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CONVENIENT SYNTHESES OF DICHLOROETHENYLIDENECYCLOPROPANES: PRECURSORS TO DIFUNCTIONAL CYCLOPROPANE DERIVATIVES[**]

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Abstract: Dichloroethenylidenecyclopropanes **4** *are obtained in good yields from olefins and tetrachloropropenes* **1** *and* **3** *or, more conveniently pentachloropropane* **7**. *The highly reactive allenes* **4** *readily add nucleophiles (such as methoxide) as well as electrophiles.*

Cheletropic addition of alkenylidenecarbenes to olefins provides a ready access to alkylsubstituted ethenylidenecyclopropanes[1], highly strained and vastly reactive allenes, which undergo a number of facile cycloadditions[2] and other transformations[3] of synthetic utility. Ethenylidenecyclopropanes with polar substituents should exhibit even greater and more specific reactivity towards nucleophilic or electrophilic reagents and thereby could more favorably serve as versatile intermediates. We here report on a convenient general entry into (dichloroethenylidene)cyclopropanes **4**.

1,1,3,3-Tetrachloropropene (**1**) [4] undergoes α-elimination with proton specific bases in ether yielding chloro-(dichlorovinyl)carbene adducts with olefins[5]. On changing the base to potassium t-butoxide and the solvent to the unpolar pentane, (dichloroethenylidenecyclopropanes **4** were formed in moderate to good yields (see table 1). This reaction most probably proceeds through 1,3,3-trichloropropyne (**2**) rather than the extremely unstable trichloroallene[6].

Since 1,2,3,3-tetrachloropropene (**3**), which is more readily available than **1** from trichloroethylene and chloroform in 2 steps[7], can also lead to **2** by β-elimination, it was treated with potassium t-butoxide/pentane in the presence of olefins **5**, too. Indeed products **4** were obtained in slightly lower yields (see table 1).

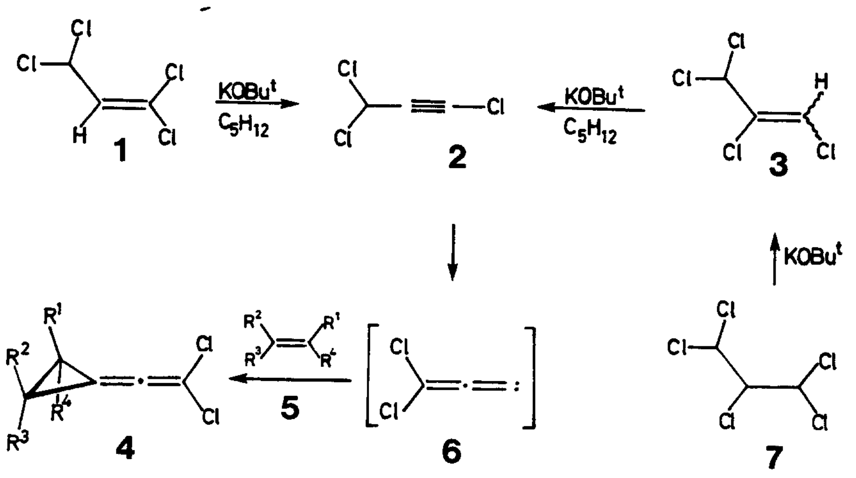


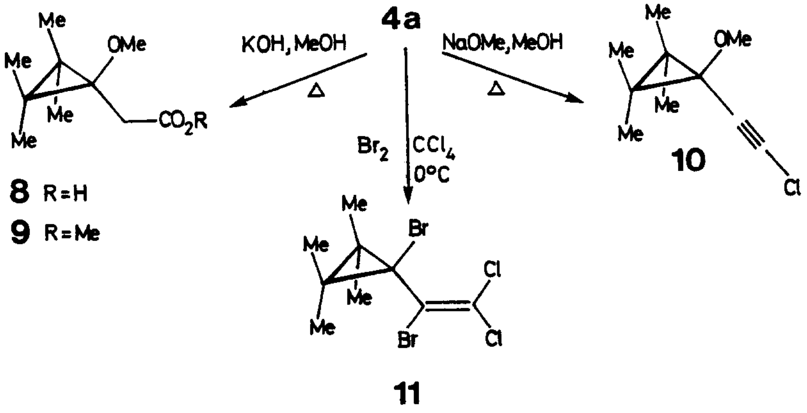
Table 1. (Dichloroethenylidene)cyclopropanes **4**[8] from olefins **5** and tetrachloropropenes **1** and **3**. Reaction conditions (molar excess of olefin) and isolated yields in %.

	Substituents	Precursor **1** **5**,Excess	 **4**,Yield	Precursor **3** **5**,Excess	 **4**,Yield
a)	R^1,R^2,R^3,R^4=Me	8	55	7	48a)
b)	R^1,R^2,R^3,R^4=Me	0.8	22	1	25a)
c)	R^1,R^2,R^3=Me, R^4=H	8	48	5	36
d)	R^1,R^2=-$(CH_2)_4$-, R^3,R^4=H	8	52	7	26
e)	R^1=n-Bu, R^2,R^3,R^4=H	8	40	7	20
f)	R^1,R^4=Me, R^2=H, R^3=CH_2OTMS	8	35	6	28
g)	R^1=OEt, R^2,R^3,R^4=H	8	0	6	0
h)	R^1,R^2=-$(CH_2)_4$-, R^3,R^4=-$(CH_2)_4$-	8	-	5	23b)

a) Isolated by sublimation. b) Isolated by Kugelrohr distillation.

Ultimately, it was obvious to try 1,1,2,3,3-pentachloropropane (**7**) directly, because it is the regular precursor to **3**[7]. In the presence of 2,3-dimethyl-2-butene (**5a**), **7** with 3.5 equivalents of potassium *t*-butoxide thus gave a 50% yield (42% after sublimation) of **4a**. Taking into account the ready access to **7**[7] and the observation that reaction mixtures from **7** can be worked-up without filtration through celite (see procedure), this alternative is by far the most convenient one for the preparation of **4**.

Compounds **4** appear to be versatile precursors to a number of highly substituted cyclopropane derivatives. E.g. reaction of **4a** with potassium hydroxide in methanol gave (1-methoxy-2,2,3,3-tetramethylcyclopropyl)acetic acid (**8**)[9] (42% isolated yield of **9** after esterification with diazomethane). The acetylene **10** is obtained (25% isolated) with sodium methoxide in methanol; bromine is added cleanly at 0°C to yield **11** (80%).



<u>General procedure for allenes **4**:</u> To a stirred suspension of 4.0 g (35 mmol) freshly sublimed t-BuOK in 50 - 60 mmol olefin **5** (e.g. 5.0 g ≙ 60 mmol **5a**) and 40 ml dry pentane, kept under nitrogen and cooled to -20°C, a solution of 2.1 g (9.7 mmol) 1,1,2,3,3-pentachloropropane (**7**) is added dropwise within 1 h. After an additional 30 min at -20°C and 30 min at room temperature, the mixture is diluted with 100 ml diethylether and hydrolyzed with 50 ml 0.5 M HCl. The organic layer is washed with 50 ml H_2O, 50 ml conc. $NaHCO_3$ solution and 2 x 50 ml H_2O and then dried over Na_2SO_4. The solvent is evaporated, the dark residue is taken up in a minimum of CH_2Cl_2 and filtered through 15 g Al_2O_3 (neutral, activity V) eluting the product with 200 ml n-pentane. Crude products can be purified by short path distillation, "Kugelrohr" distillation or sublimation. Yield of **4a**: 0.93 g (50%) crude, 0.78 g (42%) after sublimation.

References and footnotes

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[8] Products **4** were isolated by aqueous work-up, filtration through celite and short-path distillation or gaschromatography; because of their sensitivity, both thermal and towards traces of acid, gaschromatographic separation was accompanied by substantial losses. Actual crude yields are much higher. All new compounds were fully characterized by MS, ^{1}H-, ^{13}C NMR (in part) and elemental analysis (in part). E.g. **4a**, ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.23(s, 12H). - ^{13}C NMR (67.91 MHz, $CDCl_3$): δ = 20.9(C-4(5,6,7)), 31.5(C-2(3)), 98.5(C-1), 113.0(C-2'), 181.1(C-1'). - **4e**, ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.89(t, 3H, ^{3}J = 7.0), 1.21 - 1.64(m, 7H), 1.85(dd, 1H, ^{3}J = 8.5, ^{3}J = 9.0), 2.00(m, 1H).

[9] A small sample of **8** was purified by a twofold sublimation at 100°C/ 0.1 torr and had m.p. 103°C. ^{1}H NMR of **9** (270 MHz, $CDCl_3$): δ = 0.98 (s, 6H), 1.05(s, 6H), 2.67(s, 2H), 3.27(s, 3H), 3.67(s, 3H).

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