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INTERMOLECULAR REACTIONS OF NEW HALOVINYLCARBENES - VERSATILE SYNTHESIS OF (HALOVINYL)CYCLOPROPANES

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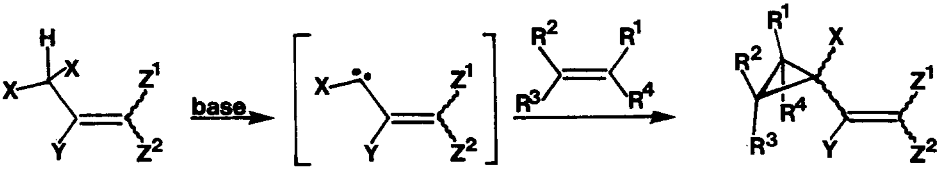
Abstract: Deprotonation of the oligohalopropenes ***1A**, **1B**, **1C** with LiTMP. or LiHMDS. in the presence of olefins **3** led to halovinylcyclopropanes **4A**, **4B**, **4C** by intermolecular trapping of the corresponding halovinylcarbenes. Mixtures **4B**/**4C** and (dichloroethenylidene)cyclopropanes **5** can be obtained from 1,1,2,3,3-pentachloropropane (**6**), LiHMDS. and olefins **3**.*

1-Chloro-1-(trichlorovinyl)cyclopropanes, readily accessible by the addition of thermally ring-opened tetrachlorocyclopropene to olefins[1], have turned out to be versatile precursors to a number of di- and trifunctional cyclopropyl derivatives[2,3], which are highly useful as building blocks in organic synthesis[4]. We have therefore developed alternative routes to similar vinylcyclopropanes which might fit into the same methodological scheme.

Since chloro-vinylcarbene, generated from 3,3-dichloropropene can intermolecularly be trapped[5], it was straightforward to try α-eliminations from other 3,3-dihalopropenes **1**. However, 1,1,2,3,3-pentachloropropene **1** (X,Y,Z = Cl)[6], when treated with proton specific bases such as lithium diisopropylamide (LDA), lithium tetramethylpiperidide (LiTMP) and lithium bis(trimethylsilyl)amide (LiHMDS) in diethylether in the presence of olefins, gave no products of type **4** from addition of an intermediate perchlorovinylcarbene or -carbenoid **2** (X,Y,Z = Cl), but rather perchloroallene through β-elimination.

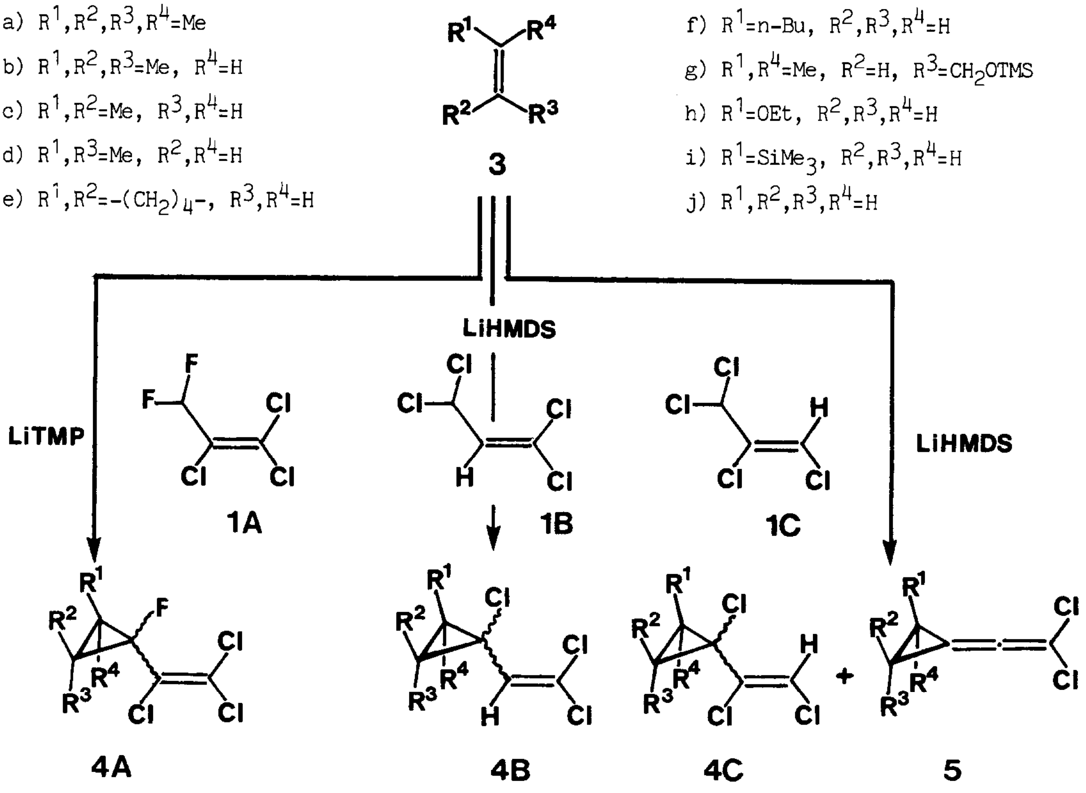


1 **2** **3** **4**

Surprisingly, α-elimination predominated in 1,1,2-trichloro-3,3-difluoropropene (**1A**) giving poor yields of 1-fluoro-1-(trichlorovinyl)cyclopropanes **4A** (see Scheme 1 and Table 1). Apparently lithium fluoride is more readily eliminated than lithium chloride, so that β-elimination is suppressed in **1A**.

Scheme 1.

a) R^1,R^2,R^3,R^4=Me
b) R^1,R^2,R^3=Me, R^4=H
c) R^1,R^2=Me, R^3,R^4=H
d) R^1,R^3=Me, R^2,R^4=H
e) R^1,R^2=-$(CH_2)_4$-, R^3,R^4=H
f) R^1=n-Bu, R^2,R^3,R^4=H
g) R^1,R^4=Me, R^2=H, R^3=CH_2OTMS
h) R^1=OEt, R^2,R^3,R^4=H
i) R^1=$SiMe_3$, R^2,R^3,R^4=H
j) R^1,R^2,R^3,R^4=H



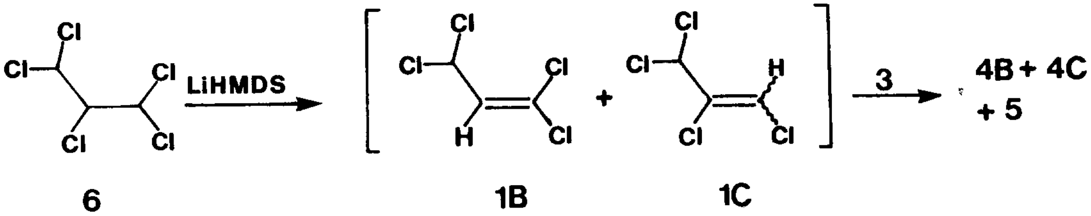
Obviously this could also be avoided in 1,1,3,3-tetrachloropropene (**1B**)[7] which does not contain a 2-chloro substituent. Moderate to good yields of 1-chloro-1-(2',2'-dichlorovinyl)cyclopropanes **4B** were thus obtained with LiHMDS in ether (Scheme 1, Table 1). On the other hand, 1,2,3,3-tetrachloropropene (**1C**) with tetramethylethylene also gave product **4Ca** (up to 20% yield) from intermolecular trapping of the corresponding 1-chloro-1-(1',2'-dichlorovinyl)carbene along with tetramethyl(dichloroethenylidene)cyclopropane (**5a**) (up to 8% yield)[8].

Table 1. Halovinylcyclopropanes **4A**, **4B**[10] from olefins **3** and oligohalopropenes **1A**, **1B**. Reaction conditions (moles excess of olefin) and isolated yields in %.

Substituents	Precursor **1A** Excess **3**	Product **4A** yield	Precursor **1B** Excess **3**	Product **4B** yield
R^1,R^2,R^3,R^4=Me	7	20 a)	8	49 c)
R^1,R^2,R^3=Me, R^4=H	5	6 (Z/E=5/2)	-	- b)
R^1,R^2=Me, R^3,R^4=H	4	9 (Z/E=2/1)	-	-
R^1,R^3=Me, R^2,R^4=H	4	13	-	-
R^1,R^2=-$(CH_2)_4$-, R^3,R^4=H	7	10	8	36
R^1=n-Bu, R^2,R^3,R^4=H	- b)	- b)	8	17
R^1,R^4=Me, R^2=H, R^3=CH_2OTMS	6	2 (E)	8	39
R^1=OEt, R^2,R^3,R^4=H	6	7 (E)		55
R^1=$SiMe_3$, R^2,R^3,R^4=H	-	-	8	31
R^1,R^2,R^3,R^4=H	-	-	8	12

a) Isolated by sublimation. b) Not tested. c) NaHMDS used; 7% **5a** isolated as byproduct.

Whereas **1B** has to be made from β,β-dichloroacroleine, **1C** is more readily prepared from 1,1,2,3,3-pentachloropropane (**6**) by dehydrochlorination with potassium hydroxide[9]. Therefore **6** was subjected to LiHMDS/ether as **1C** in the presence of tetramethylethylene (**3a**). Indeed, sequential β- and α-eliminations did occur, but led to both types of halovinylcyclopropanes



4Ba and **4Ca** and the allene **5a** in a ratio 4:3:3.

Since halovinylcyclopropanes **4B** as well as **4C** can be treated with n-butyllithium to yield cyclopropylalkynes, these new procedures appear to be the most convenient alternative for the preparation of precursors to these versatile cyclopropyl building blocks[2].

References and footnotes

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[6] **1** (X,Y,Z = Cl) was a byproduct arising from addition of HCl to perchlorovinylcarbene in the thermal reactions of tetrachlorocyclopropene[1]. It can more readily be obtained from chloroform and trichloroethylene in 4 steps. Cf. A. Roedig, E. Degener, Chem. Ber. **86**, 1469 (1953).

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[10] Products were isolated by filtration through silica gel and distillation or gaschromatography. All new compounds were fully characterized by MS, ^{1}H NMR, ^{13}C NMR (in part) and elemental analysis (in part). E.g. **4Ad**, ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$): 1.04 - 1.13(m, 1H), 1.09(dd, 3H, $^{3}J_{H,H}$ = 5.8, $^{4}J_{H,F}$ = 1.9 Hz), 1.16 - 1.33(m, 1H), 1.25(dd, 3H, $^{3}J_{H,H}$ = 5.9, $^{4}J_{H,F}$ = 1.1 Hz). (E)-**4Bh**, ^{1}H-NMR (270 MHz, $\mathrm{CDCl_3}$): 1.22(t, 3H, ^{3}J = 7.1 Hz), 1.30 (m, 1H, $^{2}J_{AB}$ = 7.8, $^{3}J_{AX,\underline{trans}}$ = 4.5 Hz), 1.51(m, 1H, $^{2}J_{AB}$ = 7.8, $^{3}J_{BX,\underline{cis}}$ = 7.5 Hz), 3.56(m, 1H, $^{3}J_{AX,\underline{trans}}$ = 4.5, $^{3}J_{BX,\underline{cis}}$ = 7.5 Hz), 3.63(q, 2H, ^{3}J = 7.1 Hz), 6.17(s, 1H). (Z)-**4Bh**, ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$): 1.27(t, 3H, ^{3}J = 7.2 Hz), 1.36(m, 1H, $^{2}J_{AB}$ = 8.0, $^{3}J_{BX,\underline{cis}}$ = 8.9 Hz), 3.33(m, 1H, $^{3}J_{AX,\underline{trans}}$ = 4.9, $^{3}J_{BX,\underline{cis}}$ = 8.9 Hz), 3.57(dq, 1H, ^{3}J = 7.2, ^{2}J = 9.0 Hz), 3.94(dq, 1H, ^{3}J = 7.2, ^{2}J = 9.0 Hz), 6.12(s, 1H).

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