Silver Ion-assisted Methanolysis of Some Functionalized Bromocyclopropane Derivatives

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gem-Dibromo- and bromocyclopropanes have been solvolyzed in methanol at 20–65 °C in the presence of silver trifluoroacetate. Acyl- and alkoxy carbonyl-substituted dibromides are unreactive whereas alkenyl-substituted analogs undergo ringopening and give mainly 1,3- and 1,4-bromodi enes and small amounts of allene. The monobromocyclopropanes are more reactive than the dibromides; thus acyl- and alkenylbromocyclopropanes, but not alkoxy carbonylbromocyclopropanes solvolyze to 1,3- and 1,4-di enes. Most 1,3-di enes are formed as E/Z mixtures with the E isomer predominating.

When gem-dihalo- and halocyclopropanes are treated with silver salts under solvolytic conditions allylic derivatives and/or dienes are generally formed due to opening of the ring.1 10 The reaction has mainly been employed to achieve ring expansion when the halocyclopropane moiety has been a part of bi- or polycyclic structures.1 4 8 10 Only a few reports1 5 have been published on the application of this reaction for the synthesis of acyclic unsaturated compounds, although the high yield obtained in several cases indicates that electrocyclic ring-opening of halocyclopropanes may represent an attractive synthetic route to such compounds.

We have for some time been interested in preparing conjugated and skipped acyclic π systems with a functional group in allylic position. Such compounds may conceivably be made from gem-dihalo- and halocyclopropanes as outlined above if unsaturated substituents are attached to the ring. In the present paper our efforts toward the preparation of allyl methyl ethers by silver ion-promoted methanolysis are reported.

RESULTS

The substrates (1 and 2) were prepared in good yields by literature procedures and were treated with silver ion in absolute methanol at 20 and 65 °C. Exploratory experiments revealed that silver nitrate and silver acetate were less reactive than silver trifluoroacetate.

\[ \text{1 and 2.} \]
\[ a, R=\text{H, } X=\text{CH}_2; \quad b, R=\text{CH}_3, X=\text{CH}_2; \quad c, R=\text{CH}_3, X=\text{O}; \quad d, R=\text{OCH}_3, X=\text{O}; \]
\[ e, R=\text{OCH}_2\text{CH}_3, X=\text{O}. \]

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Scheme 1.

\( a, \, R=H; \, b, \, R=\text{CH}_3. \)

which therefore was exclusively employed throughout this study. The reaction mixtures were analyzed by GLC prior to work-up of the products by distillation or column chromatography.

When methanol solutions of the gem-dibromocyclopropanes 1 were treated with silver trifluoroacetate the alkenyl-substituted derivatives 1a and 1b reacted whereas esters 1d and 1e were recovered unchanged even after 6 d at 65 °C. Ketone 1c reacted very sluggishly and gave a complex product mixture; after 6 d in refluxing methanol only 20% of the starting material had been converted to at least 13 minor products, none of which were identified. Both 1a and 1b reacted to give three major products, viz. the skipped diene 3, the conjugated diene 4, and the allene 5, (Scheme 1), in addition to several minor products. The product distribution varied with the reaction conditions, particularly the reactant concentrations and the reaction temperature, but under any set of conditions the allene was formed in lowest yield (3–8%) (Table 1). The presence of the allene linkage was evident from a medium IR absorption at 1960 cm\(^{-1}\) and a characteristic singlet for the \( sp \)-hybridized allene carbon atom around 207 ppm in the \( ^{13} \)C NMR spectra. In most cases the main product was the 1,4-diene which was stable under the experimental conditions employed.

The conjugated dienes (4) were formed in 20–30% yield in most reactions (Table 1). 4-Bromo-5-methoxy-3-methyl-1,3-pentadiene (4a) was obtained as a 3:2 isomeric mixture

**Table 1.** Product distribution in reactions of 1a and 1b with silver trifluoroacetate in methanol for 144 h.

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Concentration/M Ag(I)</th>
<th>Reaction temp.(^{\circ})C</th>
<th>1</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>0.12</td>
<td>0.17</td>
<td>20</td>
<td>55</td>
<td>15</td>
<td>22</td>
</tr>
<tr>
<td>1b</td>
<td>0.12</td>
<td>0.17</td>
<td>65</td>
<td>8</td>
<td>43</td>
<td>29</td>
</tr>
<tr>
<td>1a</td>
<td>1.04</td>
<td>1.49</td>
<td>65</td>
<td>6</td>
<td>52</td>
<td>14</td>
</tr>
<tr>
<td>1b</td>
<td>0.11</td>
<td>0.18</td>
<td>20</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1b</td>
<td>0.11</td>
<td>0.18</td>
<td>65</td>
<td>45</td>
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<td>1b</td>
<td>0.50</td>
<td>1.04</td>
<td>65</td>
<td>25</td>
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<td>43</td>
</tr>
</tbody>
</table>

\[^a\] Percentage of reaction mixture as determined by GLC and \( ^{1} \)H NMR analyses; for isolated yields, see Experimental.

according to $^1$H NMR spectra and GLC analysis, but the configuration of the predominant isomer is not unequivocally established. However, if the proton NMR signal, due to the methyl group attached to C-3, appears at a lower field for the Z than for the E isomer which is the case with 5-methoxy-3-methyl-1,3-pentadiene (vide infra), then 4a consists predominantly (60%) of the E isomer. This conclusion is also the most reasonable one from a mechanistic point of view (vide infra). 4-Bromo-5-methoxy-2,3-dimethyl-1,3-pentadiene (4b) was most likely formed as a single isomer; GLC analyses gave only a single peak for the compound on a variety of columns and the $^1$H NMR spectrum showed single signals, not pair of signals, for the methyl groups attached to C-2 and C-3.

When monobromides 2 were treated with silver trifluoroacetate in methanol the acetyl- and alkenyl-substituted compounds 2a–2c underwent ring-opening reactions to give product mixtures less complex than those obtained from solvolysis of the corresponding dibromides. With the exception of 2b which also gave a few minor, unidentified compounds, the products from these reactions consisted of the unconjugated and the conjugated unsaturated compounds 6 and 7 (Scheme 2). The relative yields were dependent on the reaction conditions (Table 2). Thus, solvolysis of 2-acetyl-1-bromo-2-methylcyclopropane (2c) did not take place at 20 °C, but at 65 °C 3-methoxy-3-methyl-4-penten-2-one (6c) and 5-methoxy-3-methyl-3-penten-2-one (7c) were formed as a 1:7 mixture in 64% total yield. The alkenyl-substituted bromocyclopropanes 2a and 2b, on the other hand, underwent ring-opening even at 20 °C to give mixtures of the corresponding dienes in very good yield. The conjugated dienes are formed in higher yield than the skipped ones (Table 2), a fact which reflects the relative stability of these dienes. Therefore, it is not surprising that a 1:2 mixture of 6a and 7a is completely converted to 7a when refluxed in methanol.

Dienes 7a and 7b were formed as mixtures of the E and Z isomers according to their $^1$H NMR spectra which could be used to determine the configuration of the predominant isomer. This is borne out most clearly for 7a whose proton spectrum is shown in Fig. 1. Each isomer gives rise to a signal around 1.8 ppm due to the methyl group attached to C-3. The

![Fig. 1. The 400 MHz $^1$H NMR spectrum of a 3:2 mixture of the E and Z isomers of 5-methoxy-3-methyl-1,3-pentadiene (7a). The peak marked with asteric is due to a contaminant.](image-url)

Scheme 2.

- $a$, $R=H$, $X=CH_2$; $b$, $R=CH_3$, $X=CH_2$; $c$, $R=CH_3$, $X=O$.

A low-field signal appears as a doublet with $|J|=1.6$ Hz due to allylic coupling with the proton attached to C−4. The more intense high-field signal, on the other hand, is essentially a singlet which reveals that the allylic coupling constant in this isomer is very small ($|J|<0.5$ Hz). Since $|J|_{allylic}$ generally is larger for a cis coupling than for a trans coupling in the same molecule, the $^1$H NMR spectrum indicates that 7a consists predominantly of the $E$ isomer. This conclusion is supported by nuclear Overhauser enhancement studies. Thus, irradiation of the methyl group at 1.87 ppm results in the enhancement of the high-field $H_4$ multiplet (Fig. 2a) whereas irradiation of the methyl group at 1.77 ppm results in no NOE effect, but an INDO signal for the low-field $H_4$ multiplet (Fig. 2b). Therefore, the least abundant isomer carries the methyl group cis related to $H_4$; consequently, the predominant isomer has the $E$ configuration.

5-Methoxy-2,3-dimethyl-1,3-pentadiene (7b) was not isolated as pure as 7a and conclusive evidence regarding the isomeric composition could therefore not be obtained by decoupling and NOE experiments. However, the $^1$H NMR spectrum of 7b was similar to that of 7a in several respects: (a) the minor isomer gives rise to the signal in the lowest field.

Table 2. Product distribution in reactions of 2a−2c with silver trifluoroacetate in methanol.

<table>
<thead>
<tr>
<th>Starting material $(E/Z)$</th>
<th>Concentration/M</th>
<th>Reaction Temp.$^\circ$C</th>
<th>Time/h</th>
<th>Yield/%$^a$</th>
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<tr>
<td>2a $(46/54)$</td>
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<tr>
<td>2b $(64/36)^b$</td>
<td>0.82</td>
<td>1.24</td>
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<td>2b $(64/36)$</td>
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<tr>
<td>2c $(73/27)$</td>
<td>0.75</td>
<td>1.24</td>
<td>65</td>
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<td>0.75</td>
<td>1.24</td>
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</table>

$^a$ Percentage of reaction mixture as determined by GLC and $^1$H NMR analyses; for isolated yields, see Experimental. $^b$ Several minor unidentified products were formed in 5 % total yield.

Fig. 2. Parts of the $^1$H—$^1$H NOE difference spectra of a 3:2 mixture of the $E$ and $Z$ isomers of 5-methoxy-3-methyl-1,3-penta-
diene (7a). a Irradiation of the methyl signal at 1.87 ppm. b Irradiation of the methyl signal at 1.77 ppm.

of the signals around 1.8 ppm which are due to the methyl groups attached to C-2 and C-3, (b) this low-field signal is the broadest one in this region of the spectrum, (c) the major isomer gives rise to the lower-field methoxy singlet of the two around 3.3 ppm. It is therefore reasonable to believe that also the predominant isomer of 7b has $E$ configuration.

Finally, the conjugated enone 7c was formed as a single isomer according to gas chromatographic analyses under a variety of conditions and the proton NMR spectrum which contains only one signal or one group of signals for each of the substituents and the equivalent hydrogen atoms attached to the 3-penten-2-one carbon skeleton. The NMR data permit assignment of the configuration of the C=C bond by comparison with data of pertinent analogs. One such compound is 4-ethyl-6-hydroxy-4-hexen-3-one whose $E$ and $Z$ isomers give a triplet for the olefinic proton at 6.72 and 5.65 ppm, respectively. Since 7c exhibits essentially a triplet at 6.51 ppm the configuration of 7c is most likely $E$.

Bromocyclopropane esters 2d and 2e are quite unreactive under the reaction conditions employed. Neither methyl 2-bromo-1-methylcyclopropanoate nor the corresponding ethyl ester underwent ring-opening reactions; 2d was recovered quantitatively even after 144 h in refluxing methanol whereas ethyl 2-bromo-1-methylcyclopropanoate (2e) was converted to 2d in modest yield (17%). Interestingly, only the $E$ isomer suffered transesterification (Scheme 3). This reaction is obviously catalyzed by silver trifluoroacetate since the yield of $E$-2d is only 5% when the reaction is carried out in the absence of the salt.

\[
\begin{align*}
\text{COOEt} & \quad \text{AgO}_2\text{CCl}_3 & \quad \text{MeOH} & \quad 65^\circ\text{C}/144\text{ h} \\
E/Z &= 68 / 32 & + & \text{Br} & \quad \text{COOME} \\
\text{Br} & \quad \text{COOEt} & \quad E/Z &= 50 / 33 & \quad 17\%
\end{align*}
\]

Scheme 3.

DISCUSSION

With the exception of the esters 2d and 2e, all the substrates react by initial opening of the cyclopropane ring. This transformation which is exceedingly slow in the absence of silver ion, converts the bromocyclopropanes into allylic cations in a process in which the cyclopropyl substituent cis to the leaving group rotates inward and that trans to the leaving group.
group rotates outward (Scheme 4).\textsuperscript{1,3,19} gem-Dibromocyclopropanes (X=Br) with R\neq CH\textsubscript{3} and E/Z mixtures of bromocyclopropanes (X=H) both contain two differently situated bromines. Two disrotatory processes can therefore be envisaged for each one of the starting materials 1 and 2, a) loss of the bromine atom cis to the methyl group to give a trans-allylic cation 8, and b) loss of the bromine atom cis to the R group to give the cis-allylic cation 9 (Scheme 4). Generally the two processes have different rate constants;\textsuperscript{5} if R is bulkier than the methyl group inward rotation of R to give 9 (mode b) is less favourable than rotation of R in the opposite direction to give 8 (mode a), \textit{i.e.} $k_a > k_b$. As a result of this, the gem-dibromocyclopropanes (X=Br) should ring-open mainly in one mode whereas the \textit{E} isomer of a monobromocyclopropane (X=H) should undergo ring-opening faster than the corresponding \textit{Z} isomer. Provided cation 8 is more stable than 9 and $k_b > k_9$ which is generally the case,\textsuperscript{20} one would therefore expect that the primary products from methanolysis of 1 and 2 predominantly result from quenching of 8 with methanol.

From these mechanistic considerations it is evident that the ring-opening is influenced by electronic effects. This influence is clearly demonstrated by the results compiled in Tables 1 and 2. Thus, the rate of solvolysis of the gem-dibromocyclopropanes is considerably smaller than that of the corresponding monobromocyclopropanes. Such an inhibition by a second halogen atom is characteristic of a reaction whose rate-determining step involves heterolytic cleavage of a C–Br bond to form an allylic cation with a bromine atom attached to C-2.\textsuperscript{5} Furthermore, the alkenyl-substituted cyclopropanes 1\textit{a}, 1\textit{b}, 2\textit{a}, and 2\textit{b} solvolyze much more rapidly than the corresponding acyl- and alkoxycarbonyl-substituted derivatives due to the destabilization of the allylic cation by electron-accepting substituents. As a matter of fact, alkoxycarbonyl groups render the bromo- and dibromocyclopropane moieties so unreactive that no ring-opening at all takes place under the experimental conditions employed. This may partly be caused by a deactivation of silver ion by silver-oxygen coordination.

Ring-opening of the alkenyl-substituted bromo- and dibromocyclopropanes 1\textit{a}, 1\textit{b}, 2\textit{a}, and 2\textit{b} generates the pentadienyl cation 10 (Fig. 3) which can react with methanol. Interestingly, most product mixtures consisted almost completely of dienes resulting from reaction at carbon atoms 1 and 3. In most cases, conjugated dienes are formed predominantly from 10 by reaction of methanol at the least nucleophilic, but most easily accessible carbon atom. This is in part due to the reaction conditions which favour formation.

of the thermodynamically most stable products, viz. the conjugated dienes; thus, when a mixture of 3-methoxy-3-methyl-1,4-diene (6a) and the corresponding 1,3-diene (7a), obtained by solvolysis of 2a at 20 °C, was stirred at 65 °C, the skipped diene 6a was quantitatively converted into the conjugated analog 7a. Similar results were obtained when 2-acyl-1-bromo-2-methylcyclopropane (2c) was solvolysed; the conjugated enone was formed in higher yield than the unconjugated analog (Table 2).

Most of the conjugated products (4 and 7) were formed as E/Z isomer mixtures, a result which is not surprising on the basis of the reaction mechanism presented in Scheme 4. Generally the E isomer predominates and this is the case even when a 46/54 mixture of E-2a/Z-2a is solvolysed. Cation 9 (Scheme 4) is therefore configurationally unstable and rearranges partly to 8 prior to product formation. This result is in accordance with the observation that the cis, cis and cis, trans isomers of 1,3-dimethylallyl carbocation isomerize smoothly into the trans, trans isomer at 35 °C. 20

Possible products from solvolysis of monobromide 2b and dibromides 1a and 1b are conjugated dienes resulting from pentadienyl cation 10 (Fig. 3) by reaction of methanol at C-5. However, such products were not detected which is somewhat surprising since silver ion-assisted methanolysis of 2b in the presence of 2,6-lutidine gives a compound due to such a reaction, viz. 5-methoxy-2,3-dimethyl-1,3-pentadiene, in 24% yield. 21 The formation of this compound is most likely attributable to the reaction medium which is considerably more basic than ours. However, the transient existence of conjugated dienes formed from cation 10 by methanol attack at carbon atom 5, is indicated by the formation of 4,5-dimethoxy-1,2-pentadiene derivatives (5) (Table 1) as outlined in Scheme 5. Methanol attack at C-5 (Step 2) will give, unlike attack at C-1, a substituted 2-bromo-1,3-butadiene (11) which belongs to

Scheme 5.

a group of compounds that shows remarkable solvolytic reactivity in alcoholic solvents even in the absence of silver ions. Diene 11 will therefore ionize to the mesomeric cation I2 (Step 3) with a rate comparable to that of ring-opening of the halocyclopropanes. Cation I2 contains two electrophilic centres, viz. C-2 and C-4, but generally 5-membered ring products were not detected in any reactions. Conceivably this is due to the fact that 10 does not attain the U-configuration, a prerequisite for ring-closure, before any reaction with the solvent takes place.

From a synthetic point of view, silver ion-assisted solvolyis of bromocyclopropanes has limited potential as a general method for selective preparation of conjugated and unconjugated \( \pi \) systems. Some compounds do not undergo ring-opening and in other cases mixtures of conjugated and unconjugated products are obtained. Furthermore, several of the conjugated dienes are formed as mixtures of the \( E \) and \( Z \) isomers.

**EXPERIMENTAL**

Column chromatography (CC) was carried out using Kieselgel 60 (0.063–0.200 mm) (Merck). GLC analyses were carried out on a Varian 3700 gas chromatograph equipped with thermal conductivity and flame ionization detectors. The columns were 2 m long and were packed with 3% OV17, 10% OV101, or 10% Carbowax 20M on Chromosorb W-HP, 80/100. IR spectra were recorded on a Shimadzu IR 420 spectrophotometer. NMR spectra were obtained on Jeol PMX60 si and Jeol FX 90Q spectrometers, using tetramethylsilane as internal standard. The nuclear Overhauser enhancement (NOE) studies were performed on a Bruker WH 400 spectrometer. Mass spectra were run on a Micromass 7070 H spectrometer, operated in the EI mode with an ionization potential of 70 eV. Boiling points are uncorrected.

The \( \text{gem} \)-dibromo- and bromocyclopropane derivatives were synthesized as described in the literature. **Silver trifluoroacetate-assisted methanalysis of the bromocyclopropanes; general procedure.** The reaction was carried out under dry conditions. A solution of bromocyclopropane (1.0 mmol) and silver trifluoroacetate (AgTFA) (1.4–1.6 mmol) in dry methanol (0.9–9.1 ml) was stirred at 20 or 65 °C in the dark for 0.5–144 h (see Tables 1 and 2). The reaction mixture was analyzed by GLC before the reaction was stopped by thorough extraction (6×50 ml) with ether or pentane. The combined extracts were washed with water (4×20 ml) and dried (MgSO\(_4\)). Evaporation of the solvent left a residue which was analysed by GLC and NMR-spectroscopy prior to isolation of the products by column chromatography with dichloromethane and chloroform as eluants.

The purity of the products was seldom better than 95% according to GLC analysis. Therefore, a satisfactory elemental analysis was difficult to achieve.

**Reactions of 1,1-dibromo-2-methyl-2-vinylcyclopropane** (1a). Treatment of 1a with AgTFA gave mainly two products at 20 °C and three products at 65 °C. Almost all of the starting material was consumed when the reaction was performed in a concentrated solution at 65 °C (Table 1). Work-up of this reaction mixture by CC with chloroform as eluant gave 2-bromo-3-methoxy-3-methyl-1,4-pentadiene (3a) (45%), 4-bromo-5-methoxy-3-methyl-1,3-pentadiene (4a) (8%), and fairly impure 4,5-dimethoxy-3-methyl-1,2-pentadiene (5a) (7%). 3a: IR (film): 1620, 1095, 990, 920, 895 cm\(^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\)): \( \delta \) 1.48(3H,s), 3.23(3H,s), 5.15–6.00(5H,m); \(^13\)C NMR (22.5 MHz, CDCl\(_3\)): \( \delta \) 22.6(CH\(_3\)), 50.7(CH\(_3\)), 80.3(C), 115.7(CH\(_2\)), 118.3(CH\(_2\)), 138.2(C), 139.4(CH); MS [70 eV, m/e (% rel. int.): 191(0.4), 189(0.4), 177(9.2), 175(9.4), 165(6.8), 163(7.0), 135(2.5), 133(3.1), 131(1), 129(1), 127(1), 125(1), 123(1), 121(1), 119(1)]
Reactions of 1,1-dibromo-2-isopropenyl-2-methylcyclopropane (1b). Treatment of 1b with Ag TFA gave no product at 20 °C but mainly three products at 65 °C. Most of 1b was consumed when the reaction was carried out at 65 °C in a concentrated solution. CC with dichloromethane and chloroform as eluants gave 2-bromo-3-methoxy-3,4-dimethyl-1,4-pentadiene (3b) (17 %), 4-bromo-5-methoxy-2,3-dimethyl-1,3-pentadiene (4b) (35 %), and 4,5-dimethoxy-3,4-dimethyl-1,2-pentadiene (5b) (6 %). 3b: IR (film): 1625, 1090, 995, 903 cm⁻¹; ¹H NMR (90 MHz, CDCl₃): δ 1.20 (3H, s), 1.28 (3H, m), 3.20 (3H, s), 5.05–6.01 (4H, m); ¹³C NMR (22.5 MHz, CDCl₃): δ 18.5 (CH₃), 20.5 (CH₃), 50.7 (CH₃), 82.9 (C), 114.5 (CH₂), 118.6 (CH₃), 137.5 (C), 144.8 (C); MS [70 eV, m/e (% rel. int.)]: 206 (0.6 M⁺), 204 (0.6, M⁺), 192 (0.8), 191 (10), 190 (0.8), 189 (10), 175 (2.5), 174 (2.5), 173 (2.3), 172 (2.0), 165 (41), 163 (42), 135 (7.8), 133 (8.6), 125 (10, M⁺ – Br), 110 (31), 99 (92); mol. wt., obs. 206.021, calc. for C₉H₈BrO 206.013. 4b: IR (film): 1630, 1102, 900 cm⁻¹; ¹H NMR (90 MHz, CDCl₃): δ 1.87 (3H, dd, J 1.0 and 1.5 Hz), 1.93 (3H, s), 3.37 (3H, s), 4.25 (2H, s), 4.77 (1H, broad s), 4.97 (1H, J 1.5 Hz); ¹³C NMR (22.5 MHz, CDCl₃): δ 19.6 (CH₃), 20.6 (CH₃), 57.5 (CH₃), 73.8 (CH₃), 113.1 (CH₂), 115.9 (C), 143.3 (C), 147.7 (C); MS [70 eV, m/e (% rel. int.)]: 206 (0.3, M⁺), 204 (0.3, M⁺), 191 (1.9), 189 (1.9), 165 (3.6), 163 (4.1), 121 (32), 119 (100), 117 (99), 110 (3.0), 99 (8), 86 (13). 5b: IR (film): 1960, 1120, 850 cm⁻¹; ¹H NMR (90 MHz, CDCl₃): δ 1.31 (3H, s), 1.67 (3H, t, J 3.2 Hz), 3.15 (3H, s), 3.39 (5H, s); ¹³C NMR (22.5 MHz, CDCl₃): δ 14.0 (CH₃), 20.7 (CH₃), 49.7 (CH₃), 59.1 (CH₃), 65.8 (CH₃), 75.1 (C), 77.3 (CH₂), 100.4 (C), 207.9 (C); MS [70 eV, m/e (% rel. int.)]: 156 (0.2 M⁺), 141 (4.3), 125 (4.9), 111 (100), 103 (39), 81 (15), 79 (20), 77 (16), 71 (55); mol. wt., obs. 156.115, calc. for C₈H₁₅O₂ 156.115.

Reactions of 1-bromo-2-methyl-2-vinylcyclopropane (2a). When an isomeric mixture of 2a reacted with Ag TFA at 65 °C 5-methoxy-3-methyl-1,3-pentadiene (7a) was isolated in the quantitative yield. The ¹H NMR spectrum (400 MHz) is shown in Fig. 1. IR (film): 1615, 1105, 990, 830 cm⁻¹. ¹³C NMR (22.5 MHz, CDCl₃): the E isomer δ 11.9 (CH₃), 57.6 (CH₃), 68.8 (CH₂), 112.3 (CH₂), 128.5 (CH), 136.4 (C), 140.8 (CH); the Z isomer δ 19.6 (CH₃), 57.5 (CH₃), 67.8 (CH₃), 114.9 (CH₂), 126.7 (CH), 133.3 (CH), 135.5 (C). Solvolysis of 2a at 20 °C also gave 3-methoxy-3-methyl-1,4-pentadiene (6a) which was not isolated pure. 6a: IR (film): 1630, 1100, 995, 900 cm⁻¹; ¹H NMR (60 MHz, CCl₄): δ 1.30 (3H, s), 3.12 (3H, s), 5.00–6.00 (6H, m); ¹³C NMR (22.5 MHz, CDCl₃): δ 23.0 (CH₃), 50.3 (CH₃), 77.7 (C), 114.3 (CH₂), 141.7 (CH).
Reactions of ethyl 2-bromo-1-methylcyclopropanoate (2e). A 68:32 mixture of the E and Z isomers of 2e was stirred for 144 h in methanol at 65 °C. When 1.6 equivalents of AgTFA were present, methyl (E)-2-bromo-1-methylcyclopropanoate (E-2d) was formed in 17 % yield according to NMR analyses. In the absence of silver salt, the yield of E-2d was only 5 % when the reactions were carried out under identical conditions.

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