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# AN EFFICIENT SYNTHESIS OF tert-ALKOXYETHYNES

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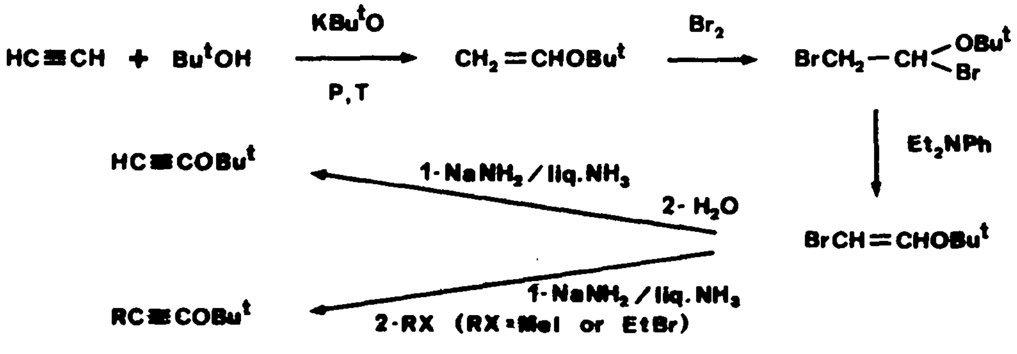
**Abstract.**- The synthesis of tert-butoxyethyne (1a) and (1-adamantyloxy)-ethyne (1b) has been performed by a three step sequence starting from ethyl vinyl ether. Overall yields are 34 and 67%, respectively. The process is insensitive to the steric hindrance of the tertiary alcohol used and can be conveniently modified for the preparation of 1-tert-alkoxy-1-alkynes in high yield, without isolation of the intermediate 1-tert-alkoxyethyne.

Acetylenic ethers have been recognized for a long time as versatile synthetic intermediates.[1,2] They are readily prepared: (i) By base induced elimination reactions starting from $\alpha$-halogenovinyl ethers,[3] $\beta$-halogenoacetals,[4] $\alpha$, $\beta$-dichlorovinyl ethers[5] or trifluorethyl ethers;[6] (ii) By addition-elimination reactions starting from acetylenic substrates,[5,7] and (iii) by 1,3-substitution on functionalised allenes.[8] On the other hand, the alkylation of metal derivatives of preformed alkoxyethynes[3a-b,5,9] and the substitution by arylcopper reagents on 2-iodo-1-ethoxyethyne[10] allow also the preparation of C-substituted compounds.

However, no general method has been reported allowing the preparation of tert-alkoxyacetylenes, a fact that can be attributed to the very weak nucleophilic character of tertiary alcohols and their alkoxides. The preparation of tert-butoxyethyne (1a) and 1-tert-butoxy-2-phenylethyne starting from 1-chloro-1-fluoroalkenes has been reported,[11] but neither the experimental details nor the characterization of the products were described. Later on, Tanaka and Miller[7] reported the preparation in very low yield of 1-tert-butoxy-2-phenylethyne starting from 1-chloro-2-phenylethyne. In fact, only the preparation of tert-butoxyethyne (1a) and some of its alkylated derivatives has been properly described by Arens and coworkers,[3a] through the sequence shown in Scheme 1.



Scheme 1

This synthesis suffers, however, from an important drawback since the preparation of tert-butoxyethene, the key intermediate in the sequence, involves the utilization of acetylene at high temperature and medium pressure, thus requiring special equipment and not being exempt of some risks. Although a more convenient synthesis of this intermediate has been recently published,[12] the starting material, 2-chloroethyl vinyl ether, is a rather expensive reagent.

In any case, tert-alkoxyethynes have a considerable synthetic interest. Thus, it is known that acetylenic ethers bearing hydrogen atoms β to oxygen in the alkyl substituent are thermally unstable, readily losing an olefin fragment and leading to a ketene[3a,3d] (Figure 1).

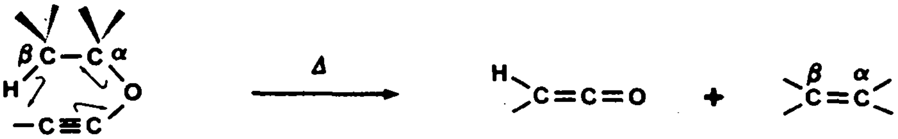


Figure 1

This elimination takes place in ethoxyethyne only at 120°C, but in tert-butoxyethyne (1a) the process occurs with appreciable rate already at 40°C.[2f] Consequently, acetylenic ethers bearing a high number of β-hydrogen atoms are an appropriate source for the generation of ketenes at low temperature under essentially neutral conditions.[13]

On the other hand, alkoxyethynes possess an electron rich triple bond, and consequently exhibit some tendency to thermal polymerisation.[1,14] Tertiary alkoxy groups, due to their steric characteristics, can modulate this behaviour by preventing the intermolecular approach necessary for the polymerisation to take place. Therefore, the synthesis of tert-alkoxyethynes bearing bulky substituents, which, for geometrical reasons, can not suffer the thermal elimination of olefin, should allow the utilization of these substances in processes requirig high temperatures.

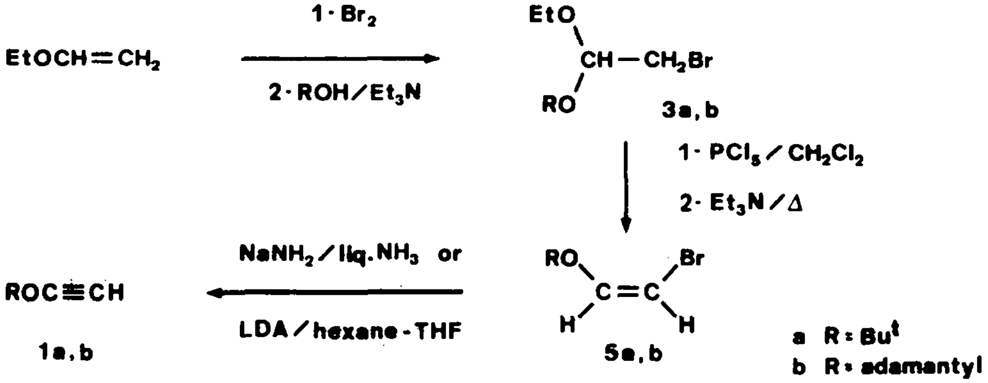
Consequently, we planned to develope a synthetic procedure of wide applicability for tert-alkoxyethynes that could obviate the lack of nucleophilic character of tertiary alcohols and could avoid the preparation of tert-alkoxyethenes as starting materials. tert-Butoxyethyne (1a) and (1-adamantyloxy)ethyne (1b) were selected as the synthetic objectives. The first one exemplifies the acetylenic ethers that readily fragment into an olefin and a ketene, whereas the second one would be an example of an acetylenic ether with presumed thermal stability owing to the anti-Bredt nature of 1-adamantene.

## RESULTS AND DISCUSSION

In order to develope the synthetic scheme, we took advantage of our previous experience in the chemistry of acetylene diethers,[15] specially on the high reactivity of α-halogenoacetals towards alcohols, and on the possibility of chemoselective cleavage of mixed acetals by phosphorus pentachloride. Ethyl vinyl ether, an inexpensive industrial chemical, would be the starting material for our synthesis, as depicted in Scheme 2.

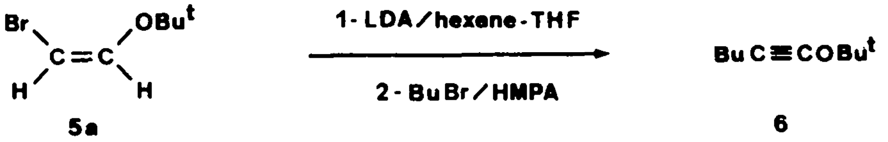
For the preparation of tert-butoxyethyne (1a), ethyl vinyl ether was brominated at low temperature in dichloromethane solution, and the resulting solution of of 1,2-dibromo-1-ethoxyethane (2) was treated with a mixture of tert-butyl alcohol and triethylamine. 2-Bromo-1-tert-butoxy-1-ethoxyethane (3a) was obtained in 67-72% yield[16] along with some (Z)-1-bromo-2-ethoxyethene arising from the base induced dehydrobromination of 2.

The cleavage of the mixed acetal group in 3a with phosphorus pentachloride in dichloromethane solution took place with high chemoselectivity, the primary ethoxy group being displaced. 2-Bromo-1-tert-butoxy-1-chloroethane (4a) was characterized spectroscopically, but was not usually isolated. Subsequent treatment of 4a with triethylamine in dichloromethane, first at 0°C in order to form a tetraalkylammonium salt, and then under reflux for 100 minutes, led to the isolation of (Z)-1-bromo-2-tert-butoxyethene (5a) in 72-76% yield. Some (Z)-1-bromo-2-ethoxyethene formed again in this reaction, thus indicating that the chemoselectivity of the reaction with $PCl_5$ was not complete. It is whorth noting that the chemoselectivity of the reaction with $PCl_5$ could be improved up to 100% by working in hexane solution. However, both steps were much slower in this solvent, and the overall yield was lower (61%).



Scheme 2

When tert-butoxyethyne (1a) itself was to be obtained, the final dehydrobromination of 5a was performed with sodium amide in liquid ammonia. This was essential in order to allow the separation of the highly volatile 1a from the reaction solvents. In this way, 1a was obtained in a 59-64% yield.[17] On the other hand, when the desired final product was an alkylated derivative of tert-butoxyethyne, the dehydrohalogenation could be performed more conveniently with lithium diisopropylamide in hexane/THF. In this way, 5a could be converted into 1-tert-butoxy-1-hexyne (6) in 47-55% overall yield by dehydrobromination and subsequent treatment of the corresponding acetylide with 1-bromobutane in the presence of HMPA (Scheme 3).



Scheme 3

The synthesis of (1-adamantyloxy)ethyne (1b ) from ethyl vinyl ether was performed by an analogous sequence. In the first place, ethyl vinyl ether was brominated at low temperature in ethanol-free chloroform, and the resulting solution of 2 was treated with 1-adamantanol, affording 1-(1-adamantyloxy)-2-bromo-1-ethoxyethane (3b) in 96% yield, on the basis of reacted 1-adamantanol.

Treatment of 3b with phosphorus pentachloride in dichloromethane led to 1-(1-adamantyloxy)-2-bromo-1-chloroethane (4b) which, in general, was not isolated. A subsequent treatment with triethylamine, first at 0°C and then under reflux, led to the isolation of (Z)-1-(1-adamantyloxy)-2-bromoethene (5b) in 93-95% overall yield from 3b. No 1-bromo-2-ethoxyehene could be detected in the final product, thus indicating that the cleavage of 3b by $PCl_5$ takes place with complete chemoselectivity.

Finally, the conversion of 5b into (1-adamantyloxy)ethyne (1b) was performed by dehydrobromination, either by sodium amide in liquid ammonia or by lithium diisopropylamide in hexane/THF. In both cases, the crude reaction product was essentially pure (1-adamantyloxy)ethyne (1b) obtained in quantitative yield. Analitically pure 1b could be isolated in 73-75% yield by column chromatography on silica gel-triethylamine, and eluting with hexane.

In summary, we have developed a method for the synthesis of acetylenic ethers derived from tertiary alcohols that seems to be insensitive to the steric bulk of the alcohol moiety and, consequently, of general applicability. The synthesis takes place in three steps starting from ethyl vinyl ether, the reagents employed are inexpensive, the overall yield is high ( 34% for 1a and 67% for 1b), and the whole process can be easily carried out at the 0.1-1.0 mol scale.

On the other hand, the synthetic intermediates involved in the sequences are themselves of synthetic interest. Thus, the 1-*tert*-alkoxy-2-bromo-1-ethoxyethanes (3) are suitable starting materials for the synthesis of mixed acetylene diethers,[18] whereas the (*Z*)-1-*tert*-alkoxy-2-bromoethenes (5) are potential precursors of (*Z*)-*tert*-alkoxyvinyl lithiums which, by analogy with *Z*-alkoxyvinyl lithiums,[19] are highly promising acetaldehyde anion equivalent reagents.

## EXPERIMENTAL

NMR spectra were recorded on a VARIAN XL-200 and HITACHI Perkin-Elmer R-24B instruments. Carbon substitution patterns in the $^{13}C$ NMR spectra were determined either by off-resonance or DEPT experiments. Mass spectra were taken on a Hewlett-Packard 5988A apparatus. Infrared spectra were recorded on a Perkin-ELmer 681 instrument. Melting points were determined on a Kofler microscope and are uncorrected. Anhydrous tetrahydrofuran (THF) was obtained by distillation from sodium benzophenone ketyl. Anhydrous hexamethylphosphoramide (HMPA) was obtained by distillation over $CaH_2$ at high vacuum and it was stored over molecular sieves. EtOH-free $HCCl_3$ was obtained by washing distillate $HCCl_3$ (1 L) with water (5x800 mL), drying over $K_2CO_3$ and filtering through alumina (10 g). 1-Adamantanol was obtained from adamantane following a literature procedure.[20]

**2-Bromo-1-*tert*-Butoxy-1-ethoxyethane (3a).-** Ethyl vinyl ether (72.2 g, 1.00 mol) was brominated in $CH_2Cl_2$ (275 mL) at -78°C under $N_2$ until persistent bromine coloration and the mixture was then decolorized with a few drops of ethyl vinyl ether. A solution of *tert*-butyl alcohol (222.0 g, 3 mol) in triethylamine (155 mL, ca. 113.2 g, 1.12 mol) was then added dropwise over 60 minutes at the same temperature with energic stirring. The cooling bath was removed and the mixture allowed to warm up to 0°C with stirring. $CH_2Cl_2$ (250 mL) was then added, and the resulting solution poured into ice-cold water (400 mL) The organic layer was separated, and the aqueous one extracted with $CH_2Cl_2$ (2x50 mL). The combined organic extracts were successively washed with 0.05 N HCl (2x150 mL) and saturated $NaHCO_3$ solution, and dried over $MgSO_4$. After solvent evaporation at reduced pressure, crude material was distilled at 18 torr through a Vigreux column collecting the fraction boiling at 83-85°C, constituted by pure 3a (150.75-162.00 g, 0.67-0.72 mol, 67-72% yield). The material distilled below this temperature was a mixture of 3a and (*Z*)-1-bromo-2-ethoxyethene.

3a.- IR ($CCl_4$) $\nu_{max.}$ = 2980, 2940, 2910, 2890, 1415, 1400, 1370, 1190, 1110, 1060, 1040, and 1010 $cm^{-1}$. $^1H$-NMR (60 MHz, $CCl_4$) $\delta$ = 4.74 (t, J= 5.5 Hz, 1H), 3.62-3.10 (m, 4H), 1.20 (s, 9H), and 1.10 (t, J= 7.0 Hz, 3H) ppm. $^{13}C$-NMR (50.3 MHz, $CDCl_3$) $\delta$ = 96.13 (d), 74.77 (s), 59.57 (t), 33.19 (t), 28.64 (q), and 15.31 (q) ppm. MS m/z : 211, 209 (14.7%, $M^+-CH_3$); 181, 189 (18.7%, $M^+$-EtO); 153, 151 (100%, $M^+$-*t*BuO); 131 (70.3%, $M^+-CH_2Br$); 125, 123 (89.1%); 103 (14.8%); 95, 93 (10.9%); 87 (19.5%); 75 (18.7%); 57 (11.7%). Calc. for $C_8H_{17}O_2Br$: C, 42.68%; H, 7.61% ; Br, 35.50%; Found: C, 42.87%; H, 7.83%; Br, 35.32%.

**(*Z*)-1-Bromo-2-*tert*-butoxyethene (5a).-** A solution of 3a (159.9 g, 0.71 mol) in $CH_2Cl_2$ (200 mL) was added dropwise with energic stirring to a suspension of phosphorus pentachloride (165 g, 0.79 mol) in $CH_2Cl_2$ (700 mL) at 0°C under a dry $N_2$ atmosphere over 15 min, and the stirring was continued for a 45 min period, until all the starting material had been converted into 2-bromo-1-*tert*-butoxy-1-chloro-ethane (4a). Triethylamine (495 mL, ca. 361.4 g, 3.57 mol) was then added dropwise at the same temperature. The cooling bath was removed, the reaction mixture heated under reflux for 105 min and finally poured into crushed ice (700 g). The organic phase was separated, the aqueous one extracted with $CH_2Cl_2$ (2x200 mL), and the combined organic extracts were successively washed with 0.5N HCl (2x100 mL) and saturated $NaHCO_3$ solution, and dried over $MgSO_4$. After solvent evaporation at reduced pressure, the crude was distilled at 22 torr through a Vigreux column, pure (*Z*)-1-Bromo-2-*tert*-butoxyethene (91.5-97.9 g, 0.51-0.54 mol, 72-76% yield) being collected at 61-63°C. The material distilled below this temperature was a mixture of 5a and (*Z*)-1-bromo-2-ethoxyethene.

4a. IR ($CCl_4$) $\nu_{max.}$ = 2990, 2940, 1430, 1400, 1380, 1370, 1310, 1270, 1250, 1190, 1140, 1050, 1020, and 920 $cm^{-1}$. $^1H$-NMR (60MHz, $CCl_4$) $\delta$ = 5.84 (t, J= 5.5 Hz, 1H), 3.65 (d, J= 5.5 Hz, 2H), and 1.34 (s, 9H) ppm.

5a. IR ($CCl_4$) $\nu_{max.}$ = 3115, 2990, 2940, 1640, 1460, 1400, 1370, 1330, 1260, 1230, 1180, 1095, and 665 $cm^{-1}$. $^1H$-NMR (200MHz, $CDCl_3$) $\delta$ = 6.63 (d, J = 4.2 Hz, 1H), 4.96 (d, J = 4.2 Hz, 1H), and 1.30 (s, 9H) ppm. $^{13}C$-RMN (50.3 MHz, $CDCl_3$) $\delta$ = 142.04 (d), 82.93 (d), 77.83 (s), and 28.03 (q) ppm. MS m/z : 180, 178 (64.4%, $M^+$); 165, 163 (29.7%, $M^+-CH_3$); 124, 122 (33.1%, $M^+-C_4H_8$); 107, 105 (12.3%); 99 (24.6, $M^+$-Br); 95, 93 (33.9%); 57 (100%); 41 (47.5%). Calc. for $C_6H_{11}OBr$: C, 40.25%; H, 6.19%; Br, 44.63%; Pound C, 39.99%; H, 6.44%; Br, 44.34%.

***tert*-Butoxyethyne (1a).-** Pure 5a (95.7 g, 0.53 mol) was added dropwise over 30 min to a stirred suspension of sodium amide in liquid ammonia at -33°C, prepared from sodium (27.60 g, 1.20 mol) and ammonia (1.2 L). After stirring for an additional 25 min period, the reaction mixture was poured into 1.3 Kg of crushed ice. The organic layer was separated, and the aqueous one was extracted with decahydronaphtalene (4x50 mL). The combined organic extracts were successively washed with $H_2O$ and pH=7 buffer solution of phosphates, and dried over $MgSO_4$. Pure *tert*-butoxyethyne (1a) (30.92-33.54 g, 0.32-0.34 mol, 59-64% yield) was obtained by distillation at room temperature and 0.5 torr, collecting at -78°C, and redistillation at room temperature and 22 torr, collecting at 0°C.

1a.- IR ($CCl_4$) $\nu_{max.}$ = 3170, 2990, 2930, 2860, 2210, 2140, 1395, 1370, 1270, 1250, 1170, 1115, 1095, and 840 $cm^{-1}$. $^1H$-NMR (60 MHz, $CDCl_3$) $\delta$ = 1.50 (s, 1H) and 1.40 (s, 9H) ppm. $^{13}C$-NMR (50.3 MHz, $CDCl_3$) $\delta$ = 87.72 (s), 86.08 (s), 29.18 (d), and 26.89 (q) ppm. MS m/z : 98 (0.25%, $M^+$), 83 (16.8%, $M^+-CH_3$), 70 (6.1%, $M^+$-CO), 57 (100%), 41 (58.7%). Calc. for $C_6H_{10}O$: C, 73.43%; H, 10.27%; Found: C, 73.53%; H, 10.66%.

**1-*tert*-Butoxy-1-hexyne (6)**.- A solution of 5a (2.15 g, 12 mmol) in THF (5mL) was added *via* syringe to a solution of lithium diisopropylamide prepared from butyl lithium 1.6 M (17.5 mL ca. 28 mmol) in THF (50 mL) and diisopropyl amide (5.0 mL, ca. 3.57 g, 35 mmol) at -60°C under $N_2$. The cooling bath was then removed and the reaction mixture was allowed to warm up to room temperature. After 2 h of stirring, a solution of 1-bromobutane (4.11 g, 30 mmol) in anhydrous hexamethylphosphoramide (20 mL) was added at 0°C and stirring was continued for 2 additional hours at room temperature. The reaction mixture was then poured into saturated $NH_4Cl$ solution (250 mL) and pethroleum ether (100 mL) was added. The organic layer was separated, the aqueous one extracted with petroleum ether (50 mL), and the combined organic extracts were successively washed with 0.5 N HCl (200mL), $H_2O$ (200 mL) and saturated $NaHCO_3$ solution (100 mL), and dried over $MgSO_4$. After solvent evaporation under reduced pressure, 1-*tert*-butoxy-1-hexyne (0.86-1.02 g, 5.60-6.62 mmol, 47-55% yield) was obtained by vacuum distillation at room temperature, collecting at -78°C. The compound may also be purified by flash chromatography through 2.5% silica gel-triethylamine and eluting with pethroleum ether.

6.- IR ($CCl_4$) $\nu_{max.}$ = 3000, 2975, 2925, 2880, 2280, 1470, 1400, 1380, 1280, 1240, 1170, 915, 900, 860, and 840 $cm^{-1}$. $^1H$-NMR (200 MHz, $CDCl_3$) $\delta$ = 2.20-2.10 (m, 2H), 1.55-1.05 (m, 4H), 1.36 (s, 9H), and 0.95-0.85 (m, 5H) ppm. $^{13}C$-NMR (50.3 MHz, $CDCl_3$) $\delta$ = 85.63 (q), 83.97 (q), 40.10 (q), 32.04 ($CH_2$), 26.94 ($CH_3$), 21.88 ($CH_2$), 17.14 ($CH_2$), and 13.59 ($CH_3$) ppm. MS m/z : 154 (0.3%, $M^+$), 139 (3.5%, $M^+-CH_3$), 98 (7.6%, $M^+-C_4H_8$), 83 (3.3%), 70 (10.7%), 69 (12.8%), 57 (100%), 55 (45.8%), 41 (72.5%).

**1-Adamantyloxy-1-ethoxy-2-bromoethane (3b)**.- Ethyl vinyl ether (9.01 g, 125 mmol) was brominated in EtOH-free $HCCl_3$ (50 mL) at -78°C under $N_2$ and a solution of 1-adamantanol (19.0 g, 125 mmol) in triethylamine (19 mL, ca. 13.9 g, 137 mmol) and EtOH-free $HCCl_3$ (250 mL) was then added dropwise at -78°C during 1 h with energic stirring. The cooling bath was removed and the mixture allowed to warm up to 0°C. After stirring for 2 additional hours at 0°, the reaction mixture was poured into $H_2O$ (100 mL), the organic phase was separated and the aqueous one extracted with $HCCl_3$ (2x50 mL). The combined organic extracts were successively washed with 0.5 N HCl, saturated $NaHCO_3$ solution, and dried over $MgSO_4$. Solvents were removed under vacuum and the residue was chromatographed through silica gel (200 g) eluting with a chloroform-hexane 1:1 mixture, to give, after removal under vacuum of some (*Z*)-1-bromo-2-ethoxyethene, pure 3b (22.2 g, 73.2 mmol) as a colourless liquid. Further elution allowed the isolation of unreacted 1-adamantanol (7.4 g, 48.7 mmol). The yield of 3b was 96% on the basis of the reacted 1-adamantanol.

3b.- IR ($CCl_4$) $\nu_{max.}$ = 2980, 2920, 2860, 1460, 1420, 1395, 1375, 1360, 1350, 1320, 1310, 1295, 1220, 1200, 1190, 1130, 1110, 1065, 1030, 940, 815, and 685 $cm^{-1}$. $^1H$-NMR (60 MHz, $CCl_4$) $\delta$ = 4.93 (t, J= 5.5 Hz, 1H), 3.72-3.17 (m, 4H), 2.15 (br. s, 3H), 1.79 (m, 6H), 1.66 (m, 6H), and 1.15 (t, J= 7.0 Hz, 3H). $^{13}C$-NMR (50.3 MHz, $CDCl_3$) $\delta$ = 94.54 (CH), 74.00 (q), 60.00 ($CH_2$), 42.60 ($CH_2$), 36.25 ($CH_2$), 33.59 ($CH_2$), 30.66 (CH), and 15.29 ($CH_3$). MS m/z: 259, 257 (0.26%, $M^+$-ETO); 209 (10%, $M^+-CH_2Br$); 180 (1.13%); 153, 151 (10%, $M^+$-AdO); 135 (100%); 125, 123 (14%); 95 (10%), 79 (8%). Calc. for $C_{14}H_{23}O_2Br$: C, 55.45%; H, 7.04%; Br, 26.35%; Found: C, 55.57%; H, 7.76%; Br, 26.29%.

**(*Z*)-1-(1-Adamantyloxy)-2-bromoethene (5b)**.- A solution of 3b (22.1 g, 72.8 mmol) in $CH_2Cl_2$ (100 mL) was added dropwise to an stirred suspension of phosphorus pentachloride (18.2 g, 87.4 mmol) in $CH_2Cl_2$ (100 mL) at 0°C under a dry $N_2$ atmosphere over 30 min, and the resulting mixture was stirred for an additional 90 min period, until all the starting material had been converted into 1-(1-adamantyloxy)-2-bromo-1-chloroethane (4b). Triethylamine (60.5 mL ca. 44.2 g, 437 mmol) was then added dropwise at 0°C, the cooling bath was removed and the reaction mixture heated under reflux for a 2.5 h period. The cold reaction mixture was poured into ice-cold water (250 mL), the organic layer was separated and the aqueous one extracted with $CH_2Cl_2$ (2x25 mL). The combined organic extracts were successively washed with 0.5 N HCl (50 mL) and saturated $NaHCO_3$ solution (50 mL), and dried over $MgSO_4$. After solvent evaporation under reduced pressure, the crude material was chromatographed through 2.5% silica gel-triethylamine (190 g) eluting with hexane, to afford pure 5b (17.4-17.8 g, 67.7-69.2 mmol, 93-95 % yield) as a white solid.

4b. IR ($CCl_4$) $\nu_{max.}$ = 2940, 2860, 1450, 1420, 1355, 1305, 1215, 1185, 1160, 1130, 1060, 1020, and 920 $cm^{-1}$. $^1H$-NMR (60 MHz, $CCl_4$) $\delta$ = 6.02 (t, J= 6.0 Hz, 1H), 3.68 (d, J= 6.0 Hz, 2H), 2.25 (br.s, 3H), 1.95 (m, 6H), and 1.68 (m, 6H) ppm.

5b. m.p. 52-3°C. IR ($CCl_4$) $\nu_{max.}$ = 2920, 2860, 1640, 1460, 1360, 1330, 1305, 1295, 1275, 1230, 1190, 1150, 1115, 1095, 1065, 1035, and 970 $cm^{-1}$. $^1H$-NMR (60 MHz, $CDCl_3$) $\delta$ = 6.91 (d, J = 4.2 Hz, 1H), 5.10 (d, J = 4.2 Hz, 1H), 2.20 (br.s, 3H), 1.86 (m, 6H), and 1.65 (m, 6H) ppm. $^{13}C$-NMR (50.3 MHz, $CDCl_3$) $\delta$ = 140.91 (CH), 82.78 (CH), 77.10 (q), 41.84 ($CH_2$), 36.00 ($CH_2$), and 30.65 (CH) ppm. MS m/z : 258, 256 (1.8%, $M^+$); 215, 213 (0.2% ); 152 (1.8%), 135 (100%), 107 (11.6%), 93 (25%), 79 (27%), and 67 (9.2). Calc. for $C_{12}H_{17}OBr$: C, 56.05%; H, 6.66%; Br, 31.07%; Found: C, 56.32%; H, 6.58%; Br, 30.93%.

**(1-Adamantyloxy)ethyne (1b).**

**a) By dehydrobromination of 5b with sodium amide in liquid ammonia.** A solution of 5b (17.7 g, 68.8 mmol) in anhydrous $Et_2O$ (30 mL) was added dropwise over 15 min to an stirred suspension of sodium amide in liquid ammonia, prepared from Na (6.90 g, 300 mmol) and ammonia (300 mL). After 2.5 h of stirring at -33°C, the reaction mixture was poured into crushed ice (200 g), the organic layer was separated and the aqueous one extracted with $Et_2O$ (3x75 mL). The combined organic extracts were successively washed with $H_2O$ and pH=7 buffer solution of phosphates, and dried over $MgSO_4$. After solvent removal at reduced pressure, the crude material was filtered through 2.5% silica gel-triethylamine (100 g), eluting with hexane, to give pure 1b (8.48-9.08 g, 48.1-51.6 mol, 70-75% yield) as a white solid.

**b) By dehydrobromination with LDA in THF-petroleum ether.** A solution of 5b (2.57 g, 10 mmol) in THF (10 mL) was added at -60°C to a solution of LDA in THF, prepared from 1.6 M n-butyl lithium (13.75 mL, 22 mmol), anhydrous petroleum ether (10 mL) and diisopropylamine (2.640 g, 26 mmol), and the mixture was stirred for 2 hours, allowing the bath to warm up to 15°C. The reaction mixture was then poured into 100 mL of saturated $NH_4Cl$ solution, the organic phase was separated and the aqueous one extracted with hexane (2x50 mL). The combined organic extracts were then successively washed with 0.5 N HCl, $H_2O$, and saturated solution of $NaHCO_3$, and finally dried over $MgSO_4$. After solvent evaporation under vacuum, the crude material was filtered through 2.5% silica gel-triethylamine (32 g) eluting with hexane, to afford pure 1b (1.283g, 7.3 mmol, 73% yield).

1b.- m.p. 49-51 °C (from $Et_2O$-pentane). IR ($CCl_4$) $\nu_{max.}$= 3320, 2910, 2850, 2190, 2130, 1450, 1365, 1195, 1040, 950, and 850 $cm^{-1}$. $^1H$-NMR (60 MHz, $CCl_4$) $\delta$ = 2.40-2.10 (m, 3H), 1.95 (m, 6H), 1.70 (m, 6H), and 1.32 (s, 1H) ppm. $^{13}C$-NMR (50.3 MHz, $CDCl_3$) $\delta$ = 86.90 (s), 84.49 (s), 40.72 (t), 35.79 (t), 21.14 (d), and 29.04 (d) ppm. M.S. m/z : 176 (0.4%, $M^+$), 148 (0.5%), 135 (100%), 119 (3.2%), 107 (16.5%), 93 (36.3%), 91 (25.3%), 79 (51.6%), 77 (29.7%), 67 (16.5%), 65 (11%), 55 (9.9%), 53 (11.0%), and 41 (30.8%). Calc. for $C_{12}H_{16}O$: C, 81.77%; H, 9.15; Found: C, 81.68%; H, 9.12%.

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