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Silver Ion-assisted Methanolysis of Some Functionalized Bromocyclopropane Derivatives

LEIV K. SYDNES and TOR H. HEMMINGSEN

Department of Chemistry, University of Tromsø, P.O.Box 953, N-9001 Tromsø, Norway

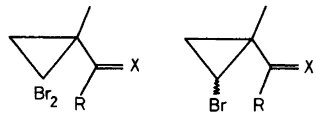
***gem*-Dibromo- and bromocyclopropanes have been solvolyzed in methanol at 20–65 °C in the presence of silver trifluoroacetate. Acyl- and alkoxycarbonyl-substituted dibromides are unreactive whereas alkenyl-substituted analogs undergo ringopening and give mainly 1,3- and 1,4-bromodienes and small amounts of allene. The monobromocyclopropanes are more reactive than the dibromides; thus acyl- and alkenylbromocyclopropanes, but not alkoxycarbonylbromocyclopropanes solvolyze to 1,3- and 1,4-dienes. Most 1,3-dienes 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 reports[1–7] 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



1 and *2*.
a, R=H, X=CH_2; *b*, R=CH_3, X=CH_2; *c*, R=CH_3, X=O; *d*, R=OCH_3, X=O; *e*, R=OCH_2CH_3, X=O.

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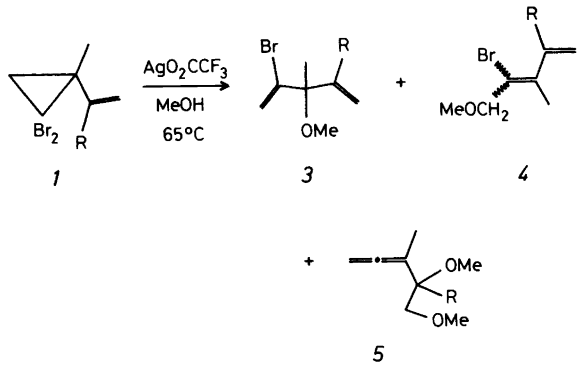


1 3 4 5

Scheme 1.

a, R=H; *b*, R=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[11] at 1960 cm^{-1} and a characteristic singlet for the *sp*-hybridized allene carbon atom around 207 ppm in the ^{13}C NMR spectra.[12] 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.

Starting material	Concentration/M		Reaction temp./°C	Yield/%[a]			
	1	Ag(I)		*1*	*3*	*4*	*5*
1a	0.12	0.17	20	55	15	22	0
1a	0.12	0.17	65	8	43	29	3
1a	1.04	1.49	65	6	52	14	8
1b	0.11	0.18	20	100	0	0	0
1b	0.11	0.18	65	45	29	23	3
1b	0.50	1.04	65	25	22	43	8

[a] Percentage of reaction mixture as determined by GLC and ^1H 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

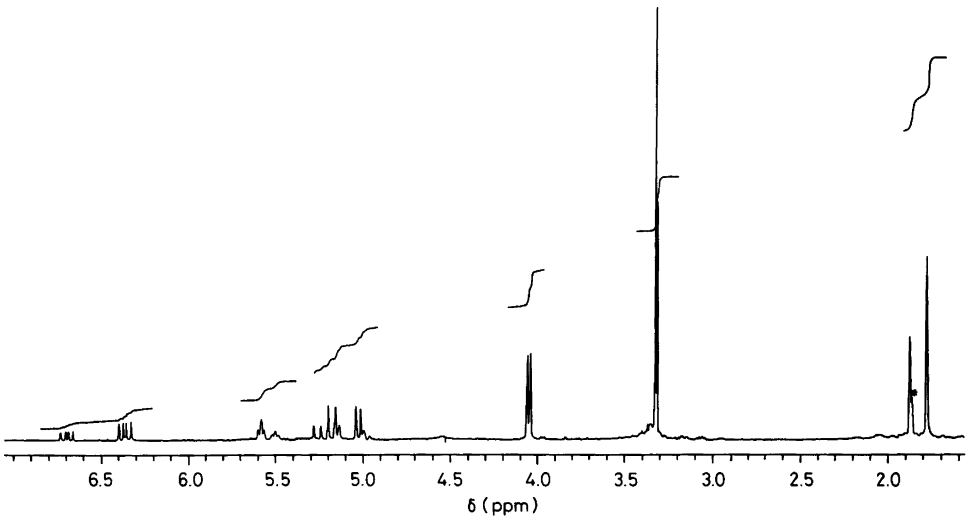
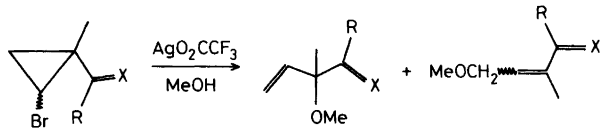


Fig. 1. The 400 MHz ^{1}H NMR spectrum of a 3:2 mixture of the *E* and *Z* isomers of 5-methoxy-3-methyl-1,3-pentadiene (*7a*). The peak marked with asteric is due to a contaminant.



2 6 7

Scheme 2.

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

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,[13] 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 INDOR 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.

Starting material (*E*/*Z*)	Concentration/M		Reaction		Yield/%[a]				
	2	Ag(I)	Temp./°C	Time/h	*2E*	*2Z*	*6*	*7E*	*7Z*
2a (46/54)	0.75	1.08	65	24.0	0	0	0	67	33
2a (46/54)	0.86	1.21	20	3.0	21	33	16	18	12
				23.0	10	22	26	26	16
				45.0	8	17	29	29	17
				68.0	5	12	30	33	20
				92.0	1	5	31	39	24
2b (64/36)[b]	0.82	1.24	65	1.5	0	13	15	46	21
2b (64/36)	0.82	1.24	20	0.5	51	34	2	8	5
				1.0	41	33	4	15	7
				4.0	24	29	7	30	10
				8.5	16	27	7	39	11
				22.5	7	24	8	48	13
				47.5	2	17	10	54	17
				98.5	0	13	11	58	18
2c (73/27)	0.75	1.24	65	144.0	25	11	8	56	0
2c (73/27)	0.75	1.24	20	144.0	73	27	0	0	0

[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.

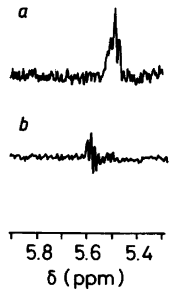
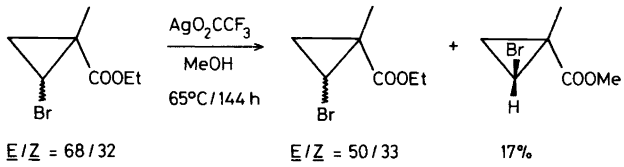


Fig. 2. Parts of the $^1H-\{^1H\}$ NOE difference spectra of a 3:2 mixture of the *E* and *Z* isomers of 5-methoxy-3-methyl-1,3-pentadiene (*7a*). *a* Irradiation of the methyl signal at 1.87 ppm. *b* Irradiation of the methyl signal at 1.77 ppm.

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.[14–18] One such compound is 4-ethyl-6-hydroxy-4-hexen-3-one[17] 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*.

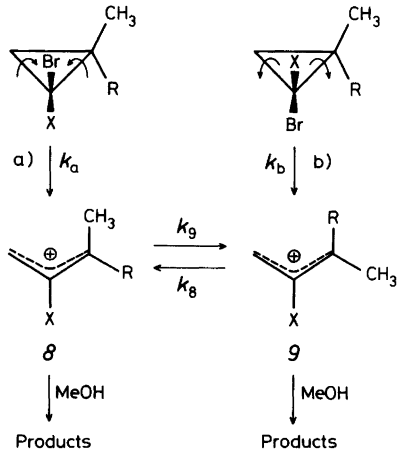
Bromocyclopropane esters *2d* and *2e* are quite unreactive under the reaction conditions employed. Neither methyl 2-bromo-1-methylcyclopropanoate nor the corresponding ethyl ester underwent ring-opening reactions; *2d* was recovered quantitatively even after 144 h in refluxing methanol whereas ethyl 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.



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

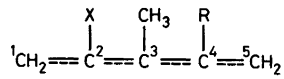


Scheme 4.

group rotates outward (Scheme 4).[1,3,19] *gem*-Dibromocyclopropanes (X=Br) with R≠CH_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;[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), *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 *E* isomer of a monobromocyclopropane (X=H) should undergo ring-opening faster than the corresponding *Z* isomer. Provided cation *8* is more stable than *9* and $k_8 > k_9$ which is generally the case,[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.[5] Furthermore, the alkenyl-substituted cyclopropanes *1a*, *1b*, *2a*, and *2b* 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 *1a*, *1b*, *2a*, and *2b* 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



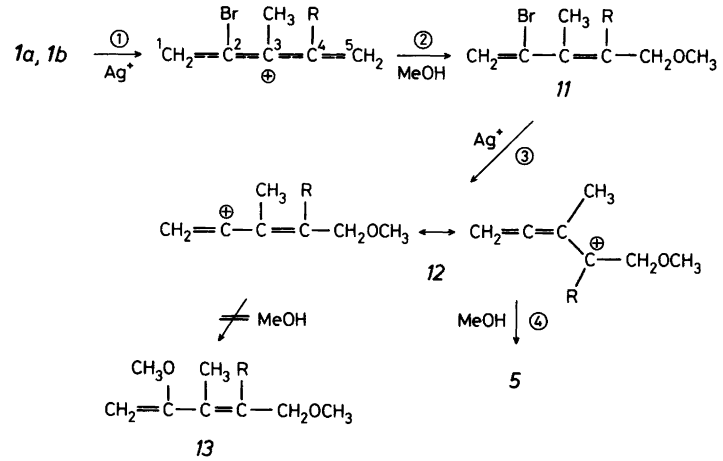
10

Fig. 3. Pentadienyl cation *10*. R=H or CH_3, X=H or Br.

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 solvolyzed; 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 solvolyzed. 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.[22,23] Diene *11* will therefore ionize to the mesomeric cation *12* (Step 3) with a rate[22] comparable to that of ring-opening of the halocyclopropanes.[5,24] Cation *12* contains two electrophilic centres, *viz.* C-2 and C-4, but generally[22] C-4 is predominantly or exclusively attacked so that allene *5* (Step 4) and not vinyl ether *13* ought to be the major product from *11*.

It should also be mentioned that although solvolysis of the alkenyl-substituted bromocyclopropanes involves pentadienyl cation *10* which tends to cyclize readily to cyclopentenyl cations,[25–28] 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 solvolysis of bromocyclopropanes has limited potential as a general method for selective preparation of conjugated and unconjugated π 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 *gem*-dibromo- and bromocyclopropane derivatives were synthesized as described in the literature.[29–30]

Silver trifluoroacetate–assisted methanolysis 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}; ^1H NMR (90 MHz, $CDCl_3$): δ 1.48(3H,s), 3,23(3H,s), 5.15–6.00(5H,m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 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),

111(100), 96(45), 85(90). *4a*: IR (film): 1625, 1090, 990, 905 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$): δ 1.95 and 2.10 (3H, 2 broad s in a ratio of 3:2), 3.20(3H,s), 4.30(2H, broad s), 5.05–6.15(3H,m); MS [70 eV,*m/e* (% rel. int.)]: 192(3.9,M^+), 190(3.7,M^+), 177(2.2), 175(2.5), 160(7.0), 158(7.1), 111(100,M^+-Br), 96(17), 81(30), 80(22), 79(74). *5a*: IR (film): 1960, 860 cm^{-1}; ^{13}C–NMR (22.5 MHz,$CDCl_3$): δ 207.4 (C).

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, $CDCl_3$): δ 1.20(3H,s), 1.28(3H,m), 3.20(3H,s), 5.05–6.01 (4H,m); ^{13}C NMR (22.5 MHz,$CDCl_3$): δ 18.5(CH_3), 20.5(CH_3), 50.7(CH_3), 82.9(C), 114.5(CH_2), 118.6(CH_2), 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(100,M^+-Br), 110(31), 99(92); mol.wt., obs. 206.012, calc. for $C_8H_{13}BrO$ 206.013. *4b*: IR (film): 1630, 1102, 900 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): 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,t,*J* 1.5 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 19.6(CH_3), 20.6(CH_3), 57.5(CH_3), 73.8(CH_2), 113.1(CH_2), 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, $CDCl_3$): δ 1.31(3H,s), 1.67(3H,t, *J* 3.2 Hz), 3.15(3H,s), 3.39(5H,s), 4.71(2H,q, *J* 3.2 Hz); in benzene the 5H singlet at 3.39 ppm is converted to 2 singlets at 3.15(3H) and 3.35(2H) ppm; ^{13}C NMR (22.5 MHz, C_6D_6): δ 14.0 (CH_3), 20.7(CH_3), 49.7(CH_3), 59.1(CH_3), 65.8(CH_2), 75.1(C), 77.3(CH_2), 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 $C_9H_{16}O_2$ 156.115.

Reactions of 1-bromo-2-methyl-2-vinylcyclopropane (2a). When an isomeric mixture of *2a* reacted with AgTFA at 65 °C 5-methoxy-3-methyl-1,3-pentadiene (*7a*)[31] was isolated in quantitative yield. The ^1H NMR spectrum (400 MHz) is shown in Fig. 1. IR (film): 1615, 1105, 990, 905, 830 cm^{-1}; ^{13}C NMR (22.5 MHz, $CDCl_3$): the *E* isomer δ 11.9 (CH_3), 57.6(CH_3), 68.8(CH_2), 112.3(CH_2), 128.5(CH), 136.4(C), 140.8(CH); the *Z* isomer δ 19.6(CH_3), 57.5(CH_3), 67.8(CH_2), 114.9(CH_2), 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, CCl_4): δ 1.30 (3H,s), 3.12(3H,s), 5.00–6.00 (6H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 23.0(CH_3), 50.3(CH_3), 77.7(C), 114.3(CH_2), 141.7(CH).

Reactions of 1-bromo-2-isopropenyl-2-methylcyclopropane (2b). Treatment of *2b* with AgTFA gave some of the *Z* isomer of the starting material and mainly three products at both 20 and 65 °C. Separation of the main products by CC using chloroform as eluant gave 10 % of 3-methoxy-2,3-dimethyl-1,4-pentadiene (*6b*) and 62 % of a 3:2 isomeric mixture of 5-methoxy-2,3-dimethyl-1,3-pentadiene (*7b*). *6b*: IR (CCl_4): 1620, 1105, 990, 920, 910 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 1.34 (3H,s), 1.68(3H,t, *J* 1.3Hz), 3.14(3H,s), 4.85–6.10(5H,m); ^{13}C NMR (22.5 MHz,$CDCl_3$): δ 18.6(CH_3), 21.4(CH_3), 50.2(CH_3), 112.7(CH_2), 113.8(CH_2), 142.2(CH), 147.4(C). *7b*: IR (film): 1620, 1100, 900 cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 1.82 (3H,d, *J* 1 Hz), 1.91 (3H,t, *J* 1 Hz), 3.30 and 3.36 (3H,2s in a ratio of 58:42), 4.15 (2H,m), 5.00–6.05 (3H,m).

Reactions of 2-acetyl-1-bromo-2-methylcyclopropane (2c). Treatment of *2c* with AgTFA gave no product at 20 °C, but 2 products were formed at 65 °C. Isolation by CC with chloroform gave 6 % of impure 3-methoxy-3-methyl-4-penten-2-one (*6c*) and 50 % of 5-methoxy-3-methyl-3-penten-2-one (*7c*). *6c*: IR(CCl_4): 1720, 1640, 1095, 995, 905 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 1.32(3H,s), 2.11(3H,s), 3.21(3H,s), 4.75–6.00(3H,m). *7c*: IR (film): 1675, 1630, 1125, 760 cm^{-1}; ^1H NMR (90 MHz,$CDCl_3$): δ 1.70(3H,d, *J* 1.0 Hz), 2.26(3H,s), 3.32(3H,s), 4.07(2H,d, *J* 5.3 Hz), 6.47(1H,txq, *J* 1.0 and 5.2 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 11.2(CH_3), 24.6(CH_3), 58.1(CH_3), 69.4(CH_2), 137.7(C), 138.0(CH), 196.0(C=O); MS [70 eV, *m/e*(% rel. int.)]: 129(4.4,M^+), 128(56,M^+), 113(20), 97(10), 95(12), 85(100), 81(18); mol. wt., obs. 128.081, calc. for $C_7H_{12}O_2$ 128.084.

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.[30] 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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