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Silver Ion-assisted Solvolysis of 2,2-Dibromo-1-phenylcyclopropanecarboxylic Acid: Solvent-dependent Competition between Decarboxylation and Ring Closure

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The solvolysis of the title compound has been studied in several alcohols (methanol, 2,2,2-trifluoroethanol, isopropyl alcohol, *tert*-butyl alcohol and 1,1,1,3,3,3-hexafluoro-2-propanol [HFP]) in the presence of an excess of silver trifluoroacetate. In all solvents the corresponding butenolide, 4-bromo-3-phenyl-2(5*H*)-furanone, was a major or the predominant product. Another product formed in all solvents but HFP was (*Z*)-4-alkoxy-3-bromo-2-phenyl-2-butenoic acid, which resulted from solvent attack on intermediate allylic cations. Furthermore, both 3-alkoxy-1-phenyl-1-propyne and 3-alkoxy-1-phenyl-1-propanone were formed except when reactions were performed in HFP; their formation involved decarboxylation and their total yield was 15–40%.

Solvolysis of 2,2-dibromocyclopropanecarboxylic acids with silver ion assistance generally results in ring opening and formation of butenolides and brominated, unsaturated acids, and, in some cases, also brominated, unsaturated esters.[1–3] The outcome of the reaction and the complexity of the reaction have proved to be both solvent- and substituent-dependent, but in spite of the fact that a number of acids have been investigated no clear connection between the variables has emerged.

During the course of our studies we also investigated the silver ion-assisted solvolysis of 2,2-dibromo-1-phenylcyclopropanecarboxylic acid (**1**). In methanol, the first solvent used, the acid afforded the expected products, but also considerable quantities of two ketones and one alkyne, making **1** unique among the cyclopropanecarboxylic acids studied so far. We therefore decided to investigate the alcoholysis of this acid further and performed reactions in 2,2,2-trifluoroethanol (TFE), isopropyl alcohol (IPA), *tert*-butyl alcohol (TBA) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP). The results of this investigation are reported here.

Results

Exploratory experiments were first performed in refluxing methanol in the presence of relatively high concentrations of selected silver salts, *viz.* silver fluoride, silver nitrate, silver perchlorate and silver trifluoroacetate (AgTFA). Generally the results were similar to those obtained with 2,2-dibromo-1-methylcyclopropanecarboxylic acid[1] and *trans*-2,2-dibromo-1,3-dimethylcyclopropanecarboxylic acid[3] under the same conditions; application of silver nitrate and silver perchlorate gave large amounts of the corresponding methyl esters, which are unreactive in keeping with expectations,[4] whereas silver fluoride furnished a reaction mixture containing almost 20 products. AgTFA, on the other hand, did not give the ester of **1** and only a limited number of products. Further studies were, therefore, limited to silver ion-assisted reactions with silver trifluoroacetate.

When **1** was refluxed in methanol under conditions preventing complete acid consumption ([**1**] = 0.36 M, $[Ag^+]$ = 0.54 M, reaction time 48 h),[1] the reaction mixture contained 61% unreacted starting material, five products which were isolated by flash chromatography, and one product which was detected by GC–MS. In keeping with the results from solvolytic studies of similar acids,[1–3] the corresponding butenolide, 4-bromo-3-phenyl-2(5*H*)-furanone (**2**), and 3-bromo-4-methoxy-2-phenyl-2-butenoic acid (**3a**) were present (see Scheme 1). The unconjugated analogue of **3a** was, however, not detected. Interestingly, **3a** was obtained as a single isomer, which was assigned the *Z* configuration by analogy: the chemical shift for

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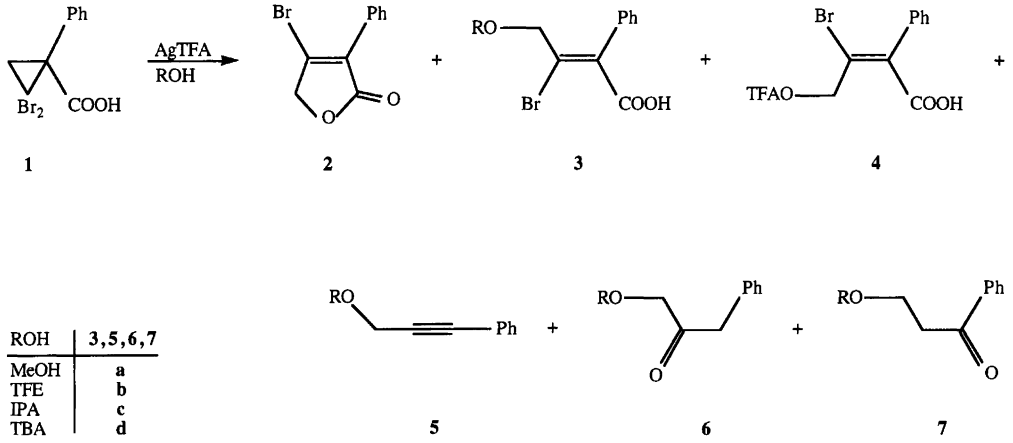


Scheme 1.

the methylene group (4.07 ppm) is identical with the shift observed for the corresponding group in the *Z* isomer of methyl 3-bromo-4-methoxy-2-phenyl-2-butenoate (4.09 ppm), but considerably smaller than in methyl (*E*)-3-bromo-4-methoxy-2-phenyl-2-butenoate (4.45 ppm), obtained in small amounts by solvolysis of **1** in methanol in the presence of silver perchlorate (see the Experimental). This analogy is supported by comparison of the NMR spectrum for **3a** with the spectra of the *E* and *Z* isomers of 3-bromo-4-methoxy-2-methyl-2-butenoic acid.[1] The three remaining isolated products were identified as 3-methoxy-1-phenyl-1-propyne (**5a**), 1-methoxy-3-phenyl-2-propanone (**6a**) and 3-methoxy-1-phenyl-1-propanone (**7a**). The identity of **5a** was proved by independent synthesis[5] and on the basis of spectroscopic data.[6] Furthermore, the spectroscopic properties of **6a** and **7a** were identical with those reported in the literature.[7,8] With respect to the yield **5a** and **6a** were both obtained in small amounts, whereas ketone **7a** was the major product formed from **1** under the reaction conditions employed (Table 1).

The sixth product detected in the reaction mixture from solvolysis of **1** in methanol was given the structure 1-phenyl-2-propen-1-one (**8**) on the basis of GC–MS analyses and the IR and ^{1}H NMR spectra of a small, but impure sample of the compound. The MS data proved the molecular formula (C_9H_8O) and also the presence of a phenyl and a vinyl group. These structural features were confirmed by the IR and NMR data as was the presence of a carbonyl group. It is also noteworthy that **8** was rather unstable, in accordance with the ease with which 1-phenyl-2-propen-1-one undergoes polymerization.[9,10] (A small amount of **8** was also detected in the reaction mixtures from solvolyses of **1** in TFE, IPA and TBA).

When methanol was replaced by 2,2,2-trifluoroethanol (TFE) or isopropyl alcohol (IPA) several significant changes in the reaction course were observed (see Table 1). First and foremost, **1** was consumed much faster, particularly in IPA which allowed complete consumption of the starting material in less than 24 h. Secondly, although the relative amount of the corresponding α,β-unsaturated acid **3** did not decrease, the amount of butenolide (**2**) increased from 28% to approximately 45% in both TFE and IPA. The increase of **2** occurred apparently at the expense of the formation of compounds **5**–**7**, whose total yield dropped from 45% in methanol to ca. 20% in TFE and IPA. Furthermore, ketone **6** was formed in neither TFE nor IPA. Finally, a new product, 3-bromo-2-phenyl-4-trifluoroacetoxy-2-butenoic acid (**4**), was isolated in both solvents, albeit in low yield. Acid **4** was obtained as a single isomer, which exhibited a singlet at 4.43 ppm for the methylene group in the ^{1}H NMR spectrum. When this value is compared with the shifts of the methylene group of the *E* and *Z* isomers of methyl 3-bromo-4-methoxy-2-phenyl-2-butenoate, 4.45 and 4.09 ppm, respectively (see Experimental), it is concluded that **4** has the *E* configuration, i.e., the carboxy group and the bromo atom are

Table 1. The distribution of products **2**–**7** in reactions of **1** with AgTFA in various solvents under reflux.

Solvent[a]	Reaction *t*/h	Distribution (%)[b] **2**	**3**	**4**	**5**	**6**	**7**	Total yield of **2**–**7** (%)[c]
a, MeOH[d]	48	28	27	0	6	3	36	38
b, TFE[d]	48	47	33	1	2	0	17	99
c, IPA[d]	24	43	30	6	16	0	5	99
d, TBA[d]	24	72	2	11	13	0	2	92
e, HFP	36	83	0	17	0	0	0	93

[a]The following abbreviations are used: TFE, 2,2,2-trifluoroethanol; IPA, isopropyl alcohol; TBA, *tert*-butyl alcohol; HFP, 1,1,1,3,3,3-hexafluoro-2-propanol. [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 Experimental. [c]Estimated on the basis of the isolated amount of **2** and the ^{1}H NMR spectrum of the crude product and the neutral fraction prior to work-up and isolation, respectively. [d]In addition traces of phenyl vinyl ketone were detected by GC–MS.

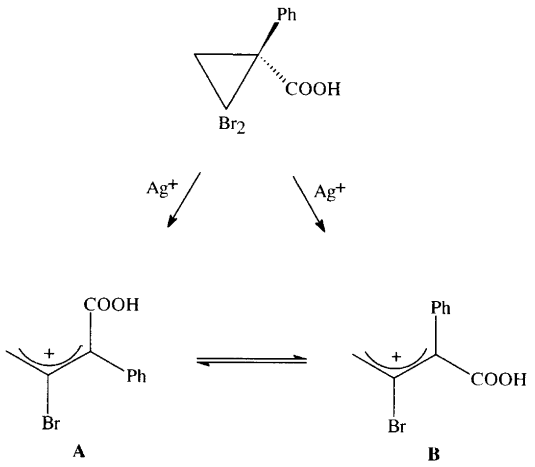
trans to each other, although a methoxy group might conceivably affect the chemical shift of the methylene group somewhat differently from a trifluoroacetoxy moiety.

Solvolysis of **1** in TBA and HFP amplified the changes observed when methanol was replaced by TFE or IPA. As borne out by the results in Table 1, the amount of both butenolide **2** and acid **4** increased whereas the yield of all other products dropped. In HFP **2** and **4** were in fact the only products isolated, amounting to 83 and 17%, respectively, of the reaction mixture obtained by 93% conversion of the starting material; in addition traces of an unknown product were detected. Consequently, products **2**–**4** are formed at the expense of compounds **5**–**7**.

Discussion

Mechanistic aspects. From the results presented above it is clear that two groups of products are formed during the solvolysis. One group consists of lactone **2** and acids **3** and **4**, which contain all the carbon atoms present in **1**, the other comprises alkyne **5** and ketones **6**, **7** and **8**, which lack one of the carbon atoms in the starting material. In spite of the difference between the two groups all the 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 **1** (Scheme 2), a general reaction for halogenated cyclopropanes.[11–14] Compounds **2**–**4** are then formed by nucleophilic trapping of the cations, butenolide **2** from **A** by intramolecular attack by the carboxy group, acid **3** from **B** by intermolecular attack by a solvent molecule, and acid **4** from **B** by intermolecular reaction with the trifluoroacetate ion.

The formation of compounds **5**–**8**, however, requires at least two elimination reactions. On the basis of work by Grob *et al.*[15] formation of **5** is likely to take place by elimination of CO_2 and HBr from 4-alkoxy-3-bromo-2-phenyl-2-butenoic acid. With **5** present in the reaction mixture acid-catalysed addition of trifluoroacetic acid or alcohol (provided the alcohol is nucleophilic enough) can take place,[16,17] giving a vinyl ester and vinyl ether, respectively, which will then afford ketones **6** and **7** during aqueous work-up under acidic conditions. This explanation is supported by experiments: when a methanol solution of **5a** and AgTFA was refluxed for 24 h, **6a** and **7a** were obtained in a 2:43 ratio after addition of hydrochloric acid. (Another transformation giving **6** can also be envisaged, *vide infra*.) Compound **8** was not detected, but it is most likely formed by elimination of alcohol from **7**.[7]

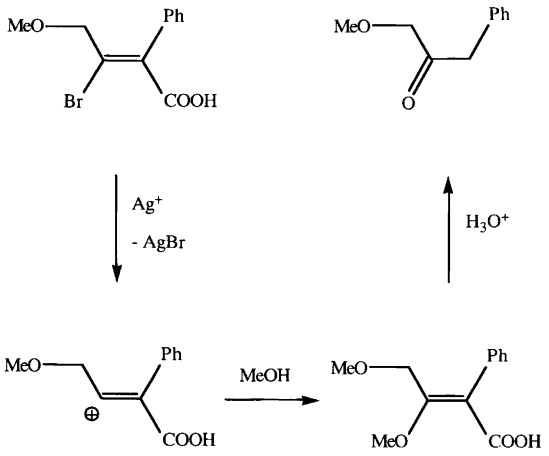


Scheme 2.

The nucleophilicity of the solvents relative to the trifluoroacetate ion is unknown, but variable because it is influenced by ion solvent interactions, the starting material's properties and pH, which vary as the reactions proceed. However, if the nucleophilicity of the neat species is regarded as an indication the trends emerging from Table 1 are reasonable. Thus, the lower the solvent nucleophilicity, the higher the intramolecular trapping (formation of **2**). Also, the lower the solvent nucleophilicity, the higher the relative reactivity of the trifluoroacetate ion, leading to a lower yield of **3** and a higher yield of **4**. Finally, when the nucleophilicity of the solvent diminishes, the triple bond in **5** will be less easily attacked, giving a smaller total quantity of ketones **6** and **7**. This was indeed observed; in methanol the ketones amounted to 39% of the products, in IPA to 5%, and in HFP the ketones were not formed at all.

Formation of **5**. The precursor of **5** is supposedly the corresponding 4-alkoxy-3-bromo-2-phenyl-2-butenoic acid which presumably undergoes decarboxylation like similar β-halo-α,β-unsaturated carboxylic acids.[15] Consequently, the elimination reaction of the precursor is expected to occur with both the *E* and the *Z* isomers and with both the carboxylic acid and the corresponding carboxylate, with the *E* isomer reacting considerably faster than the *Z* isomer and the carboxylate significantly faster than the acid.[15] However, if the *Z* isomer reacts, alkyne formation, giving **5**, is assumed[15] to be accompanied by some ketone formation, giving **6** (Scheme 3). The absence of **6** in all cases but solvolysis of **1** in methanol might indicate that **5** is not formed from (*Z*)-4-alkoxy-3-bromo-2-phenyl-2-butenoic acid, but from (*E*)-4-alkoxy-3-bromo-2-phenyl-2-butenoic acid, i.e. **3**.

If this conclusion is correct compounds **2** and **5**–**7** arise mainly from intermediate **A** whereas acids **3** and **4** originate predominantly from intermediate **B**. The **(2+5+6+7)/(3+4)** ratio does not necessarily reflect accurately the relative abundance of the two modes of disrotatory ring opening, because conversion between **A** and **B**[18] and acid-catalysed isomerization of **3** and **4**[19,20] may occur. Work to look into these matters is being planned.



Scheme 3.

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 a Jeol FX 90Q instrument and Bruker Spectrospin spectrometer models AC-200, which are 89.55 and 200 MHz for proton spectra, respectively. Unless otherwise stated the latter instrument was used. $CDCl_3$ 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 VG 7070 and VG Analytical Tribrid mass spectrometers combined with an HP 5890 gas chromatograph equipped with 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.

Thin-layer chromatography (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 sulphuric acid. The acids formed were isolated by flash chromatography using Silica gel 60 (Merck No. 9385) as the stationary phase and a mixture of hexane, ethyl acetate and/or 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. 2,2-Dibromo-1-phenylcyclopropanecarboxylic acid (**1**) was synthesized as described in the literature[21] as was 3-methoxy-1-phenyl-1-propyne[8] which was used as an authentic sample for one of the products and as the starting material for the synthesis of other products.

Exploratory experiment with **1**–*MeOH–$AgClO_4$.* Acid **1** (1.03 g, 3.23 mmol) and silver perchlorate (1.33 g, 6.03 mmol) were dissolved in methanol (9 ml) and refluxed in the dark for 60 h. The reaction was quenched by addition of 2 M hydrochloric acid (25 ml) and the resulting mixture was thoroughly extracted with ether (5 × 25 ml). The combined organic fractions were dried ($MgSO_4$) and concentrated under vacuum to give a yellowish product mixture (0.59 g). GLC analysis revealed six products. Preparative TLC allowed isolation of the *E* and *Z* isomers of methyl 3-bromo-4-methoxy-2-phenyl-2-butenoate. The stereochemical assignment of the isomers is based on the downfield shift observed for the methylene group when the carbonyl group moves from a *trans* (in the *Z* isomer) to a *cis* (in the *E* isomer) position relative to these moieties.[22]

E Isomer: ^{1}H NMR (89.55 MHz, $CDCl_3$): δ 3.43 (3 H, s), 3.74 (3 H, s), 4.45 (2 H, s), 7.20–7.50 (5 H, m).

Z Isomer: ^{1}H NMR (89.55 MHz, $CDCl_3$): δ 3.29 (3 H, s), 3.81 (3 H, s), 4.09 (2 H, s), 7.20–7.50 (5 H, m).

The mass spectra of the two isomers could not be distinguished. MS [*m/z* (rel. int.)]: 286 (M^+, 1), 284 (M^+, 1), 255 (2), 253 (2), 205 (94), 174 (10), 173 (30), 145 (100), 115 (34), 103 (15), 102 (14).

Solvolysis of **1**: *general procedure.* Acid **1** and silver trifluoroacetate were mixed with the solvent and refluxed in the dark. The concentration of the acid and of AgTFA was ca. 0.36 M and 0.54 M, respectively, in all solvents. The reaction was stopped after 24–48 h by adding 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 spectrum of the residue was taken before the product mixture was worked up further.

Unless otherwise stated the crude product mixture was then divided into neutral and acidic fractions by using the following procedure. The reaction mixture was dissolved in 25 ml of ether and washed thoroughly (4 × 15 ml) with a saturated aqueous solution of $NaHCO_3$. Since the butenolide 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 to give the neutral fraction.

The pH of the combined aqueous layers was subsequently adjusted to 1 by addition of 6 M hydrochloric acid, and the aqueous solution was then extracted with ether (4 × 25 ml). The ether extracts were combined,

dried ($MgSO_4$) and concentrated under vacuum to give the acidic fraction. The various product mixtures were analysed by TLC and their components were then separated by flash chromatography.

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

Solvolysis in methanol. The reaction mixture, composed of 1.00 g (3.12 mmol) of **1**, 1.03 g (4.68 mmol) of AgTFA, and 8.6 ml of methanol, was refluxed for 48 h. Work-up gave 0.83 g of a yellow oil, which was analysed by ^{1}H NMR spectroscopy prior to subsequent separation into a neutral fraction (0.18 g) and an acidic fraction (0.55 g). The neutral fraction was subjected to flash chromatography using hexane–ethyl acetate (95:5) as the eluent. Four products were isolated: 4-bromo-3-phenyl-2(5*H*)-furanone (**2**), 3-methoxy-1-phenyl-1-propyne (**5a**), 1-methoxy-3-phenyl-2-propanone (**6a**) and 3-methoxy-1-phenyl-1-propanone (**7a**). The acidic fraction consisted mainly of unreacted starting material and one product. Unreacted **1** prevented the isolation of a pure sample of the product, but by recording the ^{1}H NMR spectrum of an impure sample and neglecting the signals due to **1**, the product was assigned the structure (*Z*)-3-bromo-4-methoxy-2-phenyl-2-butenoic acid (**3a**). On the basis of the ^{1}H NMR spectrum of the crude product and the spectra of the isolated products the **1**:**2**:**3a**:**5a**:**6a**:**7a** ratio was determined to be 61:11:10:3:1:14. The physical data were as follows.

2: m.p. 60–61 °C. IR (KBr): 3030 (w), 2940 (w), 1735 (s), 1625 (m), 1580 (w), 1480 (w), 1415 (w), 1340 (m), 1380 (m), 1250 (m), 1160 (s), 1180 (s), 1020 (s), 990 (w), 950 (m), 910 (w), 870 (w), 775 (m), 740 (w), 685 (m), 650 (w) cm^{-1}. ^{1}H NMR (89.55 MHz, $CDCl_3$): δ 4.93 (2 H, s), 7.26–7.52 (3 H, m), 7.72–7.83 (2 H, m). ^{13}C NMR (CCl_4): δ 72.2, 128.0 (2 CH), 128.4 (2 CH), 129.4, 136.8, 167.4. MS [*m/z* (rel. int.)]: 240 (M^+, 38), 238 (M^+, 39), 183 (6), 181 (6), 160 (11), 159 (91), 131 (32), 115 (46), 103 (100), 102 (31).

3a: IR ($CHCl_3$): 3500–2400 (m), 2930 (m), 2860 (w), 1714 (s), 1620 (w), 1583 (w), 1152 (w), 1455 (w), 1440 (w), 1420 (w), 1380 (w), 1290 (w), 1235 (w), 1180 (w), 1140 (m), 1100 (w), 1020 (w), 745 (s), 655 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.26 (3 H, s), 4.07 (2 H, s), 7.21–7.50 (5 H, m), 11.85 (1 H, br s).

5a: IR (film): 3065 (w), 3020 (w), 2930 (m), 2240 (w), 1710 (w), 1600 (w), 1580 (w), 1495 (s), 1445 (s), 1380 (s), 1280 (m), 1260 (m), 1195 (s), 1100 (s), 900 (s), 760 (s), 695 (s) cm^{-1}. ^{1}H NMR data were in accordance with literature.[7] ^{13}C NMR ($CDCl_3$): δ 57.6, 60.4, 84.8, 86, 127.1, 128.3, 131.7. MS [*m/z* (rel. int.)]: 146 (M^+, 35), 145 (22), 131 (8), 129 (5), 127 (3), 118 (22), 117 (23), 116 (26), 115 (100), 103 (24), 89 (10), 78 (16), 77 (20).

6a: ^{1}H NMR data were in accordance with literature.[6] MS [*m/z* (rel. int.)]: 164 (M^+, 42), 133 (6), 132 (30), 131 (6), 105 (100), 77 (61).

7a: IR ($CDCl_3$): 3040 (w), 3000 (m), 2940 (s), 2910 (s), 2855 (m), 1715 (w), 1670 (s), 1590 (m), 1570 (w), 1440 (m), 1410 (w), 1380 (w), 1350 (w), 1325 (w), 1250 (m), 1210 (s), 1180 (m), 1170 (m), 1090 (s), 1060 (s), 1015 (w), 990 (w), 980 (w), 960 (w), 920 (w), 900 (w), 835 (w), 750 (s), 685 (m), 660 (m) cm^{-1}. ^{1}H NMR data were in accordance with the literature.[5] MS [*m/z* (rel. int.)]: 164 (M^+, 9), 133 (6), 132 (30), 131 (6), 105 (100), 77 (61).

8: MS: [*m/z* (rel. int.)]: 133 [$(M+1)^{+\cdot}$ 6], 132 (M^+, 50), 131 (10), 106 (8), 105 (100), 104 (8), 103 (4), 78 (9), 77 (77), 76 (4), 75 (3), 74 (5), 55 (12), 51 (34).

Solvolysis in 2,2,2-trifluoroethanol. The reaction mixture, composed of 1.00 g (3.12 mmol) of **1**, 1.03 g (4.68 mmol) of AgTFA, and 8.6 ml of 2,2,2-trifluoroethanol, was refluxed for 48 h. Work-up gave 0.80 g of a yellow oil, which was analysed by ^{1}H NMR spectroscopy prior to subsequent separation into a neutral fraction (0.60 g) and an acidic fraction (0.18 g). The neutral fraction was subsequently subjected to flash chromatography using hexane–ethyl acetate (95:5) as the eluent. Two compounds were isolated pure, **2** and 3-(2,2,2-trifluoroethoxy)-1-phenyl-1-propanone (**7b**); in addition an impure sample of 3-(2,2,2-trifluoroethoxy)-1-phenyl-1-propyne (**5b**) was obatined. The acidic fraction was subjected to flash chromatography with hexane–ethyl acetate–acetic acid (45:50:5) as the eluent. Pure samples of two acids were collected, (*Z*)-3-bromo-4-(2,2,2-trifluoroethoxy)-2-phenyl-2-butenoic acid (**3b**) and (*Z*)-3-bromo-2-phenyl-4-trifluoroacetoxy-2-butenoic acid (**4**). On the basis of the ^{1}H NMR spectrum of the crude product and the spectra of the isolated products the **1**:**2**:**3b**:**4**:**5b**:**7b** ratio was determined to be 1:47:32:1:2:17. The physical data were as follows.

3b: IR ($CHCl_3$): 3500–2400 (m), 3165 (w), 2930 (m), 2860 (w), 1715 (s), 1620 (w), 1585 (w), 1150 (w), 1485 (w), 1455 (w), 1440 (w), 1420 (w), 1385 (w), 1290 (w), 1235 (w), 1180 (w), 1140 (m), 1100(w), 1020 (w), 1000(w), 915 (s), 740 (s), 650 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.78 (2 H, q, *J* 8.6 Hz), 4.31 (2 H, s), 7.34–7.43 (5 H, m), 10.98 (1 H, br s). ^{13}C NMR ($CDCl_3$): δ 67.6 (q, *J* 34 Hz), 72.9, 126.7 (q, *J* 278 Hz), 123.5, 128.4, 128.9, 129.4, 133.4, 176.9. MS [*m/z* (rel. int.)]: 340 (M^+, 6), 338 (M^+, 6), 260 (4), 259 (25), 214 (5), 213 (28), 160 (15), 159 (98), 149 (3), 142 (3), 132 (5), 131 (35), 130 (4), 129 (5), 118 (2), 117 (2), 116 (10), 115 (41), 114 (4), 113 (5), 105 (5), 104 (12), 103 (100), 102 (18), 101 (3), 91 (5), 89 (7), 83 (11), 78 (3), 77 (21), 76 (4), 75 (5), 74 (3).

4: IR (KBr): 3600–2200 (m), 2985 (w), 2930 (m), 2880 (m), 1670 (s), 1630 (m), 1495 (w), 1470 (m), 1445 (m), 1414 (m), 1300 (s), 1240 (m), 1220 (s), 1095 (m), 1050 (m), 980 (m), 815 (w), 770 (w), 710 (s), 700 (s), 685 (m), 590 (m), 550 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.43 (2 H, s), 7.25–7.50 (5 H, m), 11.00 (2 H, br s). ^{13}C NMR ($CDCl_3$): δ 64.4, 114.2 (q, *J* 284 Hz), 127.7, 128.3 (2 CH), 129.2 (2 CH), 129.7, 132.8, 138.0, 161.6 (q, *J* 43 Hz), 172.8. MS [*m/z* (rel. int.)]: 258 (M^+, 2), 256 (M^+, 2), 178 (3), 177 (26), 160 (9), 159 (74), 132 (4),

131 (38), 130 (4), 129 (4), 121 (4), 120 (11), 119 (4), 105 (4), 103 (100), 102 (26), 101 (5), 91 (11), 89 (5), 78 (8), 77 (33), 76 (6), 75 (9).

5b: MS [*m/z* (rel. int.)]: 215 [$(M+1)^+$, 8], 214 (M^+, 77), 213 (10), 193 (2), 187 (1), 186 (7), 185 (2), 171 (3), 167 (1), 166 (10), 165 (7), 164 (2), 137 (2), 133 (1), 132 (1), 131 (7), 130 (2), 129 (6), 128 (1), 127 (6), 118 (6), 117 (14), 118 (19), 115 (100), 114 (5), 113 (4), 104 (4), 102 (4), 101 (2), 91 (3), 90 (1), 89 (9), 88 (4), 87 (4), 86 (3), 76 (11), 77 (15), 76 (4), 74 (5).

7b: IR (CCl_4): 3090 (w), 3065 (w), 3025 (w), 2960 (m), 2930 (m), 1770 (m), 1690 (s), 1595 (w), 1580 (w), 1575 (w), 1450 (m), 1420 (w), 1430 (w), 1360 (w), 1340 (w), 1315 (m), 1280 (s), 1285 (m), 1220 (m), 1165 (s), 1160 (s), 1100 (m), 1020 (m), 950 (m), 805 (m), 760 (s), 695 (m), 670 (m) cm^{-1}. ^{1}H NMR (CCl_4): δ 3.28 (2 H, t, *J* 6.3 Hz), 3.87 (2 H, q, *J* 8.8 Hz), 4.07 (2 H, t, *J* 6.3 Hz), 7.2–7.9 (5 H, m). ^{13}C NMR (CCl_4): δ 38.2, 67.6, 68.8 (q, *J* 34 Hz), 123.6 (q, *J* 278 Hz), 127.8 (2 CH), 128.2 (2 CH), 136.7, 195.0. MS [*m/z* (rel. int.)]: 233 [$(M+1)^+$, 4], 232 (M^+, 40), 168 (1), 167 (1), 153 (2), 149 (6), 134 (2), 133 (14), 132 (40), 131 (8), 130 (2), 113 (11), 107 (3), 106 (36), 105 (100), 104 (9), 103 (6), 102 (2), 91 (4), 83 (10), 79 (2), 78 (20), 77 (86), 76 (11), 75 (5), 74 (6).

Solvolysis in 2-propanol. The reaction mixture, composed of 1.01 g (3.16 mmol) of **1**, 1.06 g (4.82 mmol) of AgTFA, and 8.8 ml of isopropyl alcohol, was refluxed for 24 h. Work-up gave 0.68 g of a yellow oil, which was analysed by ^{1}H NMR spectroscopy prior to separation by flash chromatography with hexane–ethyl acetate (95:5) as the eluent. Five compounds were isolated: **2**, (*Z*)-3-bromo-4-isopropoxy-2-phenyl-2-butenoic acid (**3c**), the acid **4**, 3-isopropoxy-1-phenyl-1-propyne (**5c**) and 3-isopropoxy-1-phenyl-1-propanone (**7c**). On the basis of the ^{1}H NMR spectrum of the crude product and the spectra of the isolated products the **1**:**2**:**3c**:**4**:**5c**:**7c** ratio was determined to be 1:42:30:6:16:5. The physical data were as follows.

3c: IR (CCl_4): 3500–2500 (m), 3040 (w), 3010(w), 2975 (s), 2915 (m), 1720 (br s), 1615 (m), 1590 (m), 1570 (w), 1480 (m), 1455 (m), 1435 (m), 1400 (m), 1370 (m), 1320 (m), 1280 (s), 1260 (s), 1195 (s), 1170 (s), 1130 (m), 1110 (s), 1090 (s), 1060 (s), 1020 (w), 920 (w), 785 (m), 755 (w), 695 (s) cm^{-1}. ^{1}H NMR (CCl_4): δ 1.08 (6 H, d, *J* 6.1 Hz), 3.56 (1 H, sept, *J* 6.1 Hz), 4.04 (2 H, s), 7.32 (5 H, br s), 9.79 (1 H, br s). ^{13}C NMR (CCl_4): δ 21.8, 68.8, 70.9, 126.5, 128.2 (2 CH), 128.4 (2 CH), 134.0, 137.9, 171.5. MS [*m/z* (rel. int.]; 300 (M^+, 1), 298 (M^+, 1), 242 (3), 240 (5), 239 (4), 238 (2), 237 (3), 221 (4), 219 (24), 211 (2), 209 (2), 195 (3), 193 (3), 183 (4), 181 (4), 178 (6),177 (50), 176 (3), 175 (4), 161 (17), 160 (21), 159 (100), 148 (2), 142 (5), 132 (5), 131 (31), 114 (14), 115 (29), 114 (4), 107 (7), 103 (49), 102 (12), 89 (5), 77 (12), 63 (5).

5c: IR (CCl_4): 3020 (w), 2960 (w), 1715 (w), 1530 (w), 1320 (w), 1210 (s), 1190 (s), 1110 (m), 1060 (w), 1025 (m), 1005 (s), 970 (w), 670 (m) cm^{-1}. ^{1}H NMR (CCl_4): δ 1.18 (6 H, d, *J* 6.1 Hz), 3.83 (1 H, sept, *J* 6.1 Hz), 4.27 (2 H, s), 7.15–7.50 (5 H, m). ^{13}C (CCl_4): δ 22.1, 55.6, 69.8, 85.4, 86.2, 127.9 (1 CH), 128.1 (2 CH), 129.1 (C), 131.7 (2 CH). MS [*m/z* (rel. int.)]: 174 (M^+, 4), 160 (2), 159 (14), 145 (4), 131 (29), 117 (8), 116 (74), 115 (100), 104 (8), 103 (20), 102 (5), 89 (8), 77 (9), 63 (9).

7c: IR (CCl_4): 3045 (w), 2940 (s), 2910 (s), 2855 (m), 1715 (m), 1650 (w), 1590 (m), 1440 (m), 1385 (w), 1355 (w), 1250 (m), 1180 (m), 1090 (m), 1060 (m), 1015 (w), 980 (w), 980 (w), 960 (w), 920 (w), 900 (w), 660 (m) cm^{-1}. ^{1}H NMR (CCl_4): δ 1.11 (6 H, d, *J* 6.1 Hz), 3.10 (2 H, t, *J* 6.6 Hz), 3.56 (1 H, sept, *J* 6.1 Hz), 3.74 (2 H, t, *J* 6.6 Hz), 7.30–7.50 (3 H, m), 7.85–7.95 (2 H, m). ^{13}C NMR (CCl_4): δ 21.9 (2 CH_3), 38.8, 63.1, 71.3, 127.9 (2 CH), 128.0 (2 CH), 132.2 (CH), 137.2 (C), 196.1. MS [*m/z* (rel. int.)]: 192 (M^+, 1), 150 (3), 149 (25), 134 (8), 133 (15), 132 (2), 106 (10), 105 (100), 78 (5), 77 (30).

Solvolysis in 2-methyl-2-propanol. The reaction mixture, composed of 1.53 g (4.78 mmol) of **1**, 1.58 g (7.20 mmol) of AgTFA, and 13 ml of *tert*-butyl alcohol, was refluxed for 24 h. Work-up gave 0.99 g of a yellow oil, which was analysed by ^{1}H NMR spectroscopy prior to subsequent separation into a neutral fraction (0.60 g) and an acidic fraction (0.29 g). The neutral fraction was subjected to flash chromatography using hexane–ethyl acetate (95:5) as the eluent. Three compounds were isolated pure, butenolide **2**, 3-*tert*-butoxy-1-phenyl-1-propyne (**5d**) and 3-*tert*-butoxy-1-phenyl-1-propanone (**7d**). The acidic fraction was subjected to flash chromatography with hexane–ethyl acetate–acetic acid (45:50:5) as the eluent. Pure samples of two acids were collected, (*Z*)-3-bromo-4-*tert*-butoxy-2-phenyl-2-butenoic acid (**3d**) and the acid **4**. On the basis of the ^{1}H NMR spectrum of the crude product and the spectra of the isolated products the **1**:**2**:**3d**:**4**:**5d**:**7d** ratio was determined to be 7:68:1:10:12:2. The physical data were as follows.

3d: IR (CCl_4): 3500–2550 (m), 3040 (w), 2975 (s), 2915 (m), 1715 (br s), 1590 (m), 1570 (w), 1490 (m), 1455 (m), 1435 (m), 1405 (m), 1380 (m), 1350 (m), 1280 (s), 1195 (s), 1170 (s), 1130 (m), 1110 (s), 1090 (s), 1060 (s), 1020 (w), 920 (w), 695 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.14 (9 H, s), 4.23 (2 H, s), 7.22–7.46 (5 H, m), 9.92 (1 H, br s).

5d: IR (CCl_4): 3050 (w), 2945 (s), 2910 (s), 2850 (m), 1590 (w), 1505 (w), 1435 (w), 1380 (w), 1355 (m), 1270 (s), 1250 (s), 1180 (m), 1145 (m), 1090 (m), 1060 (m), 1035 (m), 1010 (m), 970 (w), 925 (w), 790 (s), 660 (m) cm^{-1}. ^{1}H NMR (CCl_4): δ 1.25 (9 H, s), 4.20 (2 H, s), 7.19–7.38 (5 H, m). ^{13}C NMR ($CDCl_3$): δ 27.3, 51.4, 74.6, 84.5, 87.3, 128.2 (2 CH), 128.9 (2 CH), 129.5 (C), 131.2 (2 CH). MS [*m/z* (rel. int.)]: 189 [$(M+1)^+$, 2], 188 (M^+, 11), 133 (6), 132 (48), 131 (71), 116 (17),115 (100), 105 (15), 104 (20), 103 (22), 102 (18), 89 (11), 78 (11), 77 (26), 63 (16), 57 (62), 56 (28), 55 (10).

7d: IR ($CDCl_3$): 3065 (w), 3040 (w), 2960 (s), 2910 (m), 1730 (m), 1640 (m), 1590 (w), 1480 (w), 1440 (m),

1380 (m), 1360 (m), 1320 (w), 1250 (s), 1225 (m), 1185 (s), 1170 (s), 1090 (s), 1065 (s), 1010 (m), 900 (s), 800 (m), 725 (s), 690 (m), 640 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.19 (9 H, s), 3.20 (2 H, t, *J* 6.8 Hz), 3.80 (2 H, t, *J* 6.8 Hz), 7.38–7.60 (3 H, m), 7.92–8.07 (2 H, m). ^{13}C NMR ($CDCl_3$): δ 26.0, 38.9, 66.4, 72.9, 127.2, 127.9, 131.3, 190.0; MS [*m/z* (rel. int.)]: 191 (1), 150 (6), 149 (15), 133 (21), 123 (34), 131 (16), 120 (6), 106 (12), 105 (100), 104 (6), 78 (10), 77 (82), 59 (13), 57 (18), 56 (32), 55 (27).

Solvolysis in 1,1,1,3,3,3-hexafluoro-2-propanol. The reaction mixture, composed of 1.01 g (3.16 mmol) of **1**, 1.06 g (4.82 mmol) of AgTFA, and 8.8 ml of HFP, was refluxed for 36 h before final work-up. However, a sample was withdrawn after 24 h and analysed by ^1H NMR spectroscopy. Final work-up gave 0.70 g of a yellow oil, which was analysed by ^1H NMR spectroscopy prior to subsequent separation into a neutral fraction (0.56 g) and an acidic fraction (0.12 g). The neutral fraction was subsequently subjected to flash chromatography using hexane–ethyl acetate (95:5) as the eluent. Only one compound was isolated pure, butenolide **2**. The acidic fraction was subjected to flash chromatography with hexane–ethyl acetate–acetic acid (45:50:5) as the eluent. Pure samples of unreacted **1** and the acid **4** were obtained. On the basis of the ^1H NMR spectrum of the crude product and the spectra of the isolated products the **1**:**2**:**4** ratio was determined to be 4:80:16.

Addition of methanol to **5a**. A mixture of **5a** (0.15 g, 1.03 mmol), AgTFA (0.20 g, 0.91 mmol) and methanol (15 ml) was refluxed for 10 h. The reaction was quenched with dilute hydrochloric acid and extracted with ether. The combined extracts were dried ($MgSO_4$), concentrated under vacuum, and analysed by GLC and ^1H NMR spectroscopy. The analyses revealed that the product mixture consisted of **5a**, **6a** and **7a** in a 55:2:43 ratio.

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