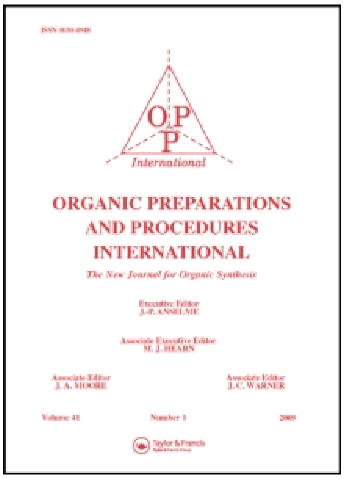

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FORMATION OF 1-CHLORO-1-ALKYNES FROM 1,1-DICHLORO-1-ALKENES UNDER PHASE-TRANSFER CONDITIONS WITHOUT SOLVENT[†]

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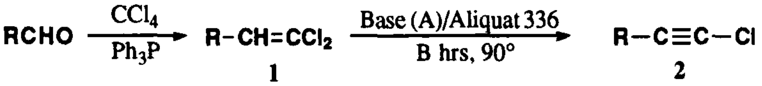
Several methods are known for the formation of 1-chloro-1-alkynes which are important intermediates in organic chemistry.[1-3] We now report a simple and effective procedure for the preparation of 1-chloro-1-alkynes from 1,1-dichloro-1-alkene (1)[4] using PTC conditions without solvent.[5]



$$\mathrm{RCHO} \xrightarrow[\mathrm{Ph_3P}]{\mathrm{CCl_4}} \underset{\mathbf{1}}{\mathrm{R{-}CH{=}CCl_2}} \xrightarrow[\text{B hrs, 90°}]{\text{Base (A)/Aliquat 336}} \underset{\mathbf{2}}{\mathrm{R{-}C{\equiv}C{-}Cl}}$$

TABLE 1. Elimination of Hydrogen Chloride from 1,1-Dichloro-1-alkenes

Entry[a]	Base	A (equiv.)	B (hrs)	Catalyst (mL/g of 1.)	Composition of Product (%)[b]		
					1	2	RC≡CH
1.	KOH	2	0.5	0.2	4	80	2
2.	KOH	2	0[c]	0.2	5	80	1
3.	KOH	1	0.5	0.2	21	60	1
4.	KOH	2	2.0	0.2	—	70	1
5.	KOH	1	2.0	0.2	4	80	—
6.	KOH	2	2.0	0.5	—	60	10
7.	KOH	4	24.0	0.2	—	60	30
8.	KOH	2	24.0	0.2	—	80	3
9.	NaOH	2	2.0	0.2	—	60	5
10.	$Ca(OH)_2$	2	2.0	0.2	40	40	1
11.	KOH	1	0.5	0.2	20	70	—
12.	KOH	2	0[c]	0.2	2	70	5
13.	KOH	2	2.0	0.2	2	70	4
14.	KOH	1	2.0	0.2	4	80	—

a) R = $CH_3(CH_2)_5$- and/or $CH_3(CH_2)_6$- for entries 1-10; and/or R = $CH_3(CH_2)_3$-; for entries 11-14.
b) Determined by GC analysis of isolated product. c) The products were distilled immediately after mixing.

This method is based on our earlier developed procedure for the synthesis of terminal alkynes from 1,2-dibromoalkanes.[6] The best results are obtained when the products (**2**) are distillable. Powdered potassium hydroxide is the most effective base for the elimination. Sodium and calcium hydroxide (formed *in situ* from water (1.0 equiv.) and CaO (1.0 equiv.)) gave similar results but lower yields (about 40%; See Table 1). If the temperature of reaction during the elimination is higher than 100°, the decomposition of PTC catalyst to tertiary amine was observed after 1 hr.

EXPERIMENTAL SECTION

^{1}H NMR (100 MHz) and ^{13}C NMR (25.2 MHz) spectra were determined on a Varian XL-100 instrument using deuterochloroform as solvent. All signals are expressed by the ppm (δ scale) down field from TMS used as an internal standard. GC analyses were made using a Perkin Elmer F22 instrument with FID detector. Carrier: N_2 (2 mL/min); Split: 1:100; Temp. of injector and detector: 240°; Column: SPB-1 (SUPELCO), 60 m x 0.25 mm i. d.; Temp. of column: 90° for 8 min then 8°/min to 240°.

General Procedure for the Preparation of 1.1-Dichloro-1-alkenes.- To the solution of triphenylphosphine (4.0 equiv.) in dichloromethane (1.5 mL/g PPh_3) was added the aldehyde ($CH_3(CH_2)_nCHO$; 1.0 equiv.) and carbon tetrachloride (2.0 equiv.). The resulting mixture was stirred for 2 hrs at 25°. The product was separated by SDC.[7] In large scale reactions, the product may be obtained by distillation, after evaporation of the reaction mixture, dilution by hexane (1.0 mL/g residue) and removal of the precipitate by filtration.

1,1-Dichloro-1-hexene (n = 3): 60% yield, colorless liquid [*Zh. Org. Khim.*, **17**, 2051 (1981)].

^{1}H NMR: δ 5.86 (t, J = 7Hz, 1H, -CH=); 2.14 (m, 2H, $-CH_2C=$); 1.30 (br.s, 4H, $-(CH_2)_2-$); 0.80 (t, J = 6Hz, 3H, $-CH_3$).

^{13}C NMR: δ 119.5 (C-1), 130.11 (C-2), 28.2 (C-3), 29.3 (C-4), 32.7 (C-5), 14.1 (C-6).

1,1-Dichloro-1-octene (n = 5): 70% yield, colorless liquid [*Tetrahedron Lett.*, **26**, 2575 (1985)].

^{1}H NMR: δ 5.87 (t, J = 7Hz, 1H, -CH=); 2.10 (m, 2H, $-CH_2C=$); 1.30 (br.s, 8H, $-(CH_2)_4-$); 0.85 (t, J = 6Hz, 3H, $-CH_3$).

^{13}C NMR: δ 119.65 (C-1), 130.10 (C-2), 28.2 (C-3), 29.2, 29.5 (C-4,5), 31.9 (C-6), 27.7 (C-7), 14.0 (C-8).

1,1-Dichloro-1-nonene (n = 6): 65% yield, colorless liquid [*Tetrahedron Lett.*, **24**, 527 (1983)].

^{1}H NMR: δ 5.89 (t, J = 7Hz, 1H, -CH=); 2.12 (m, 2H, $-CH_2C=$); 1.31 (br.s, 10H, $-(CH_2)5-$); 0.80 (t, J = 6Hz, 3H, $-CH_3$).

^{13}C NMR: δ 119.86 (C-1), 130.08 (C-2), 28.2 (C-3), 29.11,29.27, 29.67 (C-4,5,6), 31.88 (C-7), 22.71 (C-8), 14.09 (C-9)

General Method for the Preparation of Distillable 1-Chloro-1-alkynes.- A mixture of 1,1-dichloro-1-alkene (**1**; 1.0 equiv.), powdered KOH (1.0 equiv.) and Aliquat 336 (Aldrich; 0.2 mL/g **1**) was stirred at 90° for 2 hrs. The product was distilled directly from the reaction mixture.

1-Chloro-1-hexyne (n = 3): 80% yield; bp.[8] 115-117°/760 torr, lit.[8] bp. 115-116°/760 torr.

^{1}H NMR: δ 2.15 (m, 2H, $-CH_2C\equiv$), 1.2-1.6 (br.s, 4H, $-(CH_2)_2-$), 0.9 (t, J = 7Hz, 3H, $-CH_3$).

^{13}C NMR: δ 56.93 (C-1), 69.73 (C-2), 18.46 (C-3), 30.47 (C-4), 21.91 (C-5), 13.56 (C-6).

Table 2. GC Data of Compounds [$CH_3(CH_2)_n$-Z]

	Retention Time of Compounds (min)		
Z	n = 3	5	6
CHO	6	11	13
$CH=CCl_2$	13	18	21
C≡CH	4	8	10
C≡CCl	7	14	16

1-Chloro-1-octyne (n = 5): 70% yield; bp. 70°/20 torr, lit.[1] bp. 61-62°/17 torr.

^1H NMR: δ 2.14 (m, 2H, $-CH_2C\equiv$), 1.2-1.6 (br, s, 8H, $-(CH_2)_4-$), 0.9 (t, J = 7Hz, 3H, $-CH_3$).

^{13}C NMR: δ 56.89 (C-1), 69.68 (C-2), 18.51(C-3), 28.80 (C-4), 28.9,28.4 (C-5,6), 22.5 (C-7), 14.10 (C-8).

1-Chloro-1-nonyne (n = 6): 80% yield; bp.: 82°/20 torr, lit.[9] bp. 75-80°/17.5 torr.

^1H NMR: δ 2.18 (t, J = 4Hz, 2H, $-CH_2C\equiv$), 1.2-1.55 (br, s, 10H, $-(CH_2)_5-$), 0.85 (t, J = 7Hz, 3H, $-CH_3$).

^{13}C NMR: δ 56.91 (C-1), 69.8 (C-2), 18.75 (C-3), 28.7 (C-4), 28.9 (C-5), 28.38 (C-6), 31.7 (C-7), 22.6 (C-8),14.08 (C-9).

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SYNTHESIS OF TWO METHYLBENZOSUBERONES AND A DIMETHYLBENZOCYCLOHEPTENE

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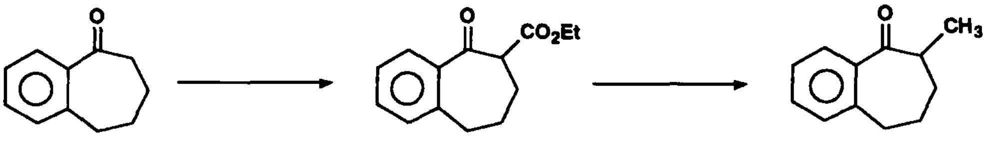
In connection with the exploration of routes to benzazaazulenes,[1] two methylbenzosuberones, **3** (6-methyl-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-one) and **7** (5-methyl-5,7,8,9-tetrahydro-6*H*-benzocyclohepten-6-one) were required. A by-product of the preparation of **7** was 5,6-dimethyl-8,9-dihydro-7*H*-benzocycloheptene (**8**).

Benzosuberone (6,7,8,9-tetrahydro-5*H*-benzocycloheptene-5-one) (**1**) was prepared and converted to **2** as previously described.[2] Treatment of **2** sequentially with NaH, MeI, and methanolic $Ba(OH)_2 \cdot 8H_2O$ gave **3** in 59% yield from **1** and 53% yield from phenylpentanoic acid. A synthesis of **3** in 37% yield from phenylpropanol has been reported.[3]



1 **2** **3**