Ring opening of some 1,1,2-trihalocyclopropanes with a polar substituent attached to C-2; evidence for regioselective attack directed by hydrogen bonding

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Dedicated to Professor Torbjörn Norin on the occasion of his 75th anniversary

Abstract
Selected members of the title family of compounds, prepared from 1,1-dibromo-2-chloro-2-diethoxymethylcyclopropane by standard chemical transformations, were dissolved in mixtures of dichloromethane and a protic, nucleophilic reagent and treated with 50% aqueous sodium hydroxide in the presence of a phase-transfer catalyst, triethylbenzylammonium chloride (TEBA), at room temperature. In all cases except two, regiospecific ring opening of the cyclopropane took place, giving one product formed by nucleophilic attack of the carbon atom to which the polar substituent was attached. This clearly lends support to the notion that hydrogen bonding contributes significantly to direct the attack of protic nucleophiles.

Keywords: Halocyclopropanes, ring opening, phase-transfer catalysis, acetylenic ketals, acetylenic acetals, hydrogen bonding

Introduction

It is well established that 2-substituted 1,1,2-trihalocyclopropanes (**1**) undergo ring opening and give mixtures of the corresponding acetylenic diethyl ketals (**2**) and acetylenic diethyl acetals (**3**) when exposed to 50% aqueous sodium hydroxide in the presence of an excess of ethanol and some triethylbenzylammonium chloride (TEBA), a phase-transfer catalyst.[1-5] Mechanistic studies have shown that the reaction under these phase-transfer conditions (PTC) is a multistep process encompassing several dehydrohalogenations and involving a cyclopropene intermediate, the corresponding 1-R-3,3-dihalocyclopropene (Figure 1), which is consumed by nucleophilic attack of ethoxide and ethanol at C-1 and C-2, respectively, affording both ketal and acetal.[4,5]

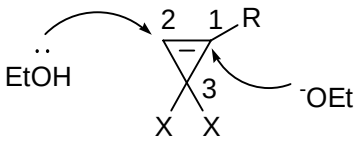
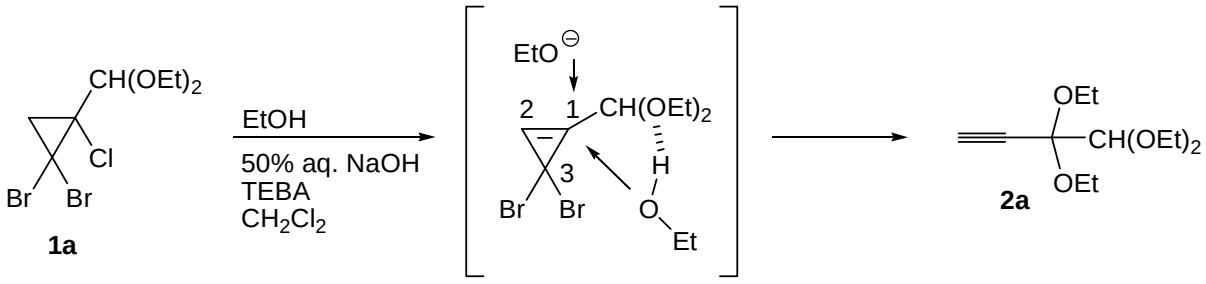


Figure 1. Ring opening of 2-R-substituted 1,1,-dihalo-2-chlorocyclopropane derivatives under PTC in the presence of ethanol occurs via the corresponding 1-R-substituted 3,3-dihalocyclopropenes, which are attacked by ethanol and ethoxide as indicated.

It has been established that the nucleophilic attack of the cyclopropene intermediate is sensitive to the steric bulk of R in such a way that the amount of acetylenic ketal decreases when R becomes sterically more demanding.[6] However, one compound that appeared to deviate from this rule, was 1,1-dibromo-2-chloro-2-diethoxymethylcyclopropane (**1a**) which afforded 3,3,4,4-tetraethoxybut-1-yne (**2a**) as the only product when treated with sodium hydroxide under standard conditions (Scheme 1).[7] Exclusive formation of this ketal requires regiospecific attack of the cyclopropene intermediate at the carbon atom bearing the polar substituent, and this suggests that the steric repulsion between ethanol molecules and R, the diethoxymethyl moiety, is more then offset by attractive forces due to hydrogen bonding between the same entities.



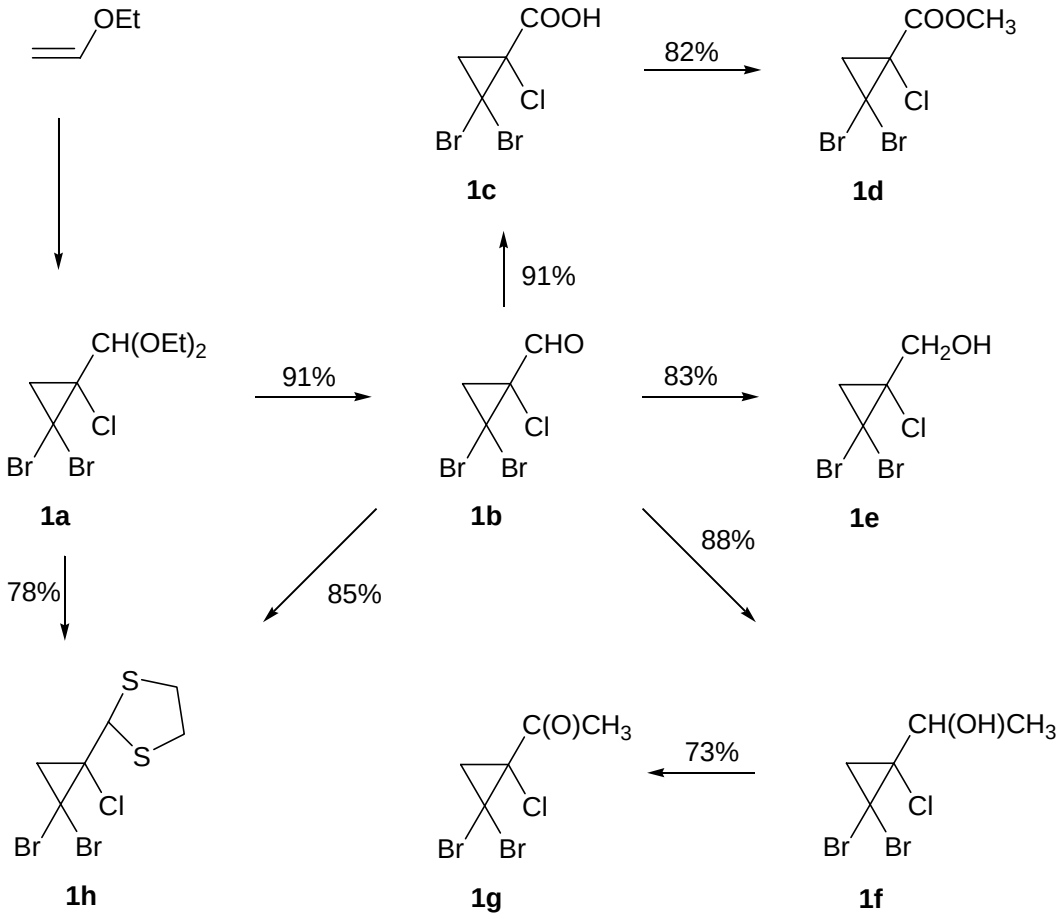
Scheme 1

It is quite conceivable that this seemingly exceptional case is not really extraordinary, but reflects a general reactivity pattern which remains to be uncovered. We therefore decided to extend the scope of our studies by reacting selected 1,1,2-trihalocyclopropanes with a different polar substituent at C-2 under the reaction conditions employed to convert **1a** to **2a**,[7] and by reacting **1a** in the presence of protic reagents other than ethanol. The results of our investigations are reported here.

Results and Discussion

Preparation of cyclopropanes

Seven 1,1-dibromo-2-chlorocyclopropanes with a polar substituent attached to C-2 were prepared from **1a** by well-established synthetic transformations (Scheme 2). Hydrolysis of **1a** to give 2,2-dibromo-1-chlorocyclopropanecarbaldehyde (**1b**) was unsatisfactory with some acids, but when 80% aqueous formic acid was employed, the corresponding aldehyde was obtained in 91% yield. Subsequent Jones oxidation of the aldehyde afforded the corresponding 2,2-dibromo-1-chlorocyclopropanecarboxylic acid (**1c**) in very good yield (91%), and conversion of this acid to the corresponding methyl ester, methyl 2,2-dibromo-1-chlorocyclopropanecarboxylate (**1d**), was uneventful when **1c** was exposed to a mixture of methanol and a catalytic amount of sulfuric acid at elevated temperature.



Scheme 2. Structures and yields of cyclopropanes **1b**-**1h** prepared from **1a** as described in this paper.The synthesis of **1a** from ethyl vinyl ether is described in refs. 7 and 8.

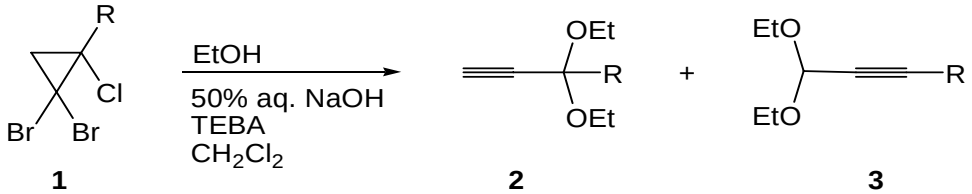
Aldehyde **1b** is also an excellent starting material for the preparation of primary and secondary alcohols. When treated with sodium borohydride in ethanol, 2,2-dibromo-1-chlorocyclopropylmethanol (**1e**) was obtained in 83% yield, and exposure of the same aldehyde to methylmagnesium iodide furnished 1-(2,2-dibromo-1-chlorocyclopropyl)ethanol (**1f**) in excellent yield (88%). It is noteworthy that no product due to reduction of the *gem*-dibromo moiety was observed in the latter case, since it is well known that this Grignard reagent has the ability to convert similar cyclopropanes to the corresponding monobromides.[9,10] With **1f** at hand formation of the corresponding ketone, 2,2-dibromo-1-chlorocyclopropyl methyl ketone (**1g**), was envisaged to take place by a simple Jones oxidation, and this was indeed achieved under standard conditions.

Exploratory experiments with **1a** revealed that this cyclopropane could be converted directly to other acetals under various conditions. This reactivity pattern was utilized to prepare a thioacetal, 2-(2,2-dibromo-1-chlorocyclopropyl)-1,3-dithiolane (**1h**), which was obtained in good yield (78%) by treating **1a** with 1,2-ethanedithiol in the presence of slightly acidic silica gel at room temperature.[11] The same dithiolane could also be synthesized, with a slightly better yield (85%), by reacting aldehyde **1b** with 1,2-ethanedithiol in the presence of boron trifluoride diethyl etherate following a somewhat modified literature procedure.[12]

Ring opening of cyclopropanes 1b-1h under PTC in the presence of ethanol

Cyclopropanes **1b** – **1h** were treated with sodium hydroxide under the same phase-transfer conditions that were applied when **1a** was converted quantitatively to 3,3,4,4-tetraethoxybut-1-yne (**2a**). All the compounds appeared to react under these conditions, and most of them gave one product only, *viz*. the alkyne analogous to **2a**, although there were exceptions, aldehyde **1b** and alcohols **1e** and **1f**.

The primary alcohol (**1e**) furnished a 1:1 mixture of terminal alkyne 2,2-diethoxybut-3-yn-1-ol (**2e**), a ketal, and the corresponding internal alkyne, 4,4-diethoxybut-2-yn-1-ol (**3e**), an acetal (Scheme 3), in a combined yield of 82%, which is lower than that of **2a** from **1a** (98%), but better than what was obtained when most of the other cyclopropanes are reacted under the same conditions (Table 1). The other alcohol, **1f**, which is secondary, reacted completely differently from the majority of the cyclopropanes and afforded the internal alkyne, 5,5-diethoxypent-3-yn-2-ol (**3f**) in 85% isolated yield. Surprisingly enough, not even traces of the terminal-alkyne analogue **2f** could be detected.



Scheme 3. R = CH_2OH (**1e**, **2e**, **3e**); R = CH(OH)Me (**1f**, **2f**, **3f**).

Table 1. Ring opening of 1,1-dibromo-2-chloro-2-R-cyclopropanes **1a** – **1h** under phase-transfer conditions in the presence of ethanol

R	**1**, **2**, **3**	Isolated yield of **2** (%)	Isolated yield of **3** (%)
$CH(OEt)_2$	**a**	96 [a]	0
CHO	**b**	0 [b]	0 [b]
COOH	**c**	39	0
COOMe	**d**	75	0
CH_2OH	**e**	41	41
CHMeOH	**f**	0	85
C(O)Me	**g**	75	0
$CH[SCH_2CH_2S]$	**h**	50	0

[a] Taken from ref. 7.
[b] All of **1b** was consumed, but neither **2b** nor **3b** could be isolated from the reaction mixture.

Aldehyde **1b** reacted much more diversely than the other trihalocyclopropanes and gave a product mixture containing at least 12 compounds as borne out by TLC analyses. IR and NMR spectra of the product mixture indicated the presence of a range of functional groups including conjugated and / or unconjugated alkyne, allene, aldehyde, and ethoxy moieties. Attempts to isolate and purify some of the products by column chromatography were unsuccessful, not only because several of the products had almost the same R_f value, but also due to the fact that some of the compounds appeared to be unstable and suffered secondary reactions.

If the regiospecificity of the ring opening of **1** were mainly determined by steric influence, the size of most of the R groups in **1** is such that formation of the internal alkynes (**3**) should be favoured. This is not the case; on the contrary, in most cases, *viz*. **1c**, **1d**, **1g** and **1h**, acetal **3** is not formed at all. This clearly indicates that the R groups in these four substrates form hydrogen bonds with ethanol that are strong enough to cause the same redirection as the hydrogen bonding between the diethoxymethyl moiety during ring opening of **1a**. As a result ethanol attacks the cyclopropene intermediates at C-1 instead of C-2 (see Scheme 1) and affords the corresponding terminal alkynes **2** only.

Although **1e** and **1f** also contain R groups that can engage in hydrogen bonding with ethanol, both substrates deviate from the pattern outlined above, **1e** by giving a mixture of the corresponding alkynes **2e** and **3e**, and in the case of **1f**, by furnishing the internal acetylene **3f** only. The reason for this behaviour is not clear, but one explanation can be that both compounds are alcohols, whose OH group can engage in hydrogen bonding with ethanol not only as an electron donor (like **1c**, **1d**, **1g** and **1h**), but also as an electron acceptor. This additional hydrogen bond is capable of facilitating ethanol attack at both C-1 and C-2, depending on conformational changes, thus preventing regiospecific ring opening by attack of C-2 to take place (Figure 2). The fact that **1f** gives no **2f** at all whereas **1e** affords a reasonable yield of **2e**

could then be explained by the larger steric crowding of the (hydroxyl)(methyl)methyl moiety as compared to the (hydroxyl)methyl group.

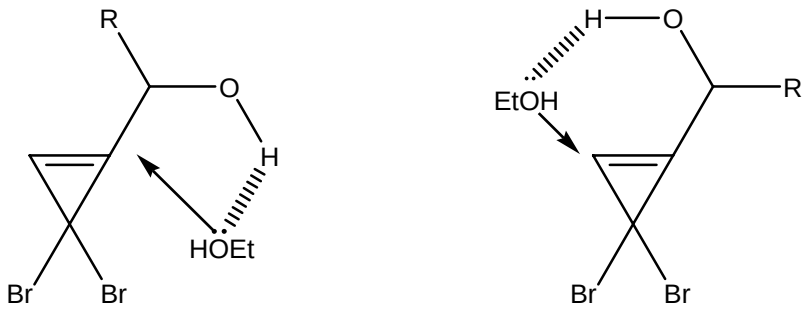


Figure 2. Two extreme conformations of **1e** (R = H) and **1f** (R = Me) engaged as electron acceptors in hydrogen bonding with ethanol.

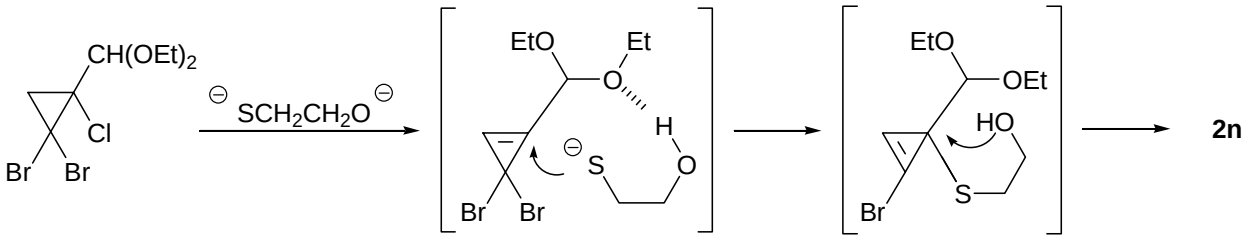
Ring opening of 1a under PTC in the presence of an alcohol or a thiol

A consequence of the results presented and discussed above is that ring opening of 1,1-dibromo-2-chloro-2-diethoxymethylcyclopropane (**1a**) with NaOH under phase-transfer conditions in the presence of alcohols other than ethanol should give terminal alkyne only. In order to test the validity of this line of reasoning **1a**, dissolved in methylene chloride containing either an alcohol different from ethanol or a thiol, was reacted with sodium hydroxide under the same phase-transfer conditions that were applied when **1a** was converted to **2a** in quantitative yield. The results, which are summarized in Table 2, exhibit at least two noteworthy trends. Most importantly, when ring opening took place only one alkyne was obtained, *viz*. **2**, the formation of which is facilitated by hydrogen bonding. Secondly, the yield of **2** drops as the acidity of the alcohol or thiol drops; thus, whereas methanol gives the corresponding ketal (**2i**) in quantitative yield, **1a** is recovered unchanged when *tert*-butyl alcohol is employed (Table 2). This very considerable difference in reactivity is closely connected to the hydroxide's ability to convert the alcohols into the corresponding alkoxides; the reaction appears to be unsuccessful with *tert*-butyl alcohol, but satisfactory with methanol (which furnishes methoxide that generates the reactive cyclopropene precursor to **2i**, see Scheme 1) because methanol is far more acidic than *tert*-butyl alcohol.[13]

Table 2. Ring opening of 1,1-dibromo-2-chloro-2-diethoxymethylcyclopropane (**1a**) under PTC in the presence of an alcohol or a thiol

Alcohol or thiol	**2**	X, Y	Isolated yield (%)
EtOH	**a**	X = Y = OEt	96
MeOH	**i**	X = Y = OMe	96
Me_2CHOH	**j**	X = Y = $OCHMe_2$	39
Me_3COH	**k**	X = Y = $OCMe_3$	0
$HOCH_2CH_2OH$	**l**	X,Y = OCH_2CH_2O	43
$H_2NCH_2CH_2OH$	**m**	X,Y = O	42
$HSCH_2CH_2OH$	**n**	X,Y = SCH_2CH_2O	51
$HSCH_2CH_2SH$	**o**	X,Y = SCH_2CH_2S	0

The importance of a proper balance between the nucleophilicity and the acidity of the organic protic reactant and its corresponding anion(s) is illustrated by the outcome of the reactions involving 1,2-ethanedithiol and 2-mercaptoethanol instead of a simple alcohol. When exposed to an excess of sodium hydroxide, the dithiol is converted to the corresponding dithiolate, which is an excellent nucleophile, but such a weak base that **1a** does not suffer elimination to give the reactive cyclopropene intermediate (Figure 1) involved in the ring-opening reaction. When 2-mercaptoethanol is exposed to the same conditions, on the other hand, formation of the corresponding thiolate takes place (because RSH is much more acidic than ROH). This hydroxythiolate is subsequently in part converted to $^-SCH_2CH_2O^-$ dianion, which is a strong base as well as a good nucleophile. Attack on **1a** by the alkoxide moiety affords 3,3-dibromo-1-diethoxymethylcyclopropene, which first reacts with the thiolate at C-1 followed by several transformations that ultimately lead to formation of 2-diethoxymethyl-2-ethynyl-1,3-oxathiolane (**2n**) (Scheme 4) in moderate yield (Table 2).



Scheme 4

The reaction involving 2-amionoethanol is a special case in the sense that the primary product, conceivably *N*,*O*-ketal **4** (a 1,3-oxazolidine), appears to be unstable under the reaction conditions and reacts further to furnish 1,1-diethoxy-3-butyn-2-one (**2m**). This secondary reaction is not surprising when the instability of *N*,*O*-ketals is taken into account.[14]

In conclusion, it has been substantiated that the regioselectivity of the ring opening of 1,1,2-trihalocyclopropanes with a polar group R attached to C-2 by protic reagents is strongly influenced by hydrogen bonding between R and the reagents. As a result attack at C-2 predominates in most cases and leads to formation of terminal alkynes.

Experimental Section

General Procedures. IR spectra were recorded on a Nicolet Impact 410 infrared spectrophotometer. NMR spectra were run on a Bruker Spectrospin AC 200 F or a Bruker Spectrospin DMX 400. Chemical shifts are reported downfield from TMS and coupling constants are given in Hz. 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, an Autospec Ultima mass spectrometer, a three-sector instrument with EBE geometry from Micromass Ltd Manchester, or JEOL AccuTOF T100GC, which were operated in the EI mode at 70 eV, the DART mode, or the CI mode as indicated for each spectrum. All boiling and melting points are uncorrected.

1,1-Dibromo-2-chloro-2-diethoxymethylcyclopropane (1a). The starting material for the synthesis of the cyclopropanes investigated, was prepared as described in the literature.[7,8]

Synthesis of 1b-1h

2,2-Dibromo-1-chlorocyclopropanecarbaldehyde (1b). A mixture of **1a** (16.8 g, 64 mmol) and 80% aqueous formic acid (250 mL) was left stirring for 24 h at 50 ^{o}C. The reaction mixture was extracted with CH_2Cl_2 (3 x 250 mL), and the combined organic extracts were washed with a saturated solution of $NaHCO_3$ in H_2O (500 mL), and dried ($MgSO_4$). Distillation afforded **1b** (15.3 g, 91%), bp. 50^{o}C/0.5 mm Hg. IR (film): 3460 (w), 3084 (m), 2998 (w), 2851 (m), 2728 (w), 1727 (s), 1410 (m), 1272 (s), 1246 (m), 1181 (s), 1130 (m), 1028 (s), 995 (s), 963 (w), 881 (m), 860 (m), 822 (w), 694 (s), 641 (s) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.50 (s, 1H), 2.82 (d, J = 9.3 Hz, 1H, A part of an AB system), 2,18 (d, J = 9.3 Hz, 1H, B part of an AB system); ^{13}C NMR (50 MHz, $CDCl_3$): δ 188.6, 53.1, 34.8, 26.9; MS (EI): *m/z* 260 (18), 246 (21), 231 (100), 171 (19), 159 (37), 145 (12), 128 (7), 57 (11); HRMS calcd for $[M]^{+\cdot}$ ($[C_4H_3Br_2ClO]^{+\cdot}$) 259.8239, found 259.8235.

2,2-Dibromo-1-chlorocyclopropanecarboxylic acid (1c). A solution of CrO_3 (1.77 g, 17.7 mmol) in a mixture of concentrated sulphuric acid (1.6 mL) and H_2O (4.8 mL) was slowly added

to a mixture of **1b** (2.6 g, 10 mmol) in acetone (8 mL), which was kept cool with an ice bath. After 1 h, H_2O (100 mL) was added and the solution was made alkaline (pH paper) by the addition of a 17% aqueous solution of NaOH. The resulting mixture was extracted once with CH_2Cl_2. The aqueous phase was then made acidic (pH paper) by adding 6 M HCl, and extracted with CH_2Cl_2. The combined organic phases from the latter extraction were dried ($MgSO_4$) and concentrated. A solid was gradually formed, and this crude product was subsequently recrystallised from pentane to yield **1c** (2.5 g, 91%) as pure white crystals, mp. 121–123 ^oC. IR (KBr): 3720- 2500 (m), 3061 (w), 2982 (s), 2934 (m), 2901 (m), 2621 (w), 1717 (s), 1444 (w), 1393 (m), 1370 (m), 1327 (m), 1268 (m), 1224 (m), 1153 (m), 1129 (s), 1089 (s), 1054 (s), 890 (w), 738 (m), 703 (m), 667 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ10.00 (s, 1H), 2.82 (d, J = 9.5 Hz, 1H, A part of an AB system), 2.10 (d, J = 9,5 Hz, 1H, B part of an AB system); ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.2, 48.1, 35.7, 26.7; MS (EI): *m/z* 279 (8), 261 (11), 233 (23), 199 (47), 171 (100), 161 (27), 153 (10), 141 (8), 135 (11), 117 (76), 107 (12), 89 (41), 79 (8), 73 (49), 61 (15); HRMS calcd. for $[M]^{+\cdot}$ ($[C_4H_3Br_2ClO_2]^{+\cdot}$) 275.8188, found 275.8180.

Methyl 2,2-dibromo-1-chlorocyclopropanecarboxylate (1d). A solution of CH_3OH (20 mL), concentrated sulphuric acid (12.0 mL), and **1c** (1.4 g, 5.0 mmol) was refluxed for 12 h. The reaction mixture was neutralised (pH paper) by adding a 10% (w/w) aqueous solution of $NaHCO_3$. H_2O (100 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated. Flash chromatography (hexane:ethyl acetate, 97.5:2.5) afforded **1d** (1.2 g, 82%) as a colourless oil. IR (film): 3502 (w), 3091 (w), 3006 (w), 2954 (w), 1746 (s), 1437 (s), 1412 (w), 1300 (s), 1234 (s), 1110 (m), 1065 (m), 1024 (s), 1003 (m), 934 (w), 857 (w), 731 (m), 694 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 3.89 (s, 3H), 2.80 (d, J = 9.4 Hz, 1H, A part of an AB stsem), 2.06 (d, J = 9,4 Hz, 1H, B part of an AB system); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.2, 53.5, 48.4, 35.2, 26.9; MS (EI): *m/z* 292 (2), 261 (10), 235 (20), 233 (30), 213 (70), 211 (52), 185 (100), 183 (72), 169 (10), 149 (20), 132 (30), 119 (8), 89 (12), 73 (40); HRMS calcd. for $[M]^{+\cdot}$ ($[C_5H_5Br_2ClO_2]^{+\cdot}$) 289.8345, found 289.8299.

(2,2-Dibromo-1-chlorocyclopropyl)methanol (1e). $NaBH_4$ (0.27 g, 7.3 mmol) was added to a solution of **1b** (2.6 g, 10.0 mmol) in CH_3CH_2OH (50 mL) and left stirring at rt for 10 h. The reaction was quenched by adding H_2O (50 mL), and the resulting solution was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. Flash chromatography (hexane:ethyl acetate, 85:15) afforded **1e** (2.2 g, 83%) as a colourless oil. IR (film): 3770-3050 (broad, s), 3625 (w), 3080 (m), 2998 (w), 2930 (m), 2877 (m), 1452 (m), 1417 (m), 1303 (m), 1283 (m), 1229 (m), 1149 (m), 1060 (s), 1009 (s), 925 (w), 899 (m), 850 (m), 737 (m), 705 (m), 695 (s), 648 (s), 624 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 4.16-3.99 (m, 2H), 2.65 (m, 1H), 2.09 (d, J = 9.3 Hz, 1H, A part of an AB system), 2.02 (d, J = 9.3 Hz, 1H, B part of and AB system); ^{13}C NMR (50 MHz, $CDCl_3$): δ 68.4, 52.5, 34.7, 29.5; MS (EI): *m/z* 264 (15), 248 (18), 234 (10), 187 (20), 169 (60), 157 (52), 151 (40), 123 (20), 121 (22), 103 (20), 82 (30), 78 (100), 73 (30); HRMS calcd. for $[M]^{+\cdot}$ ($[C_4H_5Br_2ClO]^{+\cdot}$) 261.8396, found 261.8385.

1-(2,2-Dibromo-1-chlorocyclopropyl)ethanol (1f). CH_3I (2.0 g, 14.2 mmol) was slowly added to Mg (0.28 g, 12.0 mmol) in dry diethyl ether (20 mL). The mixture was refluxed for 30 min and cooled to rt. The methylmagnesium iodide solution was slowly added to a solution of **1b** (2.6 g, 10.0 mmol) in dry diethyl ether at 0 ^oC. After addition the reaction mixture was refluxed for an additional 30 min and was then quenched by adding saturated aqueous NH_4Cl (20 mL). The hydrolysate was extracted with diethyl ether (3 x 20 mL), and the combined organic phases were dried ($MgSO_4$) and concentrated. Flash chromatography (hexane:ethyl acetate, 80:20) afforded **1f** (2.42 g, 88%) as a colorless oil. IR (film): 3800-3050 (s), 3078 (w), 2982 (s), 2958 (w), 2931 (s), 2870 (w), 1446 (m), 1420 (m), 1375 (m), 1267 (m), 1173 (m), 1110 (m), 1076 (m), 1031 (w), 1001 (m), 949 (w), 916 (m), 824 (w), 699 (m) cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$): δ 4.00 (quintet, J = 6.4 Hz, 1H), 2.29 (d, J = 6.4 Hz, 1H), 2.02 (d, J = 9.3 Hz, 1H, A part of an AB system), 1.93 (d, J = 9.3 Hz, 1H, B part of and AB system), 1.45 (d, J = 6,4 Hz, 3H); ^{13}C NMR (50 MHz; $CDCl_3$): δ 68.4, 52.5, 34.7, 29.5, 14.8; MS (EI): *m/z* 276 (12), 274 (22), 260 (12), 201 (10), 183 (20), 181 (30), 153 (42), 128 (12), 103 (25), 82 (100); HRMS calcd. for $[M]^{+\cdot}$ ($[C_5H_7Br_2ClO]^{+\cdot}$) 275.8552, found 275.8564.

1-(2,2-Dibromo-1-chlorocyclopropyl)ethanone (1g). A solution of CrO_3 (1.77 g, 17.7 mmol), concentrated sulphuric acid (1.6 mL), and H_2O (4.8 mL) was slowly added to a mixture of **1f** (2.78 g, 10.0 mmol) and acetone (8 mL) kept on ice bath. After stirring for 4 h, water (50 mL) was added and the product mixture was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. Flash chromatography (hexane:ethyl acetate, 97.5:2.5) afforded **1g** (2.0 g, 73%) as a colourless oil. IR (film): 3448 (w), 3087 (w), 3003 (w), 2925 (w), 1723 (m), 1417 (m), 1387 (w), 1359 (m), 1276 (m), 1205 (w), 1059 (w), 1030 (m), 1012 (m), 931 (w), 801 (w), 699 (m), 624m, 610m cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$): δ 2.79 (d, J = 9.1 Hz, 1H, A part of an AB system), 2.55 (s, 3H), 1.96 (d, J = 9.1 Hz, 1H, B part of an AB system); ^{13}C NMR (50 MHz; $CDCl_3$): δ 198.6, 53.1, 34.8, 27.0, 14.9; MS (EI): *m/z* 277 (12), 233 (30), 197 (88), 169 (52), 153 (9), 131 (16), 116 (100), 107 (8), 87 (27), 73 (52), 61 (7); HRMS calcd. for $[M]^{+\cdot}$ ($[C_5H_5Br_2ClO]^{+\cdot}$) 273.8396, found 273.8385.

2-(2,2-Dibromo-1-chlorocyclopropyl)-1,3-dithiolane (1h). Procedure 1. A mixture of **1a** (6.7 g, 20 mmol), 1,2-ethanedithiol (2.0 mL, 25 mmol), and silica chloride (3.0 g, 30 mmol) in CH_2Cl_2 (50 mL) was stirred at rt for 4 h. The silica chloride was removed by filtration and washed with CH_2Cl_2 (50 mL). The organic phase was washed with 10% (w/w) aqueous NaOH (50 mL), H_2O (100 mL), dried over $MgSO_4$ and concentrated. Flash chromatography (hexane:ethyl acetate, 90:10) afforded **1h** (5.3 g, 78%) as a colourless oil.

Procedure 2.[12] Aldehyde **1b** (2.6 g, 10 mmol) and 1,2-ethanedithiol (1.6 mL, 20 mmol) was dissolved in $CHCl_3$ (50 mL) and stirred for 1 h at 20 ^oC. The reaction mixture was then cooled to 0 ^oC and boron trifluoride diethyl etherate (2.0 mL, ~ 3.8 M) was added dropwise over 10 min. The reaction mixture was then stirred at 0 ^oC for further 12 h. The reaction mixture was washed with 10 % (w/w) aqueous NaOH (20 mL), H_2O (20 mL), aqueous saturated NaCl (20 mL) and dried over $MgSO_4$. The solvent was evaporated and flash chromatography (hexane:ethyl acetate, 90:10) afforded **1h** (2.6 g, 78%) as a colourless oil.

1h. IR (film): 3080 (w), 2978 (s), 2930 (m), 2897 (m), 2881 (m), 1480 (w), 1444 (m), 1422 (m), 1372 (s), 1354 (m), 1295 (w), 1268 (m), 1248 (m), 1184 (s), 1108 (s), 1072 (s), 1010 (m), 964 (w), 702 (m), 668 (m), 629 (m) cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$): δ 4.85 (s, 1H), 3.60-3.47 (m, 2H), 3.37-3.26 (m, 2H), 2,15 (d, *J* = 9.4 Hz, 1H, A part of an AB system), 2.08 (d, *J* = 9.4 Hz, 1H, B part of and AB system); ^{13}C NMR (50 MHz; $CDCl_3$): δ 61.4, 40.1, 39.8, 38.1, 31.8, 30.4; MS (EI): *m/z* 336 (9), 275 (11), 243 (14), 185 (30), 176 (12), 141 (12), 123 (7), 111 (10), 103 (74), 75 (100), 67 (9); HRMS calcd. for $[M]^{+\cdot}$ ($[C_6H_7Br_2ClS_2]^{+\cdot}$), 335.8044, found 335.8051.

Ring opening of 1b-1h under PTC in the presence of ethanol. General procedure

To a cold (0 ^oC) mixture of one of the 1,1-dibromo-2-chlorocyclopropane derivatives **1b-1h**, TEBA, and CH_3CH_2OH in CH_2Cl_2 (25-50 mL) was added 50% (w/w) aqueous NaOH. The cooling bath was removed and the reaction mixture was stirred vigorously at room temperature until all the starting material was consumed (monitored TLC). Water was added, the products were extracted with dichloromethane, and the combined extracts were dried with magnesium sulfate, filtered and evaporated under vacuum. The products, except from **1c**, were isolated from the residue by flash chromatography.

To **aldehyde 1b** (1.3 g, 5.0 mmol), TEBA (0.2 g) and CH_3CH_2OH (0.92 g, 20.0 mmol) in CH_2Cl_2 (25 mL) was added NaOH (2.1 mL, 40 mmol) dropwise during 15 min and the reaction mixture stirred for further 24 h. At this point all the starting material was consumed. H_2O (25 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were combined, dried ($MgSO_4$) and concentrated to yield a reaction crude product of 0.8 g. Chromatographic investigation showed a complex reaction mixture that contained at least 12 products from which we were not able to isolate reasonably pure samples any of the components (see text).

To **acid 1c** (1.4 g, 5.0 mmol), TEBA (0.2 g) and CH_3CH_2OH (0.92 g, 20.0 mmol) in CH_2Cl_2 (25 mL) was added NaOH (2.1 mL, 40 mmol) dropwise during 15 min and the reaction mixture stirred for further 24 h. H_2O (25 mL) was added and the water phase was washed with CH_2Cl_2 (3 x 25 mL). The water phase was then made slightly acidic (~ 4, pH paper) with 2 M HCl and then extracted with CH_2Cl_2 (3 x 25 mL). Evaporation of the solvent gave 2,2-diethoxybut-3-ynoic acid (**2c**) (0.65 g, 75%) as a semisolid which melted gradually when heated.

2c. IR (film): 3750- 2550 (m), 3252 (w), 2980 (s), 2931 (s), 2889 (m), 2628 (w), 2115 (w), 1714 (s), 1441 (m), 1396 (m), 1371 (w), 1265 (m), 1220 (m), 1153 (m), 1120 (s), 1081 (s), 1054 (s), 890 (m), 733 (w) 700 (w); ^1H NMR (200 MHz, $CDCl_3$): δ 9.28 (s, 1H), 3.90-3.42 (m, 4H), 2.62 (s, 1H), 1.29-1.05 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.1, 100.1, 83.2, 79.1, 63.0, 15.0; MS (EI): *m/z* 173 (30), 172 (40), 127 (55), 103 (100), 60 (12), 45 (15) m/z; HRMS calcd. for $[M\text{-}OEt]^+$ ($[C_6H_7O_3]^+$) 127.0402 found 127.0410.

To **ester 1d** (1.5 g, 5.0 mmol), TEBA (0.2 g) and CH_3CH_2OH (0.92 g, 20 mmol) in CH_2Cl_2 (25 mL) was added NaOH (2.1 mL, 40 mmol) dropwise during 15 min and the reaction mixture stirred for further 20 h. Water (25 mL) was added and the two phases were separated. The water phase was extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic extracts were dried

($MgSO_4$), filtered and concentrated. Methyl 2,2-diethoxybut-3-ynoate (**2d**) (0.7 g, 75%) was isolated as an light yellow oil by flash chromatography (hexane:ethyl acetate, 90:10).

2d. IR (film): 3304 (m), 2979 (s), 2931 (s), 2900 (s), 2113 (w), 1741 (s), 1630 (m), 1592 (m), 1478 (m), 1444 (m), 1418 (m), 1392 (m), 1356 (m), 1261 (s), 1219 (m), 1114 (s), 1067 (s), 962 (m), 867 (m), 806 (m), 758 (s), 701 (m), 666 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 3.92 (s, 3H), 3.81-3.67 (m, 4H), 2.61 (s, 1H), 1.29-1.17 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.4, 104.6, 79.2, 73.2, 60.8, 53.5, 17.9; MS (EI): *m/z* 271 (20%), 241 (8), 213 (48), 195 (32), 181 (18), 167 (7), 145 (22), 111 (6), 103 (100), 75 (49), 63 (13), 57 (20); HRMS calcd. for $[M\text{-}OEt]^+$ ($[C_4H_{14}O_4]^+$) 141.055, found 141.0552.

To **alcohol 1e** (2.6 g, 10.0 mmol), TEBA (0.2 g) and CH_3CH_2OH (1.84 g, 40.0 mmol) in CH_2Cl_2 was added NaOH (4.2 mL, 80 mmol) dropwise during 15 min, and the reaction mixture stirred for another 20 h. Water (50 mL) was added and the two phases were separated. The water phase was extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated. Two products were formed in a 1:1 ratio (NMR analysis). Isolation by flash chromatography (hexane:ethyl acetate, 90:10) yielded 2,2-diethoxybut-3-yn-1-ol (**2e**) (0.65 g, 41%) as an oil and 4,4-diethoxybut-2-yn-1-ol (**3e**) (0.65 g, 41%), also as an oil.

2e. IR (film): 3650-3090 (s), 3263 (s), 2989 (s), 2934 (s), 2893 (s), 2114 (m), 1480 (m), 1445 (m), 1392 (s), 1337 (m), 1262 (s), 1186 (s), 1135 (s), 1080 (s), 947 (s), 918 (m), 860 (m), 732 (m), 697 (m), 662 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 3.80-3.65 (m, 6H), 2.64 (s, 1H), 2.25 (m, 1H), 1.27-1.16 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 96.8, 78.7, 74.1, 65.6, 58.8, 14.9; MS (EI): *m/z* 186 (6), 179 (17), 168 (9), 155 (12), 141 (17), 127 (68), 113 (80), 99 (35), 85 (55), 71 (100), 53 (39); HRMS calcd. for $[M]^{+\cdot}$ ($[C_8H_{14}O_3]^{+\cdot}$) 158.0942, found 158.0938.

3e. IR (film): 3670-3140 (m), 2977 (m), 2931 (m), 2889 (m), 2180 (w), 1732 (w), 1714 (w), 1627 (w), 1481 (w), 1445 (m), 1391 (m), 1370 (m), 1329 (m), 1269 (m), 1141 (s), 1081 (s), 1051 (s), 951 (m), 912 (m), 821 (w), 737 (m), 702 (m), 666 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 5.31 (s, 1H), 4.32 (broad s, 2H), 3.80-3.55 (m, 4H), 2.23 (broad s, 1H), 1.24 (t, J = 7.3 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 96.8, 81.6, 78.6, 58.8, 51.3, 15.0; MS (EI): *m/z* 179 (1), 141 (11), 127 (72), 113 (85), 105 (80), 99 (35), 85 (55), 71 (100); HRMS calcd. for $[M\text{-}OEt]^+$ ($[C_8H_{14}O_3]^+$) 158.0942, found 158.0944.

To **alcohol 1f** (0.74 g, 2.68 mmol), TEBA (0.05 g) and CH_3CH_2OH (0.50 g, 10.71 mmol) in CH_2Cl_2 (40 mL) was added NaOH (1.1 mL, 21.4 mmol) dropwise during 15 min, and the reaction mixture stirred for further 30 h. Water (40 mL) was added and the two phases were separated. The water phase was extracted with CH_2Cl_2 (3 x 40 mL) and the combined organic extracts were combined, dried ($MgSO_4$), filtered and concentrated. 5,5-Diethoxypent-3-yn-2-ol (**3f**) (0.40 g, 87%) was isolated as an light yellow oil by flash chromatography (hexane:ethyl acetate, 85:15).

3f. IR (reflectance): 3650-3120 (w), 2977 (m), 2886 (m), 2244 (w), 1445 (m), 1369 (m), 1326 (m), 1150 (s), 1047 (s), 1005 (s), 914 (m), 886 (m), 834 (w), 793 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 5.30 (s, 1H), 4.56 (m, 1H), 3.78-3.50 (m, 4H), 2.35 (d, J = 4.7 Hz, 1H), 1.47 (d, J = 6.6 Hz, 3H), 1.24 (t, J = 6.5 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 91.1, 87.2, 79.0, 60.8, 58.0,

23.8, 14.9; MS (DART): *m/z*; 253 (50), 145 (75), 127 (100), 99 (90), 81 (70); HRMS calcd. for $[M\text{-}OEt]^+$ ($[C_7H_{11}O_2]^+$) 127.07590, found 127.06884.

To **ketone 1g** (2.2 g, 8.0 mmol), TEBA (0.2 g) and CH_3CH_2OH (1.47 g, 32 mmol) in CH_2Cl_2 (50 mL) was added NaOH (3.4 mL, 64 mmol) dropwise during 15 min and the reaction mixture stirred for further 20 h. Water (50 mL) was added and the two phases were separated. The water phase was extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated. 3,3-Diethoxypent-4-yn-2-one (**2g**) (1.0 g, 75%) was isolated as an oil by flash chromatography (hexane:ethyl acetate, 90:10).

2g. IR (film): 3246 (w), 2979 (s), 2931 (m), 2900 (m), 2113 (w), 1741 (s), 1592 (w), 1444 (w), 1418 (w), 1392 (w), 1356 (m), 1261 (s), 1219 (m), 1114 (s), 962 (w), 867 (w), 806 (m), 758 (s), 666 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 3.87-3.53 (m, 4H), 2.65 (s, 1H), 2.05 (s, 3H), 1.31-1.15 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 181.2, 100.6, 81.8, 79.0, 62.7, 15.0; MS (EI): *m/z* 279 (30), 167 (43), 157 (6), 149 (100), 127 (6), 113 (11), 83 (6), 75 (45), 57 (31); HRMS calcd. for $[M+H]^+$ ($[C_9H_{14}O_3]^+$) 171.0977, found 171.0971.

To **dithiolane 1h** (3.4 g, 10 mmol), TEBA (0.4 g) and CH_3CH_2OH (1.8 g, 40 mmol) in CH_2Cl_2 (50 mL) was added NaOH (4.2 mL, 80 mmol) dropwise over 15 min and the reaction mixture stirred for further 24 h. Water (50 mL) was added and the two phases were separated. The water phase was extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated. 2-(1,1-Diethoxypropyl-2-ynyl)-1,3-dithiolane (**2h**) (1.2 g, 51%) was isolated as an oil by flash chromatography (hexane:ethyl acetate, 90:10).

2h. IR (film): 3242 (m), 2983 (s), 2935 (m), 2909 (m), 2876 (m), 2095 (w), 1479 (m), 1465 (m), 1447 (m), 1374 (s), 1300 (m), 1161 (w), 1098 (m), 1048 (s), 938 (w), 847 (m), 634 (m), 607 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 4.42 (s, 1H), 4.19-4.10 (m, 4H), 3.93-3.46 (m, 4H), 2.58 (s, 1H), 1.30 (t, J = 7.2 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 102.8, 78.5, 76.2, 58.1, 52.0, 38.9, 14.9; MS (EI): *m/z* 207 (12), 190 (43), 187 (18), 127 (50), 105 (100), 87 (11), 73 (20); HRMS calcd. for $[M]^{+\cdot}$ ($[C_{10}H_{16}O_2S_2]^{+\cdot}$) 232.0592, found 232.0589.

Ring opening of 1a under PTC in the presence of an alcohol or a thiol. General procedure To a cold (0 ˚C) mixture of **1a,** TEBA and either CH_3OH, $(CH_3)_2CHOH$, $(CH_3)_3COH$, $HOCH_2CH_2OH$, $H_2NCH_2CH_2OH$, $HSCH_2CH_2OH$, or $HSCH_2CH_2SH$ in CH_2Cl_2 was added 50% (w/w) aqueous NaOH. The cooling bath was removed and the reaction mixture was stirred vigorously at room temperature until all the starting material was consumed (monitored by TLC). Water was added, the products were extracted with ether, and the combined extracts were dried with magnesium sulfate, filtered and evaporated under vacuum. The products were isolated from the residue by flash chromatography.

Methanol; formation of 4,4-diethoxy-3,3-dimethoxybut-1-yne (2i). Cyclopropane **1a** (2.0 g, 6.0 mmol) was dissolved in a solution of CH_2Cl_2 (25 mL), methanol (0.82 g, 25.5 mmol) and TEBA (0.2 g). NaOH (2.5 mL, 48 mmol) was added dropwise during 15 min and the reaction mixture stirred for further 24 h. Water (25 mL) was added and the two phases were separated. The water phase was extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic extracts were combined, dried ($MgSO_4$), filtered and concentrated. 4,4-Diethoxy-3,3-dimethoxybut-1-yne (**2i**)

(1.1 g, 96%) was isolated as an oil from the reaction mixture with flash chromatography (hexane:ethyl acetate, 90:10). IR (film): 3259 (m), 2977 (s), 2941 (s), 2906 (m), 2835 (m), 2115 (w), 1740 (m), 1466 (m), 1446 (w), 1392 (m), 1373 (m), 1331 (m), 1296 (w), 1243 (m), 1113 (s), 1085 (s), 980 (m), 902 (w), 654 (m) cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$): δ 4.43 (s, 1H), 3.86-3.63 (m, 4H), 3.46 (s, 6H), 2.65 (s, 1H), 1,27 (t, *J* = 7,1 Hz, 6H); ^{13}C NMR (50 MHz; $CDCl_3$): δ 102.4, 98.3, 77.1, 75.0, 64.2, 51.1, 14,9; MS (EI): *m/z* 201 (8), 177 (35), 157 (90), 141 (5), 115 (20), 103 (15), 98 (70), 97 (100), 75 (90), 69 (60), 59 (40), 55 (40); HRMS calcd. for $[M\text{-}OEt]^+$ ($[C_8H_{13}O_3]^+$) 157.0865, found 157.0863.

Isopropyl alcohol; formation of 4,4-diethoxy-3,3-diisopropoxybut-1-yne (2j). Cyclopropane **1a** (2.0 g, 6.0 mmol) was dissolved in a solution of CH_2Cl_2 (25 mL), isopropyl alcohol (1.5 g, 25.0 mmol) and TEBA (0.2 g). NaOH (2.5 mL, 48 mmol) was added dropwise during 15 min and the reaction mixture stirred for further 24 h. Water (25 mL) was added and the two phases were separated. The water phase was extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic extracts were combined, dried ($MgSO_4$), filtered and concentrated. 4,4-Diethoxy-3,3-diisopropoxybut-1-yne (**2j**) (0.6 g, 39%) was isolated from the reaction mixture with flash chromatography (hexane:ethyl acetate, 90:10). IR (film): 3311 (m), 3257 (m), 2976 (s), 2931 (s), 2899 (s), 2112 (m), 1727 (m), 1481 (m), 1467 (m), 1455 (m), 1445 (m), 1393 (s), 1381 (s), 1328 (m), 1296 (m), 1273 (m), 1217 (m), 1110 (s), 1078 (s), 981 (m), 912 (m), 896 (m), 715 (m), 699 (m) cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$): δ 4.32 (septet, *J* = 6.2 Hz, 2H), 4.17 (s, 1H), 3.83-3.57 (m, 4H), 2.60 (s, 1H), 1.28-1.16 (m, 18 H); ^{13}C NMR (50 MHz; $CDCl_3$): δ 104.9, 99.0, 78.6, 75.4, 68.5, 65.3, 65.1, 59.4, 23.7, 23.5, 15.1; MS (EI): *m/z* 287 (10), 259 (5), 213 (10), 199 (25), 185 (20), 158 (22), 155 (40), 129 (10), 103 (100), 83 (25), 75 (60); HRMS calcd. for $[M]^{+\cdot}$ ($[C_{14}H_{26}O_4]^{+\cdot}$) 258.1831, found 258.1828.

***tert*-Butyl alcohol; no reaction.** Cyclopropane **1a** (3.4 g, 10.0 mmol) was dissolved in a solution of CH_2Cl_2 (50 mL), *tert*-butyl alcohol (3.0 g, 40.0 mmol) and TEBA (0.4 g). NaOH (4.2 mL, 80 mmol) was added dropwise during 15 min. After a total reaction time of 48 h the reaction was stopped when TLC and GC showed no conversion of the starting compound. Some water was added and the reaction mixture was worked up. No product was obtained, just unreacted starting material.

Ethylene glycol; formation of 2-(diethoxymethyl)-2-ethynyl-1,3-dioxolane (2l). Cyclopropane **1a** (3.4 g, 10.0 mmol) was dissolved in a solution of CH_2Cl_2 (50 mL), ethylene glycol (1.2 g, 20.0 mmol) and TEBA (0.4 g). NaOH (4.2 mL, 80 mmol) was added dropwise during 15 min and the reaction mixture was stirred for further 24 h. Water (50 mL) was added and the two phases were separated. The water phase was extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic extracts were combined, dried ($MgSO_4$), filtered and concentrated. Diethoxymethyl-2-ethynyl-1,3-dioxolane (**2l**) (0.85 g, 43%) was isolated from the reaction mixture by flash chromatography (hexane:ethyl acetate, 90:10). IR (film): 3260 (s), 2977 (s), 2930 (s), 2897 (s), 2113 (m), 1446 (m), 1372 (s), 1344 (m), 1202 (m), 1116 (s), 1074 (s), 1039 (m), 950 (m), 903 (m), 837 (w), 699 (m), 668 (m) cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$): δ 4.43 (s, 1H), 4.18-4.02 (m, 4H), 3.88-3.64 (m, 4H), 2.57 (s, 1H), 1.30-1.18 (m, 6H); ^{13}C NMR (50 MHz;

$CDCl_3$): δ 102.4, 101.3, 78.7, 72.7, 64.9, 64.3, 15.1; MS (EI): *m/z* 201 (10), 155 (20), 149 (28), 127 (22), 103 (100), 75 (50); HRMS calcd. for $[M\text{-}OEt]^+$ ($[C_8H_{11}O_3]^+$) 155.0710, found 155.0718.

2-Aminoethanol; formation of 1,1-diethoxybut-3-yn-2-one (2m). Cyclopropane **1a** (2.0 g, 6.0 mmol) was dissolved in a solution of CH_2Cl_2 (25 mL), 2-aminoethanol (0.7 g, 12.0 mmol) and TEBA (0.2 g). NaOH (2.5 mL, 48 mmol) was added dropwise during 15 min and the reaction mixture was stirred for further 24 h. Water (25 mL) was added and the two phases were separated. The water phase was extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated. 1,1-Diethoxybut-3-yn-2-one (**2m**) (0.39 g, 42%) was isolated as an oil from the reaction mixture by flash chromatography (hexane:ethyl acetate, 90:10). The spectroscopic data were in accordance with those published in the literature with one exception, the proton NMR spectrum.[7] The chemical shift of the acetylenic proton in **2m** has been reported to be 2.66 ppm,[7] but it should be 3.39 ppm; thus the complete proton NMR spectrum is as follows: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.27 (t, *J*=7.1 Hz, 6H), 3.39 (s, 1H), 3.47-3.95 (m, 4H), 4.68 (s, 1H).

2-Mercaptoethanol; formation of 2-diethoxymethyl-2-ethynyl)-1,3-oxathiolane (2n). Cyclopropane **1a** (3.4 g, 10.0 mmol) was dissolved in a mixture of CH_2Cl_2 (50 mL), 2-mercaptoethanol (1.3 g, 20.0 mmol) and TEBA (0.4 g). NaOH (4.2 mL, 80 mmol) was added during 15 min and the reaction mixture was stirred for further 24 h. Water (25 mL) was added and the two phases were separated. The water phase was extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic extracts were combined, dried ($MgSO_4$), filtered and concentrated. 2-Diethoxymethyl-2-ethynyl-1,3-oxathiolane (**2n**) (1.0 g, 51%) was isolated from the reaction mixture with flash chromatography (hexane:ethyl acetate, 90:10). IR (film): 3259 (m), 2976 (s), 2934 (m), 2900 (s), 2111 (m), 1724 (m), 1467 (m), 1446 (m), 1381 (s), 1368 (s), 1328 (s), 1295 (m), 1274 (m), 1120 (s), 1070 (s), 984 (m), 952 (m), 937 (m), 904 (m), 838 (m), 780 (w), 697 (m), 650 (m); ^{1}H NMR (200 MHz; $CDCl_3$): δ 4.66 (s, 1H), 3.97 (m, 2H), 3.82-3.60 (m, 4H), 3.06-2.88 (m, 2H), 2.55 (s, 1H), 1.28-1.10 (m, 6H); ^{13}C NMR (50 MHz; $CDCl_3$): δ 104.8, 99.8, 82.1, 65.4, 63.8, 60.1, 48.2, 15.1; MS (EI): *m/z* 171 (20), 163 (10), 113 (100), 75 (30), 45 (20); HRMS calcd. for $[M\text{-}OEt]^+$ ($[C_8H_{11}O_2S]^+$) 171.0482 found 171.0487.

1,2-Ethanedithiol; no reaction. Cyclopropane **1a** (3.4 g, 10.0 mmol) was dissolved in a solution of CH_2Cl_2 (50 mL), 1,2-ethanedithiol (1.9 g, 20.0 mmol) and TEBA (0.4 g). NaOH (4.2 mL, 80 mmol) was added dropwise during 15 min. After 48 h the reaction was stopped since TLC and GC analysis showed no conversion of the starting compound. Some water was added and the reaction mixture was worked up to recover the starting cyclopropane.

Supplementary Information Available

The ^{1}H-NMR and ^{13}C-NMR spectra of all new compounds are compiled as supplementary material and are available from the authors on request.

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