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Synthesis and some chemical properties of 3,3,4,4-tetraethoxybut-1-yne

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Abstract—Ring opening of 1,1-dibromo-2-chloro-2-diethoxymethylcyclopropane in a mixture of ethanol and dichloromethane with 50% aqueous sodium hydroxide in the presence of triethylbenzylammonium chloride (TEBA) gave 3,3,4,4-tetraethoxybut-1-yne (TEB) in excellent yield. This alkyne appears to be thermally stable at least up to 150 °C. The compound is also stable in neutral and basic aqueous solutions. In acidic aqueous media, however, TEB is unstable and was converted to one or several products depending on the reaction conditions. The most useful reaction appears to be deketalization to give 1,1-diethoxybut-3-yn-2-one, which was obtained in quantitative yield under the optimum conditions.

1. Introduction

Substituted 1,1,2-trihalocyclopropanes (**1**) (Fig. 1), dissolved in a mixture of ethanol and some dichloromethane, undergo ring opening and give mixtures of the corresponding acetylenic diethyl ketals and acetylenic diethyl acetals when exposed to 50% sodium hydroxide in the presence of a small amount of triethylbenzylammonium chloride (TEBA), a phase-transfer catalyst.[1–5] Mechanistic studies have shown that the ring opening is a multistep process encompassing several dehydrohalogenations and involving a cyclopropene intermediate, 1-*R*-3,3-dihalocyclopropene (**2**), which is consumed by nucleophilic attack of ethoxide and ethanol at C-1 and C-2, respectively, affording ketals and acetals, respectively.[3–5] The consumption of **1** appeared to be rather sensitive to the steric bulk of the R group; attack of C-1 and subsequent formation of the corresponding acetylenic ketal decreases when R becomes sterically more demanding.[6] In keeping with this trend, for instance, 1,1-dibromo-2-*tert*-butyl-2-chlorocyclopropane undergoes ring opening to give 1,1-diethoxy-4,4-dimethylpent-2-yne as the only product; not even traces of the corresponding acetylenic ketal, 3,3-diethoxy-4,4-dimethylpent-1-yne, is observed (Scheme 1).[6]

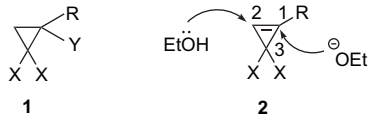
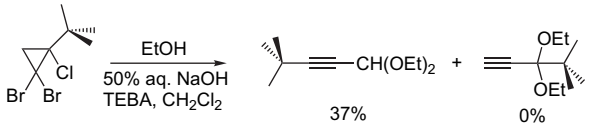


Figure 1.



Scheme 1.

On the basis of these observations it seems reasonable to anticipate that if 1,1-dibromo-2-chloro-2-diethoxymethylcyclopropane (**3**) is subjected to sodium hydroxide under the phase-transfer conditions outlined above, the intermediate cyclopropene, 3,3-dibromo-1-(diethoxymethyl)cyclopropene (**4**), would for steric reasons be predominantly attacked at C-2 and give mainly 1,1,4,4-tetraethoxybut-2-yne (**5**). However, it could also be argued that the diethoxymethyl moiety possesses sufficient hydrogen-bonding ability to redirect the ethanol attack from C-2 to C-1; as a result the main product should be 3,3,4,4-tetraethoxybut-1-yne (**6**), a structural isomer of **5** (Scheme 2). Cyclopropane **3** was therefore synthesized and exposed to sodium hydroxide under our standard conditions to determine the correct line of reasoning.[7]

Keywords: Halocyclopropane; Ring opening; Terminal alkyne; Acetals; Deacetalization.
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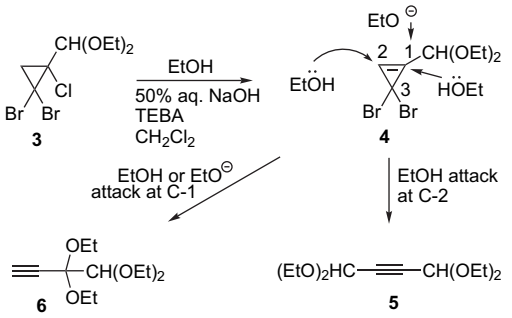
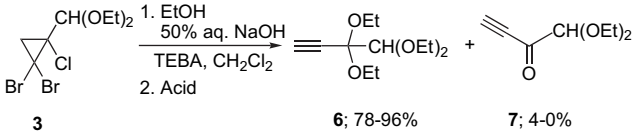


Scheme 2.

2. Results and discussion

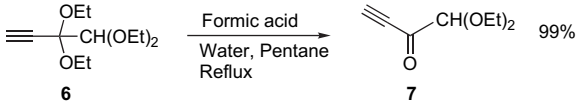
When 1,1-dibromo-2-chloro-2-diethoxymethylcyclopropane (**3**) (prepared from 2-chloroprop-2-enal diethyl acetal by Makosza's method[8]) was dissolved in a mixture of 4 equiv of ethanol and some dichloromethane and treated with 8 equiv of 50% sodium hydroxide in the presence of TEBA, a smooth and clean reaction took place. The composition of the product mixture appeared to depend on the pH of the hydrolyzate and on how quickly the extraction was carried out. When the hydrolyzate was basic, only one product was obtained, viz. 3,3,4,4-tetraethoxybut-1-yne (**6**) (denoted TEB in the following). The isolated yield of **6** turned out to depend somewhat on the scale of the reaction due to loss of product during the distillation; on a small scale (below 0.05 mol) yields in the range of 78–82% were achieved whereas yields as high as 96% were obtained when the reaction was performed on a larger scale (up to 2 mol). On the other hand, if the work-up was carried out from an acidic hydrolyzate, two products could be obtained, viz. **6** and 1,1-diethoxybut-3-yn-2-one (**7**), the corresponding ketone, depending on the work-up procedure (Scheme 3). The ratio **6/7** was sensitive to the extraction procedure; the slower the extraction operation, the higher the yield of **7**. This clearly indicates that **6** is prone to deketalization under acidic aqueous conditions (vide infra), which is no surprise since acetals and ketals are converted to the corresponding aldehydes and ketones under such conditions.[9,10]



Scheme 3.

The thermal stability of TEB (**6**) was tested by keeping the compound under nitrogen below and at rt as well as at elevated temperatures for extended periods of time, either neat or at reflux in inert solvents. The samples were analyzed at intervals by ^{1}H NMR spectroscopy. When kept neat at 100 °C and below for one week, no reaction was detected, and the same was the case when solutions of **6** in chlorobenzene and bromobenzene were refluxed at 132 and 155 °C, respectively. Thus, **6** appears to be thermally stable in the temperature range prevailing during most reactions used to carry out transformations in organic chemistry.

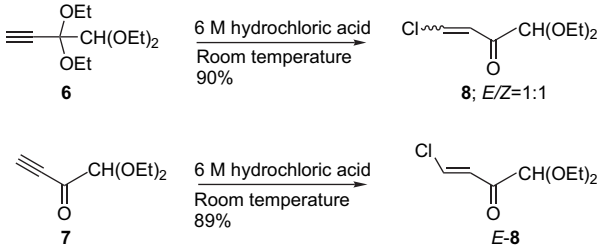
TEB was also compatible with water under neutral and basic conditions, but as indicated above, the compound reacted when exposed to acidic conditions. The outcome depended on the acid employed as well as the reaction conditions. Thus, when treated with concentrated sulfuric acid, **6** decomposed completely and gave a black, tarry residue, and when exposed to a mixture of aqueous trifluoroacetic acid and chloroform, a reagent used successfully to deketalize and deacetalize similar compounds,[11,12] an intractable product mixture was formed. However, when the compound was treated with diluted aqueous sulfuric acid, **6** was deketalized in a clean reaction and furnished 1,1-diethoxybut-3-yn-2-one (**7**), albeit in fairly low yield (about 10%). This transformation was even more successful in moist acetone containing either some beads of Dowex 50W or some drops of phosphoric acid; in both cases the ketal moiety reacted and furnished **7** in better than 90% yield. But the best results were obtained when TEB was exposed to a mixture of pentane, formic acid and water; under these conditions ketone **7** was isolated in quantitative yield (Scheme 4). In 80% aqueous acetic acid, on the other hand, no reaction occurred.



Scheme 4.

In hydrochloric acid the situation turned out to be more complex. When [HCl] was below 3 M, conditions successfully employed by De Kimpe and Stevens to achieve similar transformations,[13] TEB did not react at rt, but in more concentrated solutions such as 6 M, **6** was converted to 4-chloro-1,1-diethoxybut-3-en-2-one (**8**), which was isolated in better than 85% yield as an *E*/*Z* isomeric mixture. The ^{1}H spectrum of **8** contains two *AB quartets* in a 1:1 ratio, one for each pair of the olefinic protons with very different vicinal coupling constants (8.3 Hz as compared to 13.8 Hz), whereas its ^{13}C spectrum exhibits four pairs of signals due to the carbon atoms in the but-3-en-2-one carbon skeleton as well as partly overlapping signals from the ethyl groups (see Section 4). The $^3J_{HH}$ olefinic coupling constants are in accordance with literature values.[14,15]

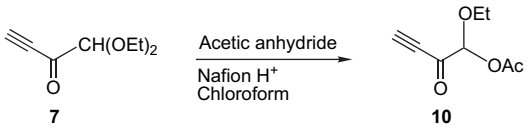
The ketone formation is conceivably a two-step process; deketalization takes place first and affords the α,β-unsaturated acetylenic ketone **7**, which is consumed by HCl addition to the conjugated triple bond in a formal Michael addition. This rationalization was supported by exposing **7** to 6 M hydrochloric acid; **7** reacted and afforded **8** as the only product. It is quite noteworthy that **8** in this case was obtained as a single isomer, viz. *E*-**8** (Scheme 5); the reason for this



Scheme 5.

specificity is not clear, but further studies will hopefully clarify the picture. There is no precedence for such a smooth and efficient addition of hydrogen chloride to α,β-unsaturated acetylenic ketones in the literature, but similar reactions carried out at elevated temperature or in the presence of a metal catalyst have been reported. Lithium chloride in acetic acid reacts in an analogous fashion with triple bonds conjugated to various carbonyl groups and furnishes the corresponding β-chloro-substituted α,β-unsaturated product(s) in fair to good yields.[15] Similar reactions involving iron and cerium catalysts have also been published.[16,17]

A number of experiments aiming at converting **7** to 2-oxobut-3-ynal (**9**) have been carried out, using reagents such as aqueous trifluoroacetic acid[11,12] and hydrochloric acid,[13] but so far with no success. The only stable modification of the diethyl acetal moiety of **7** achieved so far took place when the compound was exposed to acetic anhydride in the presence of Nafion-H^+, as described by Petrakis and Fried;[18] formally one of the ethoxy groups was replaced by an acetoxy group and 1-ethoxy-2-oxobut-3-ynyl acetate (**10**) was formed and isolated in 86% yield (Scheme 6). Conversion of **7** to **9** is still under investigation.



7 10

Scheme 6.

3. Conclusion

3,3,4,4-Tetraethoxybut-1-yne (TEB; **6**) has been prepared and been shown to be a thermally stable compound. The compound is also stable under neutral and basic conditions, but undergoes valuable transformations under acidic conditions. TEB's high density of functional groups with a range of chemical properties makes it a useful starting material for the synthesis of a variety of functionalized molecules. The scope of a number of such transformations is currently being investigated.

4. Experimental

4.1. General

IR spectra were recorded on a Nicolet Impact 410 infrared spectrophotometer. NMR spectra were run on a Bruker Spectrospin AC 200 F. Chemical shifts are reported downfield from TMS and coupling constants are given in hertz. GC analyses were performed on a HP 5890 Gas Chromatograph with a flame ionization detector and a HP Ultra 1 column (100% dimethyl-polysiloxane, 25 m, 0.2 mm i.d., 0.33 μm). Flash chromatography was carried out with silica gel (230–400 mesh) as the stationary phase and mixtures of hexane and ethyl acetate as the mobile phase. The eluent composition is given in each case. TLC analyses of the reaction mixtures were performed with silica gel (60 F_{254}) on aluminium sheets with mixtures of hexane and ethyl acetate as the mobile phase. Mass spectra were obtained on a VG 7070 Micromass spectrometer or an Autospec Ultima mass spectrometer, a three-sector instrument with EBE geometry from Micromass Ltd. Manchester, both operated in the EI mode at 70 eV. All boiling points are uncorrected.

4.2. Transformations

4.2.1. 1,1-Dibromo-2-chloro-2-diethoxymethylcyclopropane (3). A three-necked flask was charged with 2-chloro-1,1-diethoxyprop-2-ene (82.6 g, 0.50 mol), bromoform (1264.0 g, 5.00 mol) and TEBA (1.0 g), and 50% aqueous sodium hydroxide (320 g, 4.00 mol) was added over a period of 30 min while the reaction mixture, kept at 0 °C (ice-water bath), was stirred vigorously. The two-phase system was left stirring for 24 h, and water (500 mL) was then added. The phases were separated, and the aqueous phase was extracted with dichloromethane (3×150 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated in vacuo on rotary evaporator. Distillation of the crude residue gave **3** (100.6 g, 0.30 mol, 60%) as a clear liquid, bp 80–82 °C, 0.15 mmHg. IR (film): ν_{max} 3090 (w), 3000 (s), 2950 (s), 2910 (s), 2890 (s), 1740 (w), 1458 (m), 1450 (m), 1380 (s), 1360 (s), 1340 (m), 1280 (m), 1190 (s), 1115 (s), 1180 (s), 1020 (m), 970 (m), 930 (m), 845 (w), 710 (m), 675 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.15–1.33 (m, 6H), 1.93 (d, *J*=9.4 Hz, 1H), 2.06 (d, *J*=9.4 Hz, 1H), 3.48–3.84 (m, 4H), 4.50 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 15.00, 15.03, 29.3, 34.7, 51.4, 63.4, 64.0, 103.3; MS (EI): *m/z* 295 (8), 293 (35), 291 (50), 267 (2), 265 (12), 263 (16), 261 (6), 251 (6), 249 (16), 247 (20), 245 (10), 201 (6), 199 (8), 197 (3), 186 (18), 185 (75), 157 (48), 150 (62), 122 (30), 121 (13), 119 (21), 103 (80), 94 (15), 86 (5), 84 (30), 80 (28), 78 (70), 75 (100); HRMS: calcd for [$M^{+\bullet}-EtO^{\bullet}$; $C_6H_8{}^{79}Br_2{}^{35}ClO^+$] 288.8630, found 288.8602.

4.2.2. 3,3,4,4-Tetraethoxybut-1-yne (6). To a stirred mixture of **3** (168.00 g, 0.50 mol), ethanol (138.00 g, 3.00 mol), TEBA (1.0 g) and dichloromethane (700 mL) kept at 0 °C (ice-water bath) was added dropwise 50% aqueous sodium hydroxide (160.00 g, 2.00 mol). The reaction mixture was stirred vigorously at bath temperature for 24 h, before water (500 mL) was added. The phases were separated, and the aqueous phase was extracted with dichloromethane (3×100 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated in vacuo on rotary evaporator. Distillation of the crude residue gave **6** (110.8 g, 0.48 mol, 96%) as a clear liquid, bp 53–58 °C, 0.2 mmHg. IR (film): ν_{max} 3258 (m), 2977 (m), 2930 (m), 2895 (s), 2114 (w), 1725 (w), 1600 (w), 1635 (w), 1478 (w), 1447 (m), 1387 (m), 1334 (m), 1117 (s), 1080 (s), 932 (w), 885 (m), 771 (w), 651 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.17–1.31 (m, 12H), 2.60 (s, 1H), 3.63–3.86 (m, 8H), 4.40 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 15.0, 15.1, 59.4, 64.7, 74.9, 78.0, 98.4, 103.6; MS (EI): *m/z* 230 (15, M^+), 205 (30), 186 (52), 185 (52), 169 (85), 127 (98), 103 (83), 93 (85), 71 (100); HRMS: calcd for [M^+; $C_{12}H_{22}O_4^+$] 230.1518, found 230.1511.

4.2.3. 1,1-Diethoxybut-3-yn-2-one (7). *Method A*: A suspension of Dowex 50W (0.50 g) in a mixture of **6** (1.00 g, 4.34 mmol), acetone (25 mL) and water (1.0 mL) was refluxed for 8 h. The reaction mixture was filtered and concentrated in vacuo on a rotary evaporator. Purification of the

residue by flash chromatography (hexane–ethyl acetate, 95:5, v/v) provided **7**[19] (0.62 g, 4.00 mmol, 92%) as a colourless oil.

Method B: A mixture of **6** (1.00 g, 4.34 mmol), phosphoric acid (0.20 g), acetone (25 mL) and water (1.0 mL) was refluxed for 8 h. Some more water (25 mL) was added, and the resulting aqueous phase was extracted with dichloromethane (3×25 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated in vacuo on a rotary evaporator. Purification of the residue by flash chromatography (hexane–ethyl acetate, 95:5, v/v) provided **7** (0.65 g, 4.17 mmol, 96%) as a colourless liquid.

Method C. A mixture of **6** (3.50 g, 15.20 mmol), pentane (25 mL), formic acid (0.4 mL) and water (0.5 mL) was refluxed for 30 min. Water (25 mL) was added, the phases were separated, and the aqueous phase was extracted with dichloromethane (3×20 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated in vacuo on a rotary evaporator to give **7** (2.35 g, 15.05 mmol, 99%) as a pure and colourless liquid. The product was subsequently distilled, bp 52–53 °C at 1 mmHg. IR (film): ν_{max} 3369 (w), 3252 (s), 2981 (s), 2933 (s), 2887 (s), 2096 (s), 1697 (s), 1585 (w), 1481 (m), 1445 (m), 1393 (m), 1373 (m), 1320 (m), 1295 (m), 1219 (m), 1172 (s), 1070 (s), 927 (m), 909 (m), 856 (w), 838 (w), 783 (m), 699 (m), 666 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.27 (t, J=7.1 Hz, 6H), 2.66 (s, 1H), 3.62–3.95 (m, 4H), 4.68 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 15.1, 63.3, 76.6, 82.4, 101.5, 182.4; MS (EI): *m/z* 127 (4), 113 (3), 112 (35), 111 (52), 110 (3), 105 (15), 104 (91), 103 (53), 99 (12), 95 (23), 86 (5), 85 (10), 84 (84), 83 (55), 77 (16), 76 (90), 75 (52), 66 (15), 57 (45), 55 (100); HRMS: calcd for [$M^{+\bullet}-EtO^{\bullet}$; $C_6H_7O_2^+$] 111.0446, found 111.0443.

4.2.4. (*E*),(*Z*)-4-Chloro-1,1-diethoxybut-3-en-2-one ((*E*)-8, (*Z*)-8). A heterogeneous mixture of **6** (0.50 g, 2.17 mmol), dichloromethane (20 mL) and 6.0 M hydrochloric acid (15 mL) was vigorously stirred at rt for 72 h. Water (10 mL) was added, the phases were separated, and the aqueous phase was extracted with dichloromethane (3×10 mL). The combined organic phases were washed with saturated aqueous sodium hydrogencarbonate (50 mL), dried ($MgSO_4$), filtered and concentrated in vacuo on a rotary evaporator. Purification of the crude residue by flash chromatography (hexane–ethyl acetate, 95:5) provided a 1:1 mixture (determined by ^1H NMR spectra of the mixture) of *E*-**8** and *Z*-**8** (0.52 g, 2.70 mmol, 90%) as a colourless liquid. Pure samples of the two isomers, approximately 0.2 g of each obtained by flash chromatography (hexane–ethyl acetate, 95:5, v/v), were analyzed by spectroscopic and spectrometric methods.

(*E*)-**8**: IR (film): ν_{max} 3079 (w), 2979 (s), 2932 (m), 2883 (m), 1705 (s), 1686 (m), 1588 (s), 1481 (w), 1446 (w), 1320 (m), 1296 (m), 1161 (m), 1103 (s), 1063 (s), 943 (m), 903 (w), 844 (w), 734 (w), 641 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.02–1.32 (m, 6H), 3.54–3.77 (m, 4H), 4.69 (s, 1H), 6.81 (d, J=13.8 Hz, 1H), 7.53 (d, J=13.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.9, 63.2, 102.3, 127.6, 139.1, 191.7; MS (EI): *m/z* 194 (3), 193 (11), 192 (6), 191 (30), 165 (20), 163 (35), 149 (65), 147 (80), 135 (12), 129 (40), 121 (93), 119 (82), 117 (47), 107 (6), 106 (12), 103 (70), 102 (28), 93 (42), 91 (63), 83 (100), 75 (72), 73 (30), 63 (41), 61 (46); HRMS: calcd for [$M^{+\bullet}$; $C_8H_{13}{}^{35}ClO_3^+$] 192.0553, found 192.0564; calcd for [$M^{+\bullet}-EtO^{\bullet}$; $C_6H_8{}^{35}ClO_2^+$] 147.0213, found 147.0214.

(*Z*)-**8**: IR (film): ν_{max} 3077 (w), 2979 (s), 2932 (m), 2884 (m), 2179 (w), 1713 (s), 1590 (s), 1481 (w), 1446 (w), 1372 (w), 1319 (m), 1163 (m), 1101 (s), 1063 (s), 907 (m), 791 (m), 741 (m), 719 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.02–1.32 (m, 6H), 3.54–3.77 (m, 4H), 4.73 (s, 1H), 6.74 (d, J=8.3 Hz, 1H), 6.87 (d, J=8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.9, 63,1, 63.2, 102.4, 122.9, 132.6, 192.0; MS (EI): *m/z* 194 (0.5), 193 (3), 192 (0.6), 191 (4), 165 (10), 163 (12), 135 (15), 133 (14), 107 (12), 103 (100), 84 (10), 75 (78); HRMS: calcd for [$M^{+\bullet}-EtO^{\bullet}$; $C_6H_8{}^{35}ClO_2^+$] 147.0213, found 147.0221.

4.2.5. (*E*)-4-Chloro-1,1-diethoxybut-3-en-2-one ((*E*)-8). A heterogeneous mixture of **7** (0.20 g, 1.28 mmol), dichloromethane (10 mL) and 6.0 M hydrochloric acid (3 mL) was vigorously stirred at rt for 48 h. Water (10 mL) was added, the phases were separated, and the aqueous phase was extracted with dichloromethane (3×20 mL). The combined organic phases were washed with saturated aqueous sodium hydrogencarbonate (50 mL), dried ($MgSO_4$), filtered and concentrated in vacuo on a rotary evaporator. Purification of the crude residue by flash chromatography (hexane–ethyl acetate, 95:5) provided (*E*)-**8** (0.22 g, 1.14 mmol, 89%) as a colourless liquid. The spectroscopic and spectrometric data were identical to those reported above (see Section 4.2.4)

4.2.6. 1-Ethoxy-2-oxobut-3-ynyl acetate (10). Alkyne **7** (1.00 g, 6.40 mmol) was added to a stirred mixture of Nafion H^+ pellets (1.0 g), acetic anhydride (4.57 g, 44.8 mmol) and chloroform (5 mL). The reaction mixture was stirred at rt for 48 h before the pellets were removed by filtration. Water (10 mL) was added and the resulting mixture was stirred at rt for 24 h. The phases were then separated, and the aqueous phase was extracted with dichloromethane (3×10 mL). The combined organic phases were washed with water (10 mL), dried ($MgSO_4$), filtered and concentrated in vacuo on a rotary evaporator. Purification of the crude residue by flash chromatography (hexane–ethyl acetate, 95:5, v/v) provided **10** (0.94 g, 5.52 mmol, 86%) as a colourless oil. IR (film): ν_{max} 3261 (s), 2984 (s), 2939 (m), 2903 (m), 2099 (s), 1748 (s), 1705 (s), 1374 (s), 1236 (s), 1179 (s), 1105 (s), 1020 (s), 973 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.29 (t, J=7.1 Hz, 3H), 2.19 (s, 3H), 3.56 (s, 1H), 3.68–3.99 (m, 2H), 5.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.6, 20.4, 66.3, 78.6, 83.1, 95.5, 169.7, 178.3; MS (EI): *m/z* 170 (5, M^+), 143 (1), 142 (8), 141 (11), 129 (2), 128 (15), 119 (4), 118 (35), 117 (55), 110 (56), 110 (5), 100 (26), 96 (22), 95 (31), 89 (3), 87 (7), 85 (11), 84 (50), 83 (65), 77 (2), 76 (13), 75 (62), 73 (15), 69 (8), 68 (14), 61 (49), 57 (35), 55 (100); HRMS: calcd for [$M^{+\bullet}-EtO^{\bullet}$; $C_6H_5O_3^+$] 125.0239, found 125.0244.

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