction mixture using a 5-cm Vigreaux column gave a 4.6 g (82%) fraction boiling at 82-86° C/25 mm which proved to be pure **15**: ^{1}H NMR δ1.76 (br s,3H), 1.83 (br s,6H), 3.42 (br s,2H); ^{13}CNMR δ20.1, 21.2, 21.8, 53.7, 108.8, 113.9 (CF_3,q,J_{C-F}=286 Hz), 120.1, 134.8, 152.2 (C=O,q,J_{C-F}=45 Hz); IR 1818 cm^{-1} ($\nu_{C=O}$); MS: m/e 282, 280, 278 (M^+, 1.0, 6.9, 10.8%); 168, 166, 164 ($M^+-CF_3CO_2H$, 2.7, 11.0 16.8%); 83 ($M^+-CF_3CO_2CCl_2$, 89.7%). Anal. Calcd for $C_9H_{11}Cl_2F_3O_2$: C, 38.73%; H, 3.97%. Found: C, 38.50%; H, 4.02%.

Acid **17**. A mixture containing 2.00 g (7.1 mmol) of **15**, 5 mL of THF, 15 mL of water, and 2.5 g of $NaHCO_3$ was allowed to stir at room temperature for 3 h in an open 100-mL flask (caution: foaming). The pH was then adjusted to a Congo Red end point by dropwise addition of conc. HCl and the aqueous layer was saturated with NaCl. Product was extracted with ether (3 x 10 mL) and the combined extracts were dried over $MgSO_4$. After removal of volatiles by rotary evaporation, the residual liquid was distilled to give 0.67 g (74%) of pure **17**, bp 52-53° C/0.5 mm (lit.[14] bp 86-90° C/5 mm).

Ester **19**. A solution of 2.55 g (9.1 mmol) of **15** in 10 mL of absolute methanol was stirred at room temperature for 24 h. Volatile materials were removed by rotary evaporation of the reaction mixture, and the residual liquid was distilled to give 1.05 g (81%) of pure **19**, bp 85-87° C/36 mm (lit.[14] bp 61-62° C/10 mm).

Amide **20**. A mixture of 1.40 g (5.0 mmol) of **15** and 5 mL of conc. aqueous NH_3 was prepared at 0° C and then allowed to stir at room temperature for 24 h. The solution was diluted with 25 mL of brine and extracted with ether (3 x 15 mL). Extracts were combined, dried over $MgSO_4$, and concentrated by rotary evaporation. The crude solid residue was recrystallized from benzene to give 0.35 g (55%) of pure **20**, mp 135.5-136.5° C. ^{1}H NMR δ1.68 (s,9H), 2.97 (s,2H), 5.7 (br s,2H); IR 657, 1217, 1400, 1624, 1658, 3180, 3360 cm^{-1}. Anal. Calcd for $C_7H_{13}NO$: C, 66.11%; H, 10.30%. Found: C, 66.13%; H, 10.22%.

Bromochlorocarbene adduct **23**. A solution of 45.9 g (0.22 mol) of dibromochloromethane in 20 mL of hexane was added dropwise over 30 min to a mechanically stirred slurry of 40.0 g (0.36 mol) of potassium *t*-butoxide in a solution of 30.6 g (0.45 mol) of isoprene and 125 mL of hexane at 0° C. After complete addition, the reaction mixture was allowed to stir at room temperature for 18 h. Water (100 mL) was added to dissolve the salts, and the organic layer was separated

and washed with 50 mL of brine. The organic layer was dried over Na_2SO_4 and concentrated by rotary evaporation. Distillation of the residual oil gave 26.1 g (61%) of colorless liquid, bp 60-62° C/22 mm, which proved to be a 50:50 (approx.) mixture of the diastereomers [15] of **23**: ^1H NMR δ1.43-1.76 (overlapping doublets, 2H), 1.50 and 1.52 (2 singlets, 3H), 5.10-5.40 (m,2H), 5.72-6.10 (overlapping d of d, 1H); ^{13}C NMR δ (all carbon lines doubled except the non-halogenated 4°) 19.0 and 22.1, 31.9, 33.8 and 34.1, 52.9 and 53.4, 115.9 and 116.1, 138.5 and 140.9. Anal. Calcd for C_6H_8BrCl: C, 36.86%; H, 4.12%. Found: C, 36.75%; H, 4.17%.

Reaction of **23** with HCl. A mixture of 5.0 g of **23** and 10 mL of conc. HCl was heated at 100° C for 2 h. The reaction mixture was diluted with 40 mL of ice/water and extracted with ether (3 x 10 mL). Extracts were combined, dried over $MgSO_4$, and concentrated by rotary evaporation. Distillation of the residual oil gave, after a forerun of starting material, 1.8 g of a complex mixture boiling at 60-80° C/1.0 mm. The major product (36 wt %) had a vpc retention time identical to that for the major product from reaction of **21** with HBr. ^1H and ^{13}C NMR spectra of an enriched sample of this compound isolated by preparative vpc were consistent with those obtained from the major product of the reaction of **21** with HBr and in excellent agreement with the spectral data reported for **2**.[1]

Acknowledgment

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3. When a 7:1 mixture of **7**:**8** was heated at reflux for 4 h in pure water, the aqueous layer became strongly acidic. In the complex organic mixture recovered by ether extraction, two major products were observed in approximately equal concentrations: The lactone **10** and an alkene identified tentatively a 4-bromo-1,1-dichloro-4-methyl-1-pentene. Small amounts of **5** and **6** were also produced and traces of **7** and **8** were recovered.
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15. The distilled product also contained approximately 3% of 2-bromo-2-chloro-1-isopropenylcyclopropane from carbene addition to the monosubstituted double bond.