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Neighbouring-group Influence on the Ring Opening of Some 2-Alkyl-1,1,2-tribromocyclopropanes under Phase-transfer Conditions

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Summary. Several 2-alkyl-1,1,2-tribromocyclopropanes were treated with sodium hydroxide and ethanol under phase-transfer conditions. Ring opening gave mixtures of the corresponding acetylenic diethyl ketals and acetals. When the steric bulk of the alkyl substituent was increased acetal formation dominated, and in the case of 1,1,2-tribromo-2-(*tert*-butyl)cyclopropane, the acetal was formed as the only product.

Keywords. Alkynes; Halocyclopropanes; Neighbouring groups; Phase-transfer conditions; Ring opening.

Introduction

When 2-substituted 1,1,2-trihalocyclopropanes are exposed to 50% sodium hydroxide in the presence of ethanol, dichloromethane, and a small amount of a phase-transfer catalyst, triethylbenzylammonium chloride (*TEBA*), the trihalides undergo ring opening and are converted to the corresponding acetylenic diethyl ketals and corresponding 1-substituted 3,3-dibromocyclopropene, which is consumed by nucleophilic attack [1–5]. Mechanistic studies have shown that the ring-opening reaction is a multistep process involving dehydrohalogenation, formal substitution of halogen atoms by ethoxy groups, and finally ring opening [3, 5]. Furthermore, it appeared that the ketals and acetals were formed *via* a common intermediate, the corresponding 1-substituted 3,3-dibromocyclopropene, which is consumed by nucleophilic attack of ethoxide and ethanol at C-1 and C-2 (Fig. 1) [3, 5].

From the nature of this reaction it was reasonable to believe that the regioselectivity of the nucleophilic attack, and thus the acetal/ketal ratio, would be

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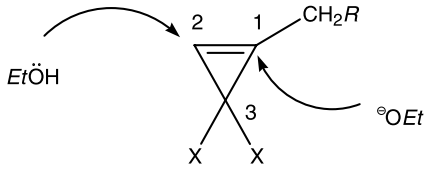


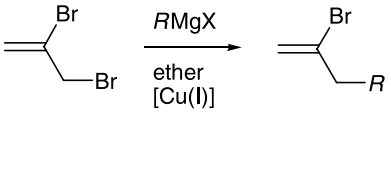
Fig. 1. Intermediate cyclopropenes are attacked regioselectively by ethanol and ethoxide

sensitive to the steric bulk of the substituent *R*. We therefore decided to examine reactions of selected 1,1,2-trihalocyclopropane derivatives containing *R* with different steric bulk, to see to what extent the acetal/ketal distribution is influenced by steric interactions. Some preliminary results have been published already [5]; this is a full account of our findings.

Results and Discussion

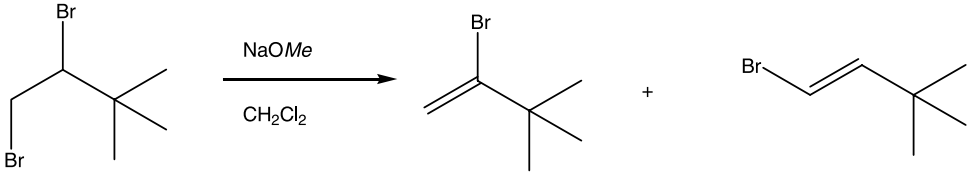
2-Bromo-1-alkenes **1** were used as starting materials for the synthesis of the 2-alkyl-1,1,2-tribromocyclopropanes **2** used in this study. Most alkenes, *viz.* **1a**–**1f**, were prepared from 2,3-dibromoprop-1-ene, which suffered nucleophilic substitution when treated with the appropriate *Grignard* reagents (Scheme 1). The yields were moderate, ranging from 42 to 61%, due to the formation of fair amounts of *Wurtz*-coupling products, which, however, were easily removed by fractional distillation rendering the method convenient to apply for our purpose. In order to improve the yields, some coupling reactions were also performed in the presence of a catalytic amount of CuCN, a salt known to catalyze such reactions, but significant improvements were not observed.

2-Bromo-3,3-dimethylbut-1-ene (**1g**) on the other hand, was synthesized from 3,3-dimethylbut-1-ene as outlined in Scheme 2. Unfortunately, a constitutional



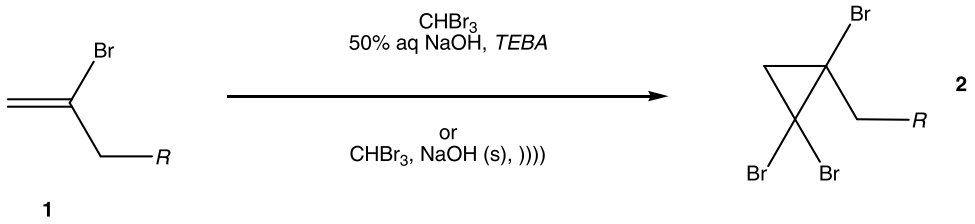
R	
ethyl	**1a**
butyl	**1b**
heptyl	**1c**
benzyl	**1d**
cyclohexyl	**1e**
i-propyl	**1f**

Scheme 1



1g **1h**

Scheme 2



Scheme 3

isomer, (*E*)-1-bromo-3,3-dimethylbut-1-ene (**1h**), was formed concomitantly (the **1g**:**1h** ratio was 76:24) and appeared to be so difficult to remove by distillation without a significant loss of the desired product that the cyclopropanation of **1g** was carried out with a sample contaminated with a fair amount of **1h** (*vide infra*).

The 2-bromoalkenes were converted to the corresponding 1,1,2-tribromocyclopropanes **2** by two different methods, either under phase-transfer conditions (PTC) using *TEBA* or hexadecyltrimethylammonium chloride (Cetrimide) as catalyst as described by *Makosza* and *Wawrzyniewicz* [6], or by employing finely ground NaOH and ultrasound irradiation in accordance with the *Xu-Brinker* procedure (Scheme 3) [7]. Generally, the yields were fair to good irrespective of the method employed, but the steric influence seemed to be slightly more important under PTC than when the latter method was utilized; thus, under the former conditions the yield decreased somewhat when the steric bulk of the alkyl group increased, from 77 to 60% when *R* changed from propyl to *tert*-butyl and afforded **2a** and **2g** (Table 1). It is also noteworthy that when a mixture of **1g** and **1h** was reacted under standard phase-transfer conditions, only the former alkene appeared to react and furnished the corresponding cyclopropane, 1,1,2-tribromo-2-(*tert*-butyl)cyclopropane (**2g**), in rather good yield (60% based on **1g**). Consequently, **1g** and **1h** exhibit the same reactivity difference as 1-bromo-1-phenylethene and 2-bromo-1-phenylethene under the same reaction conditions [2], a pattern which conceivably is intimately connected to the larger polarisation of the carbon-carbon double bond in the 1,1-disubstituted alkene than the 1,2-disubstituted isomer.

Table 1. Preparation of 1,1,2-trihalo-2-CH_2R-cyclopropanes from 2-bromoalkenes under phase-transfer conditions (PTC) as well as ultrasound irradiation (USI)

Entry	*R*	Product	Isolated yield/%	
			PTC	USI
1	Ethyl	**2a**	77	77
2	Butyl	**2b**	70	57
3	Heptyl	**2c**	72	–
4	Benzyl	**2d**	77	–
5	Cyclohexyl	**2e**	68	75
6	*i*-Propyl	**2f**	69	–
7	*a*	**2g**	60	–

a RCH_2 = *tert*-butyl

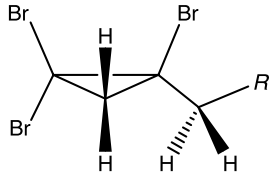
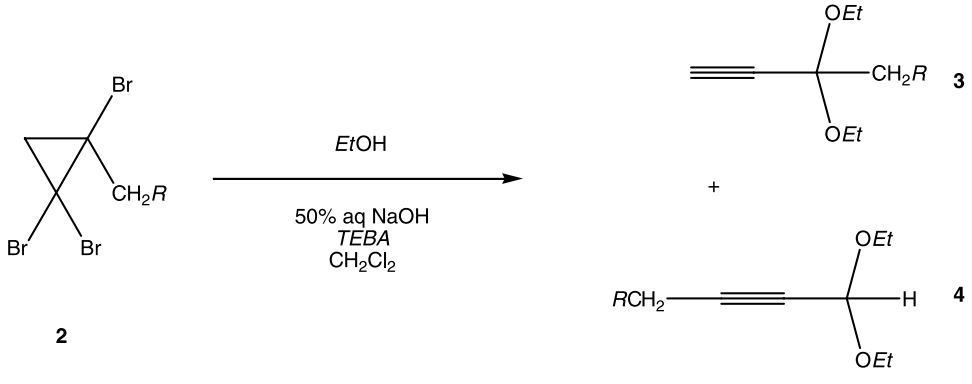


Fig. 2. Long-range coupling is observed between methylene groups in **2d** ($R = CH_2Ph$) and **2f** ($R = i$-propyl)

The structures of the tribromides were elucidated on the basis of their spectroscopic and spectrometric properties, which are as expected. However, a remark about the proton NMR spectra of **2d** and **2f** is appropriate, because both compounds exhibit long-range coupling between one of the cyclopropyl protons and one of the protons in the methylene group next to the ring. Both coupling constants are small, 0.6 Hz in **2d** to 1.0 Hz in **2f**, but their values are similar to those displayed by a large number of 2,2-disubstituted 1,1-dihalocyclopropanes [8, 9]. For both **2d** and **2f** the cyclopropyl proton involved in long-range coupling appears at a lower field than the other cyclopropyl proton; this clearly indicates that it is the proton *cis* to two bromo atoms that is engaged in the ^4J coupling (Fig. 2) [9].

When the 1,1,2-tribromocyclopropanes **2** were subsequently reacted with 50% aqueous sodium hydroxide in the presence of ethanol and a small amount of *TEBA*, the substrates suffered ring opening and gave in general a mixture of the acetylenic diethyl ketal **3** and the corresponding acetylenic acetal **4** (Scheme 4). In most cases the combined yield of **3** and **4** was moderate; in the best case, which involved **2c** as starting material, only 60% yield was obtained (Table 2). Another important feature is how difficult it is to separate the ketal from the corresponding acetal. In most cases separation is not achieved without a significant drop in yield for both compounds, and in three cases the loss was so significant that one of the compounds (**4a**, **3e**, and **3f**) could not be properly analyzed. The formation and structures of **4a**, **3e**, and **3f** were therefore substantiated by independent synthesis. The only mixture that allowed straightforward separation of ketal and acetal, was that of 3,3-diethoxy-5-phenylpent-1-yne (**3d**) and 1,1-diethoxy-5-phenyl-pent-2-yne (**4d**) obtained from **2d**; pure samples of both **3d** and **4d** were obtained fairly easily without a significant loss of material.



Scheme 4

Table 2. Combined isolated yield of acetal **4** and ketal **3** and the acetal/ketal ratio (**4**/**3**) in ring opening of 1,1,2-tribromocyclopropanes **2**

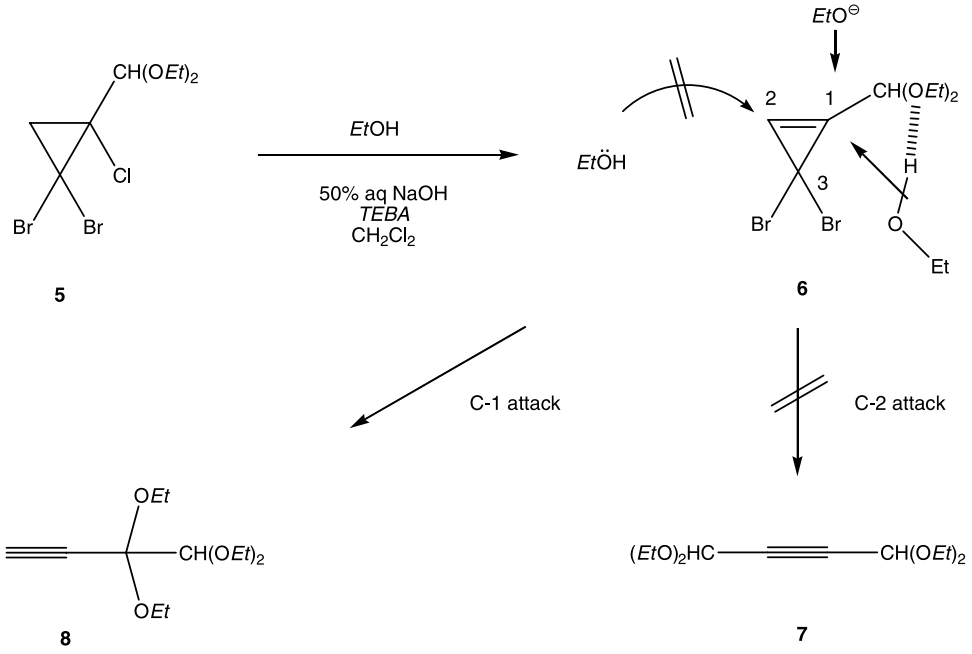
Entry	Cyclopropane	**4**/**3**[a]	Isolated yield/%[b]
1	**2a**	1.2	55
2	**2b**	1.2	43
3	**2c**	1.4	60
4	**2d**	1.5	54
5	**2e**	1.8	57
6	**2f**	3.5	36
7	**2g**	>80	37

[a] The ratios are based on GC and ^{1}H NMR analyses; some of the numbers differ somewhat from data published earlier [5]; this is due to different conditions during the reaction; [b] combined yield of **3** and **4** except for **2g**, which gave no **3g**, only **4g**

In order to try to improve the reaction and increase the yield of **3** and/or **4**, the ring opening was carried out under different conditions (reactant concentrations, excess of sodium hydroxide and ethanol, and reaction temperature). These experiments did not significantly improve the total yield of the products, but based on data from GC and ^{1}H NMR analyses of the crude product mixtures, it became evident that the acetal/ketal ratio **4**/**3** was somewhat sensitive to the conditions prevailing during the reaction. It was therefore important to carry out the ring opening of **2** under identical conditions so that it would be possible to detect the steric influence of *R* on the course of the reaction.

After some consideration it was decided to run the reaction in the same amount of dichloromethane containing the same amount of *TEBA*, to have the same initial concentrations of **2**, *Et*OH, and NaOH, and to cool the reaction mixtures in the same fashion during the reaction. Thus, it appeared that the **4**/**3** ratio increased as the steric crowding of RCH_2 increased (Table 2). The smallest alkyl groups, propyl and pentyl, gave a ratio of 1.2, which is slightly above the 1.0 ratio observed for the methyl group [2]. The ratio increases to 3.5 when $R = i\text{-}Pr$, and ring opening of **2g** afforded the corresponding acetal only; no signals were detected, which could be ascribed to the presence of the corresponding ketal. It is therefore clear that attack of the alkyl-substituted carbon atom, *viz*. C-1, in the 3,3-dibromocyclopropene formed as intermediate during the reaction, is hampered when the steric bulk of the alkyl group becomes significant and is completely prevented when a *t-Bu* group is attached to C-1.

The observation that alkyl substitution renders attack of C-1 and thus ketal formation more difficult when the steric influence of the alkyl group increases, suggests that from a steric point of view, acetal predominance should be the rule when the alkyl group is sterically demanding. On this basis it was expected that when **5** was exposed to the reaction conditions used to trigger ring opening of **2**, formation of **6** would occur, followed by predominant attack of C-2 and generation of **7**. To our surprise, that did not take place at all; instead **8** was formed exclusively (Scheme 5). Exclusive formation of **8** requires regiospecific attack of **6** at C-1, and this is conceivably achieved because the steric repulsion between ethanol molecules and the diethoxymethyl moiety is more than compensated by attractive forces



Scheme 5

due to hydrogen bonding between the same entities. Studies are currently under way to see if other polar substituents with hydrogen-bonding properties are capable to redirect the course of reaction in a similar fashion.

Experimental

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% dimethylpolysiloxane, 25 m, 0.2 mm i.d., 0.33 μm). Flash chromatography was performed with Silica gel (230–400 mesh) as the stationary phase and mixtures of *n*-hexane and ethyl acetate as the mobile phase. TLC analyses of the reaction mixtures were carried out with Silica gel (60 F_{254}) on aluminum sheets with mixtures of *n*-hexane and ethyl acetate as the mobile phase. Mass spectra were obtained on a VG 7070 Micromass spectrometer operated in the EI mode at 70 eV. Melting points were measured on a Gallenkamp apparatus.

THF and diethyl ether were distilled from sodium-benzophenone ketyl under N_2 immediately prior to use. Extremely dry *Et*OH was prepared by refluxing absolute *Et*OH with Na and diethyl succinate for 2 h, before distilling at atmospheric pressure [10]. Absolute ethanol was used as purchased. CH_2Cl_2 was dried over 4 Å molecular sieves prior to use. Mg turnings for the *Grignard* reactions were dried at 130°C before use. Solutions of $NaOCH_3$ were prepared immediately prior to use from Na and *p.a. Me*OH.

*Synthesis of 2-Bromo-1-alkenes **1a–1f**; General Procedure*

All the *Grignard* reagents were prepared from an alkyl bromide or alkyl chloride, Mg, and a few crystals I_2 in diethyl ether under N_2. A few drops of the halide were added, and when the reaction started (indicated by the disappearance of the dark colour of I_2) the solution was diluted with more

diethyl ether. A mixture of halide and diethyl ether (1:1) was then added dropwise to achieve a gentle reflux of the solution. When the addition was completed the reaction mixture was stirred at room temperature for 2 h and finally at reflux for another hour. The concentration of some of the *Grignard*-reagent solutions was determined by titration prior to use.

The freshly prepared *Grignard* reagent was added dropwise to a solution of 2,3-dibromoprop-1-ene in diethyl ether or *THF* under N_2 at 0°C (in a few cases CuCN was added to catalyze the reaction). Two layers were formed and Mg halide separated. After vigorous stirring for 2 h at reflux, the solution was decanted into a beaker filled with ice. The hydrolysate was acidified with 6 *M* HCl, and the products were extracted with diethyl ether. The combined organic phases were dried, filtered, evaporated, and the product was isolated by distillation or flash chromatography.

2-Bromopent-1-ene (**1a**)
The synthesis was carried out with CH_3CH_2MgBr (1.21 *M*, 132 cm^3, 160 mmol), and 30.46 g of 2,3-dibromoprop-1-ene (150 mmol) in 100 cm^3 *THF*. The alkene **1a** was isolated as a colourless oil (10.26 g, 46%) by distillation through a 20 cm packed column, bp 68–70°C/300 mm Hg (Ref. [11] 106°C/760 mm Hg).

2-Bromohept-1-ene (**1b**)
The synthesis was carried out with 13.89 g of 1-chlorobutane (150 mmol), 3.65 g Mg (150 mmol), and 20.04 g of 2,3-dibromoprop-1-ene (100 mmol) in 100 cm^3 of diethyl ether. Distillation through a 20 cm packed column yielded 9.32 g **1b** (53%) as a colourless liquid, bp 48°C/16 mm Hg (Ref. [12] 34°C/0.3 mm Hg). Traces of octane, formed by *Wurtz* coupling, could be observed in the ^1H NMR spectra [13]. A similar reaction carried out in the presence of CuCN gave **1b** in 38% yield.

2-Bromodec-1-ene (**1c**)
The synthesis was carried out with 17.94 g of 1-bromoheptane (100 mmol), 2.43 g Mg (100 mmol), and 15.94 g of 2,3-dibromoprop-1-ene (80 mmol) in 100 cm^3 of diethyl ether. Distillation of the residue through a 20 cm packed column gave 7.28 g **1c** (42%) as a colourless oil, bp 58–62°C/0.5 mm Hg (Ref. [14] 76–77°C/3 mm Hg). In addition 3.73 g of tetradecane were isolated as a colourless liquid, bp 69–79°C/0.2 mm Hg (Ref. [15] 254°C/760 mm Hg). A similar reaction performed in the presence of CuCN gave **1c** in 16% yield.

2-Bromo-4-phenylbut-1-ene (**1d**)
The synthesis was carried out with 12.66 g of benzyl chloride (0.10 mol), 2.43 g Mg (0.10 mol), and 15.99 g of 2,3-dibromoprop-1-ene (0.08 mol) in 80 cm^3 of diethyl ether [14]. Purification by flash chromatography (*n*-hexane) gave 10.36 g pure **1d** (61%) as a colourless oil. In addition 3.14 g of bibenzyl were isolated as crystals [15].

2-Bromo-3-cyclohexylprop-1-ene (**1e**)
The synthesis was carried out with 56 cm^3 of cyclohexylmagnesium bromide (1.84 *M*, 103 mmol), and 20.51 g of 2,3-dibromoprop-1-ene (103 mmol) in 100 cm^3 of diethyl ether. Some CuCN was added as a catalyst. Distillation yielded 11.67 g **1e** (56%) as a colourless oil, bp 84–92°C/13 mm Hg (Ref. [16] 88–89°C/14 mm Hg). Traces of bicyclohexyl could be observed in the NMR spectra [13]. When the reaction was repeated in the absence of CuCN, **1e** was obtained in 23% yield.

2-Bromo-4-methylpent-1-ene (**1f**)
The synthesis was carried out with 18.45 g of 2-bromopropane (150 mmol), 3.69 g Mg (150 mmol), and 23.97 g of 2,3-dibromoprop-1-ene (120 mmol) in 120 cm^3 *THF*. Distillation through a 20 cm packed column yielded 8.72 g **1f** (46%) as a colourless liquid, bp 63–64°C/100 mm Hg (Ref. [17] 126–127°C/760 mm Hg).

2-Bromo-3,3-dimethylbut-1-ene (**1g**)

The reaction was performed according to Ref. [18]. 1,2-Dibromo-3,3-dimethylbut-1-ene (36.60 g, 0.15 mol) was dissolved in 100 cm^3 CH_2Cl_2 and 180 cm^3 $NaOCH_3$ (1.0 *M*, 0.18 mol) were added dropwise at 0°C. The solution was magnetically stirred for 1 h, heated to rt, and stirred for another hour. After reflux for 24 h, the reaction mixture was quenched with 50 cm^3 sat NH_4Cl and extracted with pentane (4×150 cm^3). After evaporation of the solvents, the residue was distilled through a 20 cm packed column. Distillation afforded 19.52 g (80%) of a colourless liquid, which was proved to be a 76:24 mixture (GC and NMR analyses) of **1g** and **1h**, bp 60–63°C/96 mm Hg. IR (film): $\bar{\nu} = 2967$s, 2910s, 2874s, 1627m, 1608m, 1462br, 1365m, 1262w, 1240w, 1207w, 1093s, 945br, 888br, 740w cm^{-1}. The ^{1}H NMR spectrum of the mixture was as expected from the corresponding literature data for **1g** and **1h** in Refs. [18, 19].

1g: ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 29.0$ (3 CH_3), 39.5 (C), 113.9 (=CH_2), 147.0 (CBr) ppm.

1h: ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 28.9$ (3 CH_3), 35.6 (C), 101.7 (CHBr), 148.3 (=CH) ppm.

Preparation of 2-Substituted 1,1,2-Tribromocyclopropanes ***2***

All cyclopropanes were made by using the phase-transfer method described in Ref. [6]. For comparison cyclopropanes **2a**, **2b**, and **2e** were also synthesized by employing finely ground NaOH and ultrasound irradiation according to Ref. [7].

Makosza's method; General Procedure. A mixture of **1** and $CHBr_3$ (8 equivalents) was treated with 50% aq NaOH (6 equiv) at 0°C with vigorous mechanical stirring and 0.2–0.4 g *TEBA* or hexadecyltrimethylammonium chloride (Cetrimide) as a catalyst. The reactions were monitored by GC or TLC, and the stirring was continued at rt for 15–36 h. After quenching with H_2O and 6 *M* HCl, the products were extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), filtered, and evaporated under vacuum. The products were isolated by flash chromatography, distillation, or recrystallization.

Xu-Brinker's method; General Procedure. To a mixture of 12.0 g finely ground NaOH (0.30 mol) and 50 cm^3 CH_2Cl_2 in a round-bottom flask were added **1** (50 mmol) and *TEBA*. The flask was then immersed into an ultrasound bath with H_2O, some 0.5 cm from the bottom. After adding a 1:1 mixture of 25.4 g $CHBr_3$ (0.10 mol) and CH_2Cl_2, the mixture was ultrasonicated for 1 h. Celite® (5 g) was added, and the resulting mixture was filtered with suction through a 1-cm thick bed of Celite®. The filtrate was washed with CH_2Cl_2 (4×50 cm^3). The combined filtrates were concentrated on a rotavapor, and the product was isolated by distillation of the residue.

1,1,2-Tribromo-2-propylcyclopropane (**2a**, $C_6H_9Br_3$)

Prepared from 7.49 g **1a** (50 mmol), 100.59 g $CHBr_3$ (398 mmol), 27.05 g 50% aq NaOH (338 mmol), and *TEBA*. Purification by flash chromatography (*n*-hexane) gave 12.31 g **2a** (77%) as a colourless oil. IR (film): $\bar{\nu} = 2961$br, 2872s, 1459s, 1421m, 1380w, 1145m, 1089w, 1051m, 1014s, 955w, 740w, 666br cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.00$ (t, $J = 7.3$ Hz, CH_3), 1.56–2.13 (m, 3 CH_2) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.3$ (CH_3), 21.0 (CH_2), 33.0 (CBr_2), 37.9 (CH_2), 43.4 (CH_2), 45.5 (CBr) ppm; MS (EI): m/z (%) = 318 (M^+, 4), 243/241/239 (6/12/6), 201/199/197 (16/32/16), 79 (56), 51 (100); HRMS (EI): m/z calcd for M^+, $C_6H_9Br_3$, 317.8254; found 317.8268. When the synthesis was performed using the *Xu-Brinker* method **2a** was isolated in 77% yield.

1,1,2-Tribromo-2-pentylcyclopropane (**2b**, $C_8H_{13}Br_3$)

The compound was synthesized from 9.00 g **1b** (51 mmol), 101.38 g $CHBr_3$ (401 mmol), 25.93 g 50% aq NaOH (324 mmol), and *TEBA*. Distillation of the residue yielded 12.48 g **2b** (70%) as a colourless liquid, bp 88–92°C/0.4 mm Hg. IR (film): $\bar{\nu} = 2952$s, 2930s, 2862s, 1459m, 1422m, 1378w, 1145w, 1051w, 1016m, 684s, 672s cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.88$–0.98 (m, CH_3), 1.28–1.42 (m, 2 CH_2), 1.62–2.16 (m, 3 CH_2) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.9$ (CH_3), 22.4 (CH_2), 27.2 (CH_2), 31.0 (CH_2), 33.1 (CBr_2), 37.9 (CH_2), 41.6 (CH_2), 45.7 (CBr) ppm; MS (EI): m/z (%) = 346 (M^+, 1), 201/199/197 (8/16/8), 189/187 (10/10), 107 (73), 41 (100); HRMS (EI): m/z calcd for

M^+, $C_8H_{13}Br_3$, 345.8567; found 345.8595. When the synthesis was performed using the *Xu-Brinker* method **2b** was isolated in 57% yield.

1,1,2-Tribromo-2-octylcyclopropane (**2c**)
The compound was synthesized from 7.16 g **1c** (33 mmol), 66.32 g $CHBr_3$ (262 mmol), 17.02 g 50% aq NaOH (213 mmol), and *TEBA*. Purification by flash chromatography (*n*-hexane) gave 9.28 g **2c** (72%) as a colourless liquid [20, 21]. IR (film): $\bar{\nu} = 2925$br, 2856s, 1459s, 1423m, 1375w, 1144w, 1052m, 1016m, 885w, 722w, 691s, 672m cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.85$–0.92 (m, CH_3), 1.28–1.31 (m, 5 CH_2), 1.55–2.15 (m, 3 CH_2) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.0$ (CH_3), 22.5 (CH_2), 27.6 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 31.7 (CH_2), 33.1 (CBr_2), 37.9 (CH_2), 41.6 (CH_2), 45.7 (CBr) ppm; MS (EI): m/z (%) = 394 (M^+, 1), 201/199/197 (7/14/7), 69 (90), 42 (100); HRMS (EI): m/z calcd for M^+, $C_{11}H_{19}{}^{81}Br_3$, 393.8975, found 393.8993.

1,1,2-Tribromo-2-(2-phenylethyl)cyclopropane (**2d**, $C_{11}H_{11}Br_3$)
The compound was prepared from 10.05 g **1d** (48 mmol), 101.07 g $CHBr_3$ (400 mmol), 26.46 g 50% aq NaOH (331 mmol), and *TEBA*. Purification by flash chromatography (*n*-hexane) gave 14.07 g **2d** (77%) as a colourless oil. IR (film): $\bar{\nu} = 3066$w, 3026m, 2951w, 2925w, 2860w, 1495w, 1450m, 1422w, 1180w, 1054w, 1009m, 748s, 695s cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.73$ (d, $J = 9.4$ Hz, CH), 1.92 (dd, $J = 9.4$, 0.6 Hz, CH), 2.16–2.47 (m, CH_2), 2.86–3.16 (m, CH_2), 7.15–7.35 (m, Ph) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 32.6$ (CBr_2), 33.8 (CH_2), 37.8 (CH_2), 43.6 (CH_2), 45.0 (CBr), 126.2 (CH), 128.37 (2 CH), 128.39 (2 CH), 140.3 (C) ppm; MS (EI): m/z (%) = 301 (M^+-Br, 3), 223/221 (33/33), 91 (100) and 65 (74); HRMS (EI): m/z calcd for M^+-Br, $C_{11}H_{11}Br_2$, 300.9227; found 300.9233.

1,1,2-Tribromo-2-cyclohexylmethylcyclopropane (**2e**, $C_{10}H_{15}Br_3$)
The compound was synthesized from 10.16 g **1e** (50 mmol), 103.58 g $CHBr_3$ (410 mmol), 25.36 g 50% aq NaOH (317 mmol), and *TEBA*. Purification by flash chromatography (*n*-hexane) gave 12.79 g **2e** (68%) as a colourless oil. In the freezer white crystals were formed and subsequently recrystallized (*n*-hexane), mp 29–30°C. IR (film): $\bar{\nu} = 2924$br, 2849s, 1446m, 1420m, 1346w, 1267w, 1207w, 1149w, 1054m, 1017m, 974m, 902w, 851w, 690m cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.79$–1.42 (m, 3 CH_2), 1.66–2.15 (m, 4 CH_2 and CH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 26.0$ (CH_2), 26.2 (CH_2), 26.3 (CH_2), 32.1 (CH_2), 32.9 (CH_2), 33.5 (CBr_2), 38.0 (CH), 38.2 (CH_2), 44.3 (CBr), 47.3 (CH_2) ppm; MS (EI): m/z (%) = 372 (M^+, 1), 297/295/293 (2/4/2), 215/213 (13/13), 133 (45), 109 (60), 83 (98) and 55 (100); HRMS (EI): m/z calcd for M^+, $C_{10}H_{15}Br_3$, 371.8724; found 371.8732. When the synthesis was performed using the *Xu-Brinker* method **2e** was isolated in 75% yield.

1,1,2-Tribromo-2-isobutylcyclopropane (**2f**)
The compound was prepared from 8.48 g **1f** (54 mmol), 108.47 g $CHBr_3$ (429 mmol), 25.90 g 50% aq NaOH (322 mmol), and Cetrimide [21]. Purification of the crude product by flash chromatography (*n*-hexane) yielded 12.42 g **2f** (69%) as a colourless liquid.

1,1,2-Tribromo-2-(tert-butyl)cyclopropane (**2g**, $C_7H_{11}Br_3$)
The compound was synthesized from 7.49 g of a 76:24 mixture of **1g** and **1h** (46 mmol), 98.42 g $CHBr_3$ (361 mmol), 22.24 g 50% aq NaOH (278 mmol), and *TEBA*. Flash chromatography (*n*-hexane) of the residue yielded 6.97 g (60% based on the amount of **1g**) of pure **2g** as a colourless liquid. IR (film): $\bar{\nu} = 2967$s, 2875m, 1466br, 1410m, 1263w, 1211w, 1058m, 1032w, 1058br, 948w, 878w, 670s, 600s cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.34$ (s, 3 CH_3), 1.90 (d, $J = 9.9$ Hz, CH), 2.21 (d, $J = 9.9$ Hz, CH) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 29.8$ (3 CH_3), 30.6 (C), 34.7 (CH_2), 38.7 (CBr_2), 55.8 (CBr) ppm; MS (EI): m/z (%) = 331 (M^+-H, 1), 176/174 (2/2), 150/148 (55/55), 69 (77), 41 (100); HRMS (EI): m/z calcd for M^+-H, $C_7H_{10}Br_3$, 330.8333; found 330.8333.

*Ring Opening of **2** Under Phase-transfer Conditions; General Procedure*

To a cold (0°C) mixture of **2** (5 mmol), 0.2 g *TEBA*, and 0.92 g *Et*OH (20 mmol) in 15 cm^3 CH_2Cl_2 were added 3.26 g 50% aq NaOH (40 mmol). The cooling bath was removed and the reaction mixture was stirred vigorously at rt until all the starting material was consumed (monitored by GC or TLC). Water was added, the products were extracted with ether, and the combined extracts were dried ($MgSO_4$), filtered, and evaporated *in vacuo*. The products were isolated from the residue by flash chromatography.

3,3-Diethoxyhex-1-yne (**3a**, $C_{10}H_{18}O_2$) *and 1,1-Diethoxyhex-2-yne* (**4a**, $C_{10}H_{18}O_2$)

Cyclopropane **2a** (1.63 g, 5.0 mmol) gave a mixture of two products in a 45:55 ratio (GC analysis). Isolation by flash chromatography (*n*-hexane:ethyl acetate = 97.5:2.5) yielded 0.47 g of a mixture of **3a** and **4a** (55%) as a yellow oil, from which 0.21 g pure **3a** (25%) were obtained. IR (film): $\bar{\nu} = 3302$m, 2970s, 2933s, 2883s, 2116w, 1455m, 1388m, 1301m, 1286m, 1257m, 1152s, 1113s, 1059s, 988s, 845w, 806w, 652m cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7.3$ Hz, CH_3), 1.18–1.27 (m, 2 CH_3CH_2O), 1.43–1.65 (m, CH_2), 1.75–1.84 (m, CH_2), 2.52 (s, ≡C*H*), 3.48–3.73 (m, 2 CH_3CH_2O) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.8$ (CH_3), 15.0 (2 CH_3CH_2O), 17.3 (CH_2), 40.1 (CH_2), 57.7 (2 CH_3CH_2O), 72.6 (≡*C*H), 81.1 (≡C), 98.2 ($C(OEt)_2$) ppm; MS (EI): m/z (%) = 125.0969 (M^+-OEt, 100), 97 (40), 41 (100); HRMS (EI): m/z calcd for M^+-OEt, $C_8H_{13}O$, 125.0966; found 125.0969. Attempts to isolate a pure sample of **4a** were unsuccessful. The compound was therefore made by independent synthesis (*vide infra*).

3,3-Diethoxyoct-1-yne (**3b**, $C_{12}H_{22}O_2$) *and 1,1-Diethoxyoct-2-yne* (**4b**, $C_{12}H_{22}O_2$)

Cyclopropane **2b** (1.75 g, 5.0 mmol) gave a mixture of two products in a 46:54 ratio (GC analysis). Isolation by flash chromatography (*n*-hexane:ethyl acetate = 98:2) gave 0.43 g of a mixture of **3b** and **4b** (major product) (43%) as a yellow liquid, from which 0.08 g **3b** (8%) and 0.20 g **4b** (20%) were isolated.

3b: IR (film): $\bar{\nu} = 3303$m, 2959s, 2931s, 2873s, 2112w, 1459m, 1386m, 1281m, 1227m, 1149s, 1057s, 1009s, 957m, 886w, 651m cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.87$–0.93 (m, 5H), 1.18–1.58 (m, 12H), 1.76–1.85 (m, CH_2), 2.52 (s, ≡C*H*), 3.48–3.73 (m, 2 CH_3CH_2O) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.9$ (CH_3), 15.1 (2 CH_3CH_2O), 22.4 (CH_2), 23.6 (CH_2), 31.5 (CH_2), 37.9 (CH_2), 57.8 (2 CH_3CH_2O), 72.6 (≡*C*H), 81.2 (≡C), 98.4 ($C(OEt)_2$) ppm; MS (EI): m/z (%) = 153 (M^+-OEt, 100), 127 (98), 71 (57), 55 (58); HRMS (EI): m/z calcd for M^+-OEt, $C_{10}H_{17}O$, 153.1279; found 153.1260.

4b: IR (film): $\bar{\nu} = 2967$s, 2932s, 2877s, 2243w, 1457m, 1358m, 1332m, 1152s, 1056s, 1009s, 912w, 815w cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.83$–0.91 (m, CH_3), 1.18–1.59 (m, 12H), 2.22 (dt, $J = 7.0$, 1.6 Hz, CH_2), 3.47–3.80 (m, 2 CH_3CH_2O), 5.24 (t, $J = 1.6$ Hz, $(EtO)_2CH$) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.7$ (CH_3), 14.9 (2 CH_3CH_2O), 18.4 (CH_2), 22.0 (CH_2), 27.8 (CH_2), 30.9 (CH_2), 60.4 (2 CH_3CH_2O), 76.3 (C), 86.3 (C), 91.3 ($(EtO)_2CH$) ppm; MS (EI): m/z (%) = 153 (M^+-OEt, 100), 103 (10), 81 (50), 55 (40); HRMS (EI): m/z calcd for M^+-OEt, $C_{10}H_{17}O$, 153.1279; found 153.1268.

3,3-Diethoxyundec-1-yne (**3c**, $C_{15}H_{28}O_2$) *and 1,1-Diethoxyundec-2-yne* (**4c**, $C_{15}H_{28}O_2$)

Cyclopropane **2c** (1.95 g, 5 mmol) afforded 0.72 g (60%) of an essentially pure mixture of **3c** and **4c** in a 42:58 ratio, respectively (^{1}H NMR analysis). Further purification by flash chromatography (a 99:1 mixture of *n*-hexane and ethyl acetate) yielded pure, yellowish samples of 0.20 g **3c** (17%) and 0.12 g **4c** (10%).

3c: IR (film): $\bar{\nu} = 3307$m, 2927s, 2858s, 2115w, 1460m, 1386m, 1300m, 1278m, 1249m, 1148s, 1057s, 990s, 886w cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.85$–0.91 (m, CH_3), 1.18–1.53 (m, 18H), 1.78–1.85 (m, CH_2), 2.52 (s, ≡C*H*), 3.48–3.74 (m, 2 CH_3CH_2O) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.9$ (CH_3), 15.0 (2 CH_3CH_2O), 22.5 (CH_2), 23.9 (CH_2), 29.1 (CH_2), 29.3 (2 CH_2), 31.7 (CH_2), 37.9 (CH_2), 57.7 (2 CH_3CH_2O), 72.6 (≡*C*H), 81.2 (≡C), 98.3

(C(OEt)$_2$) ppm; MS (EI): m/z (%) = 195 (M^+-OEt, 100), 127 (93); HRMS (EI): m/z calcd for M^+-OEt, $C_{10}H_{17}O$, 195.1749; found 195.1765.

4c: IR (film): $\bar{\nu}$ = 2927s, 2861s, 2241w, 1459m, 1358m, 1331m, 1260w, 1152s, 1057s, 1009s, 910w, 811w cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.85–0.91 (m, CH_3), 1.20–1.60 (m, 18H), 2.24 (dt, J = 7.0, 1.6 Hz, CH_2), 3.49–3.82 (m, 2 CH_3CH_2O), 5.26 (t, J = 1.6 Hz, ((EtO)$_2$C*H*) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9 (CH_3), 14.9 (2 *C*H_3CH$_2$O), 18.4 (CH_2), 22.4 (CH_2), 28.1 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 31.6 (CH_2), 60.3 (2 CH_3*C*H$_2$O), 75.4 (C), 86.3 (C), 91.3 ((EtO)$_2$*C*H) ppm; MS (EI): m/z (%) = 240 (M^+, 1), 195 (M^+-OEt, 100), 81 (45), and 55 (55); HRMS (EI): m/z calcd for M^+-OEt, $C_{10}H_{17}O$, 195.1749; found 195.1721.

3,3-Diethoxy-5-phenylpent-1-yne (**3d**, $C_{15}H_{20}O_2$)
and 1,1-Diethoxy-5-phenylpent-2-yne (**4d**, $C_{15}H_{20}O_2$)
Cyclopropane **2d** (1.91 g, 5.0 mmol) afforded a mixture of **3d** and **4d** in a 40:60 ratio (GC analysis). Subsequent purification by flash chromatography (a 96:4 mixture of *n*-hexane and ethyl acetate) yielded pure, yellowish samples of 0.23 g **3d** (20%) and 0.40 g **4d** (34%).

3d: IR (film): $\bar{\nu}$ = 3287m, 3027m, 2975s, 2932s, 2890m, 2112w, 1600w, 1494w, 1450m, 1389m, 1292m, 1274m, 1222m, 1167s, 1114s, 1053br, 1009s, 961m, 878w, 822w, 745m, 700s, 659m cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.22 (t, J = 7.1 Hz, 2 C*H*$_3$CH$_2$O), 2.09–2.17 (m, 2H), 2.58 (s, ≡CH), 2.79–2.88 (m, 2H), 3.52–3.79 (m, 2 CH_3C*H*$_2$O), 7.12–7.32 (m, Ph) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.0 (2 *C*H_3CH$_2$O), 30.4 (CH_2), 39.6 (CH_2), 58.0 (2 CH_3*C*H$_2$O), 73.2 (≡*C*H), 80.8 (≡C), 98.0 (C(OEt)$_2$), 125.7 (CH), 128.2 (4 CH), 141.4 (C) ppm; MS (EI): m/z (%) = 187 (M^+-OEt, 35), 127 (56), 91 (100), 77 (21); HRMS (EI): m/z calcd for M^+-OEt, $C_{13}H_{15}O$, 187.1123; found 187.1142.

4d: IR (film): $\bar{\nu}$ = 3062w, 3028m, 2976s, 2928s, 2887s, 2240w, 1605w, 1494m, 1449m, 1357s, 1334s, 1150s, 1056br, 1009s, 911w, 746m, 700s cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.21 (t, J = 7.2 Hz, 2 C*H*$_3$CH$_2$O), 2.49–2.58 (m, 2H), 2.81–2.88 (m, 2H), 3.45–3.76 (m, 2 CH_3C*H*$_2$O), 5.24 (t, J = 1.7 Hz, (EtO)$_2$C*H*), 7.16–7.33 (m, Ph) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.9 (2 *C*H_3CH$_2$O), 20.6 (CH_2), 34.4 (CH_2), 60.4 (2 CH_3*C*H$_2$O), 76.2 (C), 85.3 (C), 91.2 ((EtO)$_2$*C*H), 126.1 (CH), 128.16 (2 CH), 128.18 (2 CH), 140.2 (C) ppm; MS (EI): m/z (%) = 232 (M^+, 1), 91 (100), 77 (8); HRMS (EI): m/z calcd for M^+-OEt, $C_{13}H_{15}O$, 187.1123; found 187.1150.

3,3-Diethoxy-4-cyclohexylbut-1-yne (**3e**, $C_{14}H_{24}O_2$)
and 1,1-Diethoxy-4-cyclohexylbut-2-yne (**4e**, $C_{14}H_{24}O_2$)
Cyclopropane **2e** (1.91 g, 5.0 mmol) afforded a product mixture of **3e** and **4e** in a 36:64 ratio (^{1}H NMR analysis). Subsequent purification by flash chromatography (a 95:5 mixture of *n*-hexane and ethyl acetate) yielded 0.64 g (57%) of a pure, yellowish sample of the two alkynes, from which 0.40 g **4e** (34%) were isolated. IR (film): $\bar{\nu}$ = 2975s, 2925s, 2855s, 2242w, 1448m, 1331m, 1152s, 1055s, 1007s, 912m, 817w cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.83–1.83 (m, 17H), 2.14 (dd, J = 6.8, 1.7 Hz, CH_2), 3.50–3.82 (m, 2 CH_3C*H*$_2$O), 5.27 (t, J = 1.7 Hz, (EtO)$_2$C*H*) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.0 (2 *C*H_3CH$_2$O), 25.9 (2 CH_2), 26.1 (CH_2), 26.3 (CH_2), 32.6 (2 CH_2), 36.9 (CH), 60.2 (2 CH_3*C*H$_2$O), 76.4 (C), 85.2 (C), 91.4 ((EtO)$_2$*C*H) ppm; MS (EI): m/z (%) = 223 (M^+-H, 10), 179 (M^+-OEt, 100), 55 (41); HRMS (EI): m/z calcd for M^+-OEt, $C_{12}H_{19}O$, 179.1436; found 179.1441. Attempts to isolate a pure sample of **3e** were unsuccessful. The compound was therefore made by independent synthesis (*vide infra*).

3,3-Diethoxy-5-methylhex-1-yne (**3f**, $C_{11}H_{20}O_2$)
and 1,1-Diethoxy-5-methylhex-2-yne (**4f**, $C_{11}H_{20}O_2$)
Cyclopropane **2f** (1.68 g, 5 mmol) gave a product mixture of **3f** and **4f** in a 22:78 ratio (GC and ^{1}H NMR analyses). Subsequent work-up by flash chromatography (*n*-hexane:ethyl acetate = 97.5:2.5) afforded 0.33 g of a yellow liquid, which consisted of almost pure **4f** (36%), but contained traces of both **3f** and an aldehyde [2, 3]. IR (film): $\bar{\nu}$ = 2964s, 2928br, 2241w, 1462m, 1361m, 1334m, 1279w, 1257w, 1151s, 1058br, 1009s, 911w, 817br cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.98 (d, J = 6.5 Hz,

2 CH_3), 1.23 (t, $J = 7.1$ Hz, 2 OCH_2CH_3), 1.74–1.94 (m, $(CH_3)_2CH$), 2.14 (dd, $J = 6.5$, 1.7 Hz, CH_2), 3.50–3.82 (m, 2 OCH_2CH_3), 5.27 (t, $J = 1.7$ Hz, $(EtO)_2CH$) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.9$ (2 CH_3CH_2O), 21.8 (2 CH_3), 27.55 (CH_2), 27.61 ($(CH_3)_2CH$), 60.3 (2 CH_3CH_2O), 76.4 (C), 85.1 (C), 91.3 ($(EtO)_2CH$) ppm; MS (EI): m/z (%) = 183 (M^+-H, 2), 139 (M-OEt, 100), 127 (4), 57 (4); HRMS (EI): m/z calcd for M^+-H, $C_{11}H_{19}O_2$, 183.1385; found 183.1388. Attempts to isolate a pure sample of **3f** were unsuccessful, but the compound was made by independent synthesis (*vide infra*).

1,1-Diethoxy-4,4-dimethylpent-2-yne (**4g**, $C_{11}H_{20}O_2$)

When 1.67 g **2g** (5.0 mmol) were reacted following the general procedure, only one product was obtained (GC analysis). Work-up by flash chromatography (*n*-hexane:ethyl acetate = 97.5:2.5) gave 0.34 g **4g** (37%) as a yellow liquid. IR (film): $\bar{\nu} = 2971$s, 2932s, 2887s, 2243w, 1718m, 1672m, 1621m, 1456m, 1363m, 1332m, 1263m, 1204m, 1117s, 1054s, 1009s, 904w, 856w, 808m cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.20$–1.27 (m, 15H), 3.49–3.81 (m, 2 CH_3CH_2O), 5.26 (s, $(EtO)_2CH$) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.9$ (2 CH_3CH_2O), 27.1 (C), 30.5 (3 CH_3), 60.3 (2 CH_3CH_2O), 74.0 (C), 91.3 ($(EtO)_2CH$), 94.1 (C) ppm; MS (EI): m/z (%) = 183 (M^+-H, 25), 155 (72), 139 (M^+-OEt, 100), 57 (90); HRMS (EI): m/z calcd for M^+-OEt, $C_9H_{15}O$, 139.1123; found 139.1124.

Alternative Synthesis of 1,1-Diethoxyhex-2-yne (**4a**)

The compound was synthesized by treating 1.60 g **2a** (20 mmol) with 1.53 g of 1,8-diazabicyclo[5.4.0]undec-7-ene (*DBU*) (20 mmol) in 25 cm^3 of extremely dry ethanol, following the procedure in Ref. [3]. Work-up of the residue by flash chromatography (*n*-hexane:ethyl acetate = 96:4) afforded 0.39 g **4a** (46%) as a colourless liquid, along with 0.21 g recovered **2b** (13%). IR (film): $\bar{\nu} = 2971$s, 2933s, 2881s, 2245w, 1455m, 1333m, 1152s, 1056s, 1009s, 914m, 816w cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.91$ (t, $J = 7.3$ Hz, CH_3), 1.15 (t, $J = 7.2$ Hz, 2 CH_3CH_2O), 1.39–1.57 (m, CH_2), 2.14 (dt, $J = 7.0$, 1.6 Hz, CH_2), 3.41–3.73 (m, 2 CH_3CH_2O), 5.17 (t, $J = 1.6$ Hz, $(EtO)_2CH$) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 12.9$ (CH_3), 14.5 (2 CH_3CH_2O), 20.0 (CH_2), 21.3 (CH_2), 60.0 (2 CH_3CH_2O), 75.4 (C), 85.6 (C), 91.0 ($(EtO)_2CH$) ppm; MS (EI): m/z (%) = 125 (M^+-OEt, 100), 103 (7), 97 (62); HRMS (EI): m/z calcd for M^+-OEt, $C_8H_{13}O$, 125.0966; found 125.0981.

Alternative Synthesis of 3,3-Diethoxy-4-cyclohexylbut-1-yne (**3e**)

The compound was synthesized by treating 1.87 g **2e** (5.0 mmol) with 0.68 g $NaOC_2H_5$ (10 mmol) in 16 cm^3 dry *THF*, following the procedure in Ref. [3]. Work-up of the residue by flash chromatography (*n*-hexane:ethyl acetate = 95:5) afforded 0.51 g **3e** (46%) as a light yellow liquid. IR (film): $\bar{\nu} = 3306$m, 2974s, 2925s, 2853s, 2114w, 1448m, 1388m, 1342m, 1279m, 1235m, 1180s, 1147s, 1111s, 1058s, 997s, 936w, 884w, 824w, 650m cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.84$–1.36 (m, 12H), 1.60–1.73 (m, 5H), 1.87–1.90 (m, 2H), 2.54 (s, ≡C*H*), 3.52–3.68 (m, 2 CH_3CH_2O) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.0$ (2 CH_3CH_2O), 26.2 (2 CH_2), 26.3 (CH_2), 33.7 (CH), 34.1 (2 CH_2), 44.9 (CH_2) 57.8 (2 CH_3CH_2O), 73.1 (≡*C*H), 81.4 (≡C), 98.3 (*C*$(OEt)_2$) ppm; MS (EI): m/z (%) = 179 (M^+-OEt, 31), 149 (10), 135 (35), 127 (15), 107 (41), 83 (20), 41 (100); HRMS (EI): m/z calcd for M^+-OEt, $C_8H_{13}O$, 179.1436; found 179.1427.

Alternative Synthesis of 3,3-Diethoxy-5-methylhex-1-yne (**3f**)

The compound was synthesized by treating 1.67 g **2f** (5.0 mmol) with 0.68 g $NaOC_2H_5$ (10 mmol) in 16 cm^3 dry *THF*, following the procedure in Ref. [3]. Work-up of the residue by flash chromatography (*n*-hexane:ethyl acetate = 95:5) afforded 0.52 g **3f** (57%) as a light yellow liquid. IR (film): $\bar{\nu} = 3306$m, 2958s, 2894s, 2112w, 1464m, 1388m, 1361m, 1265m, 1148s, 1060br, 996s, 922w, 810br, 651m cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.99$ (d, $J = 6.5$ Hz, 2 CH_3), 1.20 (t, $J = 7.1$ Hz, 2 CH_3CH_2O), 1.73 (d, $J = 1.7$ Hz, CH_2), 1.90–2.09 (m, 1H), 2.55 (s, ≡C*H*), 3.49–3.73 (m, 2 CH_3CH_2O) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 15.0$ (2 CH_3CH_2O), 23.5 (2 CH_3), 24.5 (CH), 46.0 (CH_2), 57.8 ((2 CH_3CH_2O), 73.2 (≡*C*H), 81.3 (≡C), 98.3 ($(EtO)_2C$) ppm; MS (EI): m/z (%) = 139 (M^+-OEt, 100), 138 (M^+-

EtOH, 2), 127 (82), 111 (30), 57 (6); HRMS (EI): m/z calcd for M^+-EtOH, $C_9H_{14}O$, 138.1045; found 138.1051.

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