Silver Ion-assisted Solvolysis of *trans*-2,2-Dibromo-1,3-dimethylcyclopropanecarboxylic Acid: Selective Formation of 4-Bromo-3,5-dimethyl-2(5*H*)-furanone

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The title compound has been solvolysed in 2,2,2-trifluoroethanol (IFE), isopropyl alcohol (IPA), 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) and *tert*-butyl alcohol (TBA) in the presence of silver trifluoroacetate. The product distribution is sensitive to the solvent used. In TFE and IPA two major products were formed, the butenolide 4-bromo-3,5-dimethyl-2(5*H*)-furanone and the corresponding (*Z*)-4-alkoxy-3-bromo-2-methyl-2-pentenoic acid, but, in addition, minor amounts of 2-alkoxy-3-bromo-2-methyl-3-pentenoic acid and 3-bromo-2-hydroxy-2-methyl-3-pentenoic acid were also obtained. In HFP and TBA the furanone was formed in better than 80% yield, the other products being 3-bromo-2-hydroxy-2-methyl-3-pentenoic acid and 3-bromo-2-methyl-2,4-pentadienoic acid. The outcome of the reactions is discussed on the basis of the nucleophilicity, the hydrogen-bonding ability and the polarity of the solvents.

Solvolysis of 2,2-dibromo-1-methylcyclopropanecarboxylic acid (1) in the dark in the presence of silver trifluoroacetate (AgTFA) results in ring opening via an allylic cation and formation of a mixture of compounds.[1,2] Generally, the corresponding butenolide 4-bromo-3-methyl-2(5*H*)-furanone (2) is a major product, but the yield of this γ-lactone depends on the solvent employed. In methanol, furanone formation is inefficient due to solvent trapping of the intermediate,[1] but when the reaction is carried out in refluxing 2,2,2-trifluoroethanol (TFE) the yield increases considerably, giving the γ-lactone in 90% isolated yield in a large-scale experiment under the best conditions.[2]

A compound that reacts similarly to 1 when exposed to AgTFA in refluxing methanol is *trans*-2-2-dibromo-1,3-dimethylcyclopropanecarboxylic acid (3).[1] But in spite of the fact that 3 both reacts faster and affords a smaller number of products than 1 under these conditions, the selectivity of the ring-opening reaction of 3 is rather low. In order to improve the selectivity methanol was replaced by TFE, a measure which was successful with 1.[2] As it turned out, this change of solvent was a minor success with 3, and we therefore decided to study the silver ion-assisted solvolysis of 3 more closely to see whether selective product formation could be achieved

under any other conditions. The results of this investigation are reported here.

Results

The importance of the solvent properties for the Ag^{+}-assisted ring opening of 2,2-dibromocyclopropanecarboxylic acids became clear when 1 was reacted in various solvents. Not only did the number of identifiable products drop from 17 to 3 when methanol was replaced with TFE, 4-bromo-3-methyl-2(5*H*)-furanone also became the predominant product under the optimum conditions. We therefore anticipated that the silver-assisted ring opening of *trans*-2,2-dibromo-1,3-cyclopropanecarboxylic acid in TFE should give almost exclusively 4-bromo-3,5-dimethyl-2(5*H*)-furanone (4). When 3 was reacted under the best conditions worked out for 1 (an acid concentration of 0.070 M and a silver concentration of 0.084 M),[1] however, lactone 4 was obtained in only 54% yield; the rest of the product mixture consisted essentially of two compounds, 3-bromo-4-(2,2, 2-trifluoroethoxy)-2-methyl-2-pentenoic acid (5b) and 3-bromo-2-(2,2,2-trifluoroethoxy)-2-methyl-3-pentenoic acid (6b), which were formed in 35 and 11% yield, respectively (Scheme 1, Table 1). Acid 6b was formed as a mixture of stereoisomers. The conjugated analogue 5b, however, was a single isomer,

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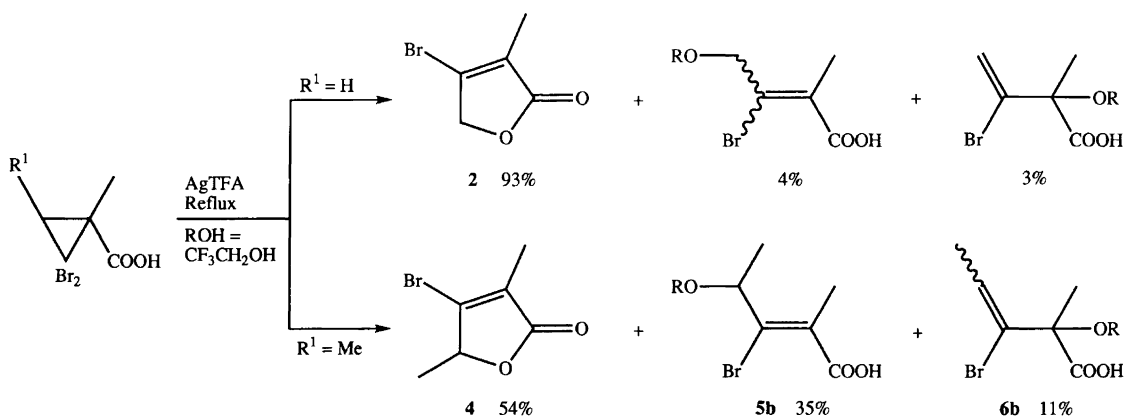
Scheme 1.

Table 1. The distribution of products **4–8** in reactions of **3** with AgTFA in refluxing solvents.

| Solvent[a]	Distribution (%)[b]					Total yield of **4–8** (%)[c]
	4	**5**	**6**	**7**	**8**	
a, MeOH[d]	23	30	47	0	0	92
b, TFE	54	35	11	0	0	100
c, IPA	41	43	6	10	0	100
d, HFP	82	0	0	11	7	94
e, TEA	86	0	0	10	4	94

[a]The following abbreviations are used: TFE, 2,2,2-trifluoroethanol; IPA, isopropyl alcohol; HFP, 1,1,1,3,3,3-hexafluoro-2-propanol; TBA, *tert*-butyl alcohol. [b]Percentage of the reaction mixture as determined by ^{1}H NMR analyses of the crude product mixture prior to work-up; for isolated yields, see the Experimental. [c]Estimated on the basis of the isolated amount of **4** and the ^{1}H NMR spectrum of the crude product prior to work-up. [d]The results are taken from Ref. 1.

which was assigned the *Z* configuration by analogy: the chemical shift of the methyl group attached to the C=C bond is almost identical with the shift observed for the corresponding group in (*Z*)-3-bromo-4-methoxy-2-methyl-2-butenoic acid, but significantly different from that observed for (*E*)-3-bromo-4-methoxy-2-methyl-2-butenoic acid, (*E*)-3-bromo-4-methoxy-2-methyl-2-pentenoic acid, and several similar compounds.[1] Consequently, the outcome of the solvolysis of **3** in TFE was comparable to the results obtained in methanol (Table 1). This observation† prompted us to perform silver-catalysed ring-opening reactions of **3** in other solvents as well. To increase the span of the solvents' nucleophilicity, reactions were carried out in both isopropyl alcohol (IPA) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) as well as *tert*-butyl alcohol (TBA).[3–6] By using TBA, we would also be able to compare the results achieved with those obtained with **1** under the same conditions.

In IPA **3** gave a reaction mixture consisting of four compounds according to TLC analyses. The main products were the corresponding conjugated acid, 3-bromo-4-isopropoxy-2-methyl-2-pentenoic acid (**5c**) (Scheme 1,

† Similar interceptions of allylic cations by TFE have been observed by Banwell and coworkers when performing ring opening of several *gem*-dihalocyclopropanes containing a nucleophilic substituent elsewhere in the molecule. Banwell, M. G., Harvey, J. E. and Wu, A. W. *Unpublished work.*

R = i-Pr), and butenolide **4**, both obtained in approximately 40% yield, whereas the skipped, unsaturated acid, 3-bromo-2-isopropoxy-2-methyl-3-pentenoic acid (**6c**) (Scheme 1, R = i-Pr), was formed in less than 10% yield. Consequently, the combined yield of products **4**, **5** and **6** in IPA was comparable to those achieved in TFE (Table 1). Just like **5b**, the conjugated acid **5c** was formed as a single isomer, which was assigned the *Z* configuration for the same reason given for **5b**. Acid **6c**, on the other hand, was formed as a mixture of stereoisomers. In addition a fourth product, 3-bromo-2-hydroxy-2-methyl-3-pentenoic acid (**7**), which was spectroscopically and
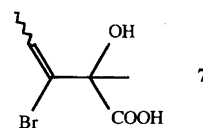

chromatographically identical with an authentic sample isolated from reactions in TBA (*vide infra*), was formed in low yield (10%). This compound was, however, not a primary product because its ^{1}H NMR signals were not present in the spectrum of the crude product mixture. Acid **7** is, therefore, formed during the separation of the crude product mixture into neutral and acidic fractions. Since **7** was not observed when **3** was solvolysed in MeOH and TFE a probable precursor is 3-bromo-2-

methyl-2-trifluoroacetoxy-3-pentenoic acid, which conceivably affords **7** by saponification.

When solvolysis of **3** was performed in HFP or TBA instead of in MeOH, TFE and IPA, the course of reaction changed significantly. Interestingly, the number of products increased, but more significantly, butenolide **4** predominated completely in both solvents and was obtained in better than 80% yield. Furthermore, acids **5** and **6** were not formed at all, whereas **7** was afforded in low yield (10–11%, Table 1). In addition, a second minor product was isolated, *viz.* 3-bromo-2-methyl-2,4-pentadienoic acid (**8**). TLC analyses and the ^{1}H NMR

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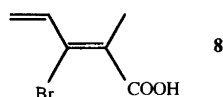
spectrum of the latter compound indicated clearly that **8** was obtained as a single isomer, which was assigned the *Z* configuration by comparing the NMR data with those of similar compounds. Thus, the chemical shift of the methyl group attached to the C=C bond is almost identical with the shift observed for the corresponding group in (*Z*)-3-bromo-4-methoxy-2-methyl-2-butenoic acid, but significantly different from that observed for (*E*)-3-bromo-4-methoxy-2-methyl-2-butenoic acid, (*E*)-3-bromo-4-methoxy-2-methyl-2-pentenoic acid and several similar compounds.[1] Furthermore, by comparison with the ^{1}H NMR spectra of (*E*)- and (*Z*)-2-methyl-2,4-pentadienoic acid[7] it is clear that the hydrogen atom attached to C-4 in **8** appears at a much higher field than expected for an isomer with an *E* configuration (Scheme 2). The assignment is also supported by the fact that (*Z*)-2-methyl-2,4-pentadienoic acid is unstable and isomerizes quantitatively to the more stable *E* isomer under acidic conditions,[7] which prevail during part of the work-up of our reaction mixtures. Consequently, it may well be that both *E*-**8** and *Z*-**8** are formed, but the *E* isomer is converted into the *Z* isomer during work-up and thus escapes detection. In any case the isolation of **8** is noteworthy because alkyl-substituted 2-bromo-1,3-butadienes belong to a group of compounds that show remarkable solvolytic reactivity in alcoholic solvents even
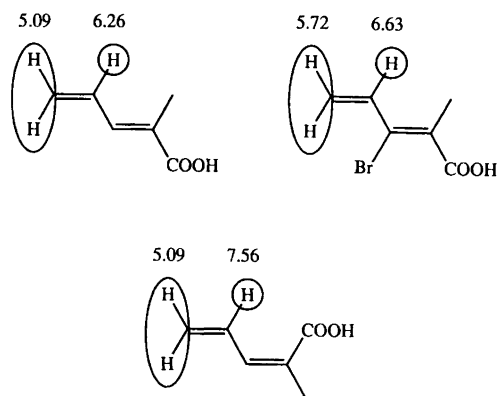
in the absence of silver ions.[8,9] The activating effect of the methyl group is therefore more than compensated by the deactivating influence of the carboxy group.

In order to try to achieve the same results by using less HFP **3** was solvolysed in mixtures of HFP and acetone. It soon became clear that the composition of the product mixture did not change very much when HFP was partly replaced. A reaction was therefore carried out in pure acetone and, indeed, lactone **4** was obtained in 62% isolated yield. A small amount of acids **7** and **8** was also formed.

Discussion

Mechanism. All the major products (**4**–**8**) obtained by solvolysis of **3** were isolated and characterized, giving a material balance of better than 92% for all the reactions. These products can be accounted for by invoking two isomeric intermediates, the allylic cations **A** and **B** which result from silver-assisted, disrotatory ring opening of **3** (Scheme 3).[10–13] Compounds **4**–**7** are subsequently formed by nucleophilic trapping of the cations and diene **8** by proton abstraction from the same intermediates. However, not all the products can be formed from *both* allylic cations; **6**, **7** and **8** can, but butenolide **4** can only be obtained from cation **A** and acid **5** only from cation **B**. Consequently, the composition of the product mixture depends on the relative rate of the two competing disrotatory ring-opening processes as well as the configurational stability of **A** and **B**. Furthermore, it is relevant to point out that **4** is formed by an intramolecular reaction whereas products **5**–**8** result from intermolecular
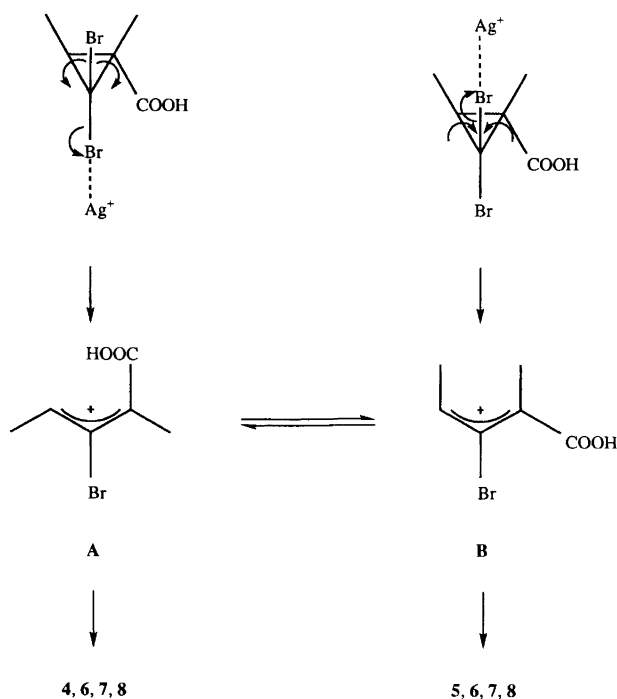
Scheme 2.

Scheme 3.

reactions. It is therefore reasonable to predict a variation in the composition of the reaction mixture when the solvolysis is carried out in different solvents.

Table 1 clearly reveals that the product distribution is sensitive to the solvent properties. From a synthetic point of view it is satisfying to see that butenolide formation can be made predominant by performing the reaction in TBA. *tert*-Butyl alcohol is in fact much more suitable for this purpose than 2,2,2-trifluoroethanol and also better than 1,1,1,3,3,3-hexafluoro-2-propanol; this is surprising considering the properties of HFP.[6] The results achieved with 3 in TBA are also surprising on the basis of the outcome of the reactions with 1 in TBA and TFE; in TFE 1 furnishes the corresponding butenolide with a selectivity far better than that achieved in TBA (93% as compared to 38%).[2]

A rather general pattern also apparent in Table 1 is the preference for attack of the γ position of the cation intermediates. If the diene formation (8) and the results obtained in methanol are disregarded, the γ/α ratio is larger than 5, similar to what was observed with 1 in TBA and TFE. This γ preference conceivably results from the larger electrophilicity of the γ carbon combined with relatively more steric crowding around the α carbon.

Solvent influence. The most striking result in Table 1 is the solvent's influence on the 5/4 ratio. In methanol, TFE and isopropyl alcohol this ratio is 0.7–1.3, but when HFP and *tert*-butyl alcohol are used it drops to 0, i.e., 5 is not formed. Since 4 and 5 can only be formed from cations A and B, respectively, it is tempting to conclude that cation B is not formed at all in HFP and TBA. Such a conclusion would, however, be rather unlikely because, since the reactions occur at almost the same temperature in all solvents, the relative ease of the two modes of the ring opening of 3 will largely be determined by the molecule's intrinsic properties, which are not expected to differ to a considerable extent. What will differ under the various conditions, however, are the nucleophilicity, the polarity and the hydrogen-bonding capability of the solvent. Of the solvents used in this study HFP is the most extreme in all these respects.[6] Its very low nucleophilicity explains *both* the lack of products containing the hexafluoroisopropoxy moiety (e.g., compounds like 5 and 6) *and* the presence of acid 7, which results from primary attack of A and/or B at C-α by trifluoroacetate, a nucleophile too poor to be able to compete under more normal circumstances. Furthermore, the low nucleophilicity and the high polarity of HFP also makes the conversion of B into A more likely, thus making intramolecular trapping leading to butenolide 4 more easily achievable.

When the results in HFP are compared with those obtained in other solvents, it becomes clear that the total picture is very complex. For instance, TFE is less nucleophilic and more polar and forms stronger hydrogen bonds than IPA,[3,14] but in spite of this the results of the reactions in TFE and IPA are very similar. Likewise,

although the solvent properties of TBA are closer to those of IPA than of both TFE and HFP, the outcome of the solvolysis in TBA resembles much more the results achieved in HFP than in IPA (and TFE). Furthermore, it is also strange that the results obtained with 1 and 3 under comparable conditions in several solvents are so different. It is therefore quite clear that the transformations depend on a number of factors that have to be studied more thoroughly before a detailed description of the reaction can be presented.

Finally, it should be mentioned that silver ion-assisted solvolysis has also been studied with several other 2,2-dibromocyclopropanecarboxylic acids. Generally the compounds react, but predominant formation of one product was less easily achieved than in the case of 1 and 3. With one exception, a detailed account of the results of these reactions has therefore not appeared. The exception is 2,2-dibromo-1-phenylcyclopropanecarboxylic acid (9), which exhibits reactions not observed with other 2,2-dibromocyclopropanecarboxylic acids studied by us. The results obtained with 9 are therefore published separately.[15]

Experimental

General. IR spectra were recorded on a Perkin–Elmer 1310 infrared spectrophotometer and on Nicolet Impact 400 FT-IR and 410 FT-IR instruments. The absorption intensities are described as (s) for strong, (m) for medium, and (w) for weak. ^{1}H NMR, ^{13}C NMR and NOESY spectra were obtained on Bruker Spectrospin spectrometer models AC-200 and -400, which are 200 MHz and 400 MHz for proton spectra, respectively. $CDCl_3$ and CCl_4 were used as solvents with added tetramethylsilane (TMS) as an internal reference. Chemical shifts are reported in ppm downfield from TMS. Signal multiplicity is given as (s) for singlet, (d) for doublet, (t) for triplet, (q) for quartet, (sept) for septet, (br s) for broad singlet, and (dd) for double doublet. Mass spectrometry was performed on a VG 7070 mass spectrometer combined with an HP 5890 IIA gas chromatograph equipped with an HP1 column (50 m × 0.2 mm i.d. with a film layer of 0.33 μm). The spectrometer was operated in the EI mode at 70 eV. GC analyses were carried out on an HP 5720 gas chromatograph equipped with a 4 m packed column (15% SP 2100 on Supelcoport) and FID. Response ratios were not determined. Melting points, which are uncorrected, were measured on a Gallenkamp melting-point instrument.

TLC was carried out using commercial aluminium sheets covered with silica gel 60 F_{254} from Merck. The resulting chromatograms were developed by UV irradiation or by spraying with a solution of anisaldehyde and phosphomolybdenic acid in a mixture of ethanol and concentrated sulfuric acid. The acids formed were isolated by flash chromatography using Silica gel 60 (Merck No. 9385) as the stationary phase and a 9:10:1 (v/v)

mixture of hexane, ethyl acetate and acetic acid as the mobile phase.

Chemicals. All solvents were analysed and could be used in the reactions without further purification. 2,2,2-Trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) were purchased from Aldrich. The starting material, *trans*-2,2-dibromo-1,3-dimethylcyclopropanecarboxylic acid (3), was synthesized as described in the literature.[16]

Solvolysis of 3: general procedure. Acid 3 and silver trifluoroacetate were mixed with the solvent and refluxed in the dark. The concentration of the acid and of AgTFA was ca. 0.070 M and 0.084 M, respectively, except in the reactions performed with HFP as the solvent. The reaction was stopped after 24 h by addition of 1.0 M hydrochloric acid. The hydrolysate was extracted with ether (4 × 25 ml), and the combined extracts were dried (MgSO$_4$) and concentrated under reduced pressure. The ^{1}H NMR spectra of the residue were taken before the product mixtures were worked up.

The reaction mixture was then dissolved in 25 ml of diethyl ether and washed thoroughly (4 × 15 ml) with a saturated aqueous solution of NaHCO$_3$. Since the buten-olide turned out to be quite soluble in water at alkaline pH, the combined aqueous layers were extracted with ethyl acetate (2 × 25 ml). The organic extracts were combined with the ether solution. The combined organic phases were dried (MgSO$_4$) and then concentrated under vacuum.

The pH of the combined aqueous layers was adjusted to 1 by addition of 6 M hydrochloric acid. The acidic solution was then extracted with ether (4 × 25 ml) and the extracts were combined, dried (MgSO$_4$) and concentrated under vacuum.

The neutral and acidic extracts were analysed by TLC. Their components were then separated by flash chromatography.

The following solvolyses were carried out according to the general procedure.

Solvolysis in 2,2,2-trifluoroethanol. The reaction mixture was composed of 0.80 g (2.94 mmol) of 3, 0.75 g (3.41 mmol) of AgTFA, and 44 ml of 2,2,2-trifluoroethanol. Work-up gave 0.58 g of an oil, which was analysed by ^{1}H NMR spectroscopy prior to subsequent separation in a neutral fraction (0.28 g) and an acidic fraction (0.29 g).

The neutral fraction was essentially pure 4-bromo-3,5-dimethyl-2(5*H*)-furanone (4).[1] The acidic fraction was subjected to flash chromatography, which gave pure samples of two acids, (*Z*)-3-bromo-4-(2,2,2-trifluoroethoxy)-2-methyl-2-pentenoic acid (*Z*-5b) and an *E/Z* mixture of 3-bromo-2-(2,2,2-trifluoroethoxy)-2-methyl-3-pentenoic acid (6b).

Z-5b: IR (CCl$_4$): 3100–2500 (s), 1690 (s), 1600 (m), 1160 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.38 (3 H, d, *J*

6.4 Hz), 2.18 (3 H, s), 3.50–4.00 (2 H, m), 5.07 (1 H, q, *J* 6.4 Hz), 9.2 (1 H, br s). ^{13}C NMR (CCl$_4$): δ 20.5 (CH$_3$), 20.9 (CH$_3$), 65.8 (CH$_3$, q, *J* 34.4 Hz), 76.0 (CH), 126.7 (CF$_3$, q, *J* 278 Hz), 131.4 (C), 143.4 (C), 171.3 (C=O). MS [*m/z* (% rel. int.)]: 212 (5), 211 (63), 210 (9), 193 (6), 191 (14), 189 (9), 177 (25), 175 (27), 165 (69), 151 (26), 127 (47), 121 (8), 119 (9), 112 (27), 111 (100), 110 (6), 83 (25), 82 (9).

6b: IR (CCl$_4$): 3150–2560 (s), 1705 (s), 1600 (m), 1160 (s) cm^{-1}. ^{1}H NMR (CCl$_4$): δ 1.75 (3 H, s), 1.90 (3 H, d, *J* 6.5 Hz), 3.60–4.00 (2 H, m), 6.35 (1 H, q, *J* 6.5 Hz), 11.0 (1 H, br s).

On the basis of the ^{1}H NMR spectrum of the crude product and the spectra of the isolated products the 4: *Z*-5b:6b ratio was determined to be 54:35:11.

Solvolysis in 2-propanol. The reaction mixture was composed of 1.60 g (5.88 mmol) of 3, 1.56 g (7.07 mmol) of AgTFA, and 84 ml of isopropyl alcohol. Work-up gave 1.04 g of an oil, which was analysed by ^{1}H NMR spectroscopy prior to subsequent separation into a neutral fraction (0.43 g) and an acidic fraction (0.53 g). The neutral fraction was essentially pure 4. TLC analysis of the acidic fraction showed at least three compounds, but when the mixture was subjected to flash chromatography, pure samples of the products could not be isolated. A ^{1}H NMR spectrum of the fraction was recorded and showed the presence of acid 8 as well as peaks compatible with (*Z*)-3-bromo-4-isopropoxy-2-methyl-2-pentenoic acid (*Z*-5d) (main product) and an *E/Z* mixture of 3-bromo-2-isopropoxy-2-methyl-3-pentenoic acid (6d) (minor product). Esterification using ethanol and boron trifluoride–diethyl ether according to Marshall *et al.*[17] made isolation of ethyl (*Z*)-3-bromo-4-isopropoxy-2-methyl-2-pentenoate (10) possible.

8: See later.

10: IR (CCl$_4$): 2970 (s), 2950 (m), 2870 (m), 1716 (s), 1600 (w), 1550 (w), 1465 (m), 1445 (m), 1360 (m), 1370 (m), 1335 (w), 1260 (s), 1150 (m), 1120 (m), 1090 (s), 1070 (m), 1030 (m), 1020 (m), 990 (m), 885 (w), 790 (s), 770 (s) cm^{-1}. ^{1}H NMR (CCl$_4$): δ 1.05 (3 H, d, *J* 6.1 Hz), 1.10 (3 H, d, *J* 6.1 Hz), 1.21 (3 H, d, *J* 6.2 Hz), 1.32 (3 H, t, *J* 7.1 Hz), 2.07 (3 H, s), 3.44 (1 H, sept, *J* 6.1 Hz), 4.19 (2 H, q, *J* 7.1 Hz), 4.67 (1 H, q, *J* 6.2 Hz). ^{13}C NMR (CCl$_4$): δ 14.2, 20.7, 20.8, 23.2, 60.4, 68.1, 71.1, 129.6, 143.9, 165.8. MS [*m/z* (% rel. int.)]: 280 (*M*$^+$, <1), 278 (*M*$^+$, <1), 265 (1), 263 (1), 238 (3), 237 (7), 236 (3), 235 (38), 223 (8), 221 (18), 219 (9), 199 (10), 193 (65), 192 (24), 191 (100), 109 (20), 189 (88), 177 (51), 175 (53), 169 (6), 165 (14), 163 (14), 157 (49), 113 (15), 112 (15), 111 (84), 110 (9), 95 (9), 87 (13), 83 (39), 69 (20), 67 (53).

On the basis of the ^{1}H NMR spectrum of the crude product and the acidic fraction and the spectra of the isolated products 4 and 10, the 4:5d:6d:7 ratio was determined to be 43:41:10:6.

Solvolysis in 1,1,1,3,3,3-hexafluoro-2-propanol. The reaction mixture was composed of 0.57 g (2.10 mmol) of **3**, 0.55 g (2.50 mmol) of AgTFA, and 5 ml of HFP. Work-up gave 0.22 g of an oil, which was analysed by ^{1}H NMR spectroscopy. The spectrum showed almost exclusively peaks due to butenolide **4** and acids **7** and **8**. From this spectrum the **4:7:8** ratio was 82:11:7. The reaction mixture was not worked up further.

Solvolysis in 2-methyl-2-propanol. The reaction mixture consisted of 2.15 g (7.90 mmol) of **3**, 2.09 g (9.50 mmol) of AgTFA, and 118 ml of *tert*-butyl alcohol. Work-up gave 1.16 g of an oil, which was analysed by ^{1}H NMR spectroscopy and subsequently separated into a neutral fraction (0.90 g) and an acidic fraction (0.20 g).

The neutral fraction was essentially pure **4**. The acidic fraction was subjected to flash chromatography. Two compounds were isolated, 3-bromo-2-hydroxy-2-methyl-3-pentenoic acid (**7**) and 3-bromo-2-methyl-2,4-pentadienoic acid (**8**). Minor amounts of unidentified products were also isolated.

7: IR (CCl$_4$): 3600–2500 (w), 2970 (s), 2925 (m), 2850 (w), 1720 (m), 1660 (w), 1560 (w), 1465 (w), 1420 (w), 1265 (s), 1100 (s), 1015 (s), 915 (m), 865 (w), 790 (s), 750 (s), 670 (m) cm^{-1}. ^{1}H NMR (CCl$_4$): δ 1.65 (3 H, s), 1.83 (3 H, d, *J* 6.5 Hz), 6.30 (1 H, q, *J* 6.5 Hz), 9.36 (2 H, br s). ^{13}C NMR (CCl$_4$): δ 17.1, 23.9, 77.6, 126.4, 129.0, 176.7. MS [*m/z* (% rel. int.)]: 209 [(*M* − 1)$^+$, 8], 207 [(*M* − 1)$^+$, 8], 193 (3), 192 (4), 191 (13), 190 (3), 189 (14), 188 (3), 177 (7), 175 (7), 166 (5), 165 (98), 164 (6), 163 (100), 160 (12), 149 (6), 147 (6), 129 (8), 121 (4), 119 (4), 117 (4), 113 (10), 112 (5), 111 (22), 83 (7), 69 (22).

8: IR (CDCl$_3$): 3600–2400 (m), 2970 (m), 2910 (m), 1745 (s), 1680 (s), 1554 (m), 1450 (w), 1435 (m), 1400 (m), 1370 (m), 1310 (m), 1270 (s), 1185 (w), 1100 (m), 1060 (m), 1040 (m), 1010 (m), 900 (s), 725 (s), 640 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.13 (3 H, s), 5.55 (1 H, d, *J* 10.5 Hz), 5.89 (1 H, d, *J* 16.2 Hz), 6.63 (1 H, dd, *J* 10.5 and 16.2 Hz), 9.83 (1 H, s). ^{13}C NMR (CDCl$_3$): δ 21.7, 124.3, 132.8, 138.7, 140.3, 173.4. MS [*m/z* (% rel. int.)]: 192 (*M*$^+$, 41), 191 (38), 190 (*M*$^+$, 43), 189 (26), 177 (21), 175 (17), 131 (19), 129 (17), 111 (70), 107 (27), 105 (32), 97 (34), 95 (25), 92 (31), 85 (39), 83 (68), 71 (66), 69 (58), 67 (66), 65 (57), 60 (100).

On the basis of the ^{1}H NMR spectrum of the crude product and the spectra of the isolated products the **4:7:8** ratio was determined to be 86:10:4.

Solvolysis in acetone. The reaction mixture consisted of 1.20 g (4.41 mmol) of **3**, 1.16 g (5.27 mmol) of AgTFA,

and 66 ml of acetone. Work-up gave 0.60 g of a yellow oil, which was analysed by ^{1}H NMR spectroscopy and subsequently separated into a neutral fraction (0.53 g) and an acidic fraction (0.05 g). The neutral fraction consisted of essentially pure 4-bromo-3,5-dimethyl-2(5*H*)-furanone (**4**), which was thus obtained in 62% yield. The acidic fraction was subjected to flash chromatography and afforded acids **7** and **8** as well as minor amounts of several unidentified products.

The ^{1}H NMR spectrum of the crude product showed that the **4:7:8** was 90:7:3.

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