A new general method for the generation of (alk-1-ynyl)halocarbenes by base solvolysis of 3-substituted 1,1,1,3-tetrahalopropanes

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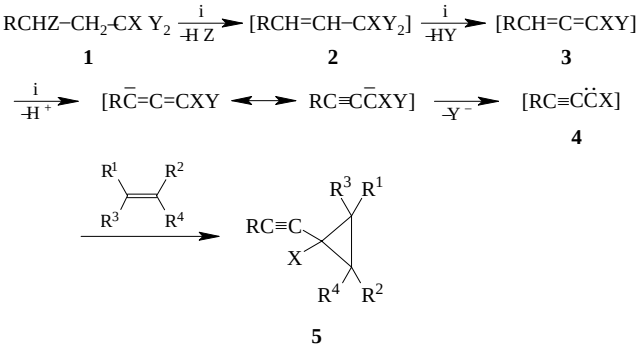
The (alk-1-ynyl)halocarbenes **4** have been generated from 3-substituted 1,1,1,3-tetrahalopropanes **1** *via* elimination of three molecules of hydrogen halide by treatment with Bu^{t}OK or with alkali metal hydroxides under phase-transfer catalysis conditions and have been trapped by alkenes to form 1-(alk-1-ynyl)-1-halocyclopropanes **5** in 40–70% yields.

Previously (alk-1-ynyl)halocarbenes **4** have been generated by base solvolysis of the corresponding 1,1-dihaloalk-2-ynes[1] or by photolysis of 3,3-dimethyl-5-(bromoethynyl)-3*H*-pyrazole.[2] These carbenes readily add to the double bond of olefins with formation of 1-(alk-1-ynyl)-1-halocyclopropanes **5**.

We have found that upon interaction with Bu^{t}OK or with alkali metal hydroxides under phase-transfer catalysis conditions, 3-substituted 1,1,1,3-tetrahalopropanes eliminated three molecules of hydrogen halides to give carbenes **4**, which were trapped by excess alkene, resulting in the formation of 1-(alk-1-ynyl)-1-halocyclopropanes[†] **5** in up to 70% yield (Scheme 1).

The following experimental results point to the fact that the generation of carbenes **4** proceeds *via* the reaction pathway presented in Scheme 1.

(*a*) Upon interaction of Bu^{t}OK with a 1.5–2.5-fold molar excess of 3,3-dichloro-1-phenylpropyne **6** in hexane at 20 °C for 0.5–1.5 h, a mixture of starting dichloride **6** (55–80 %) and 1,1-dichloro-3-phenylpropadiene **3a** (45–20%) was formed in a ratio depending on the reaction time and amount of Bu^{t}OK added. On treatment of these mixtures with excess Bu^{t}OK in the presence of tetramethylethylene, 1-chloro-2,2,3,3-tetramethyl-1-(phenylethynyl)cyclopropane **5a** was formed in 55% yield based on both dichlorides. The latter is equal to the yield of cyclopropane **5a** from uncombined dichloride **6** and is unaffected by the content of halides **6** and **3a** in the mixture. Therefore, the formation of cyclopropane **5a** arises from acetylene **6** as well as from allene **3a**, *i.e.* both of these dihalides are precursors of chloro(phenylethynyl)carbene **4a** (Scheme 2).



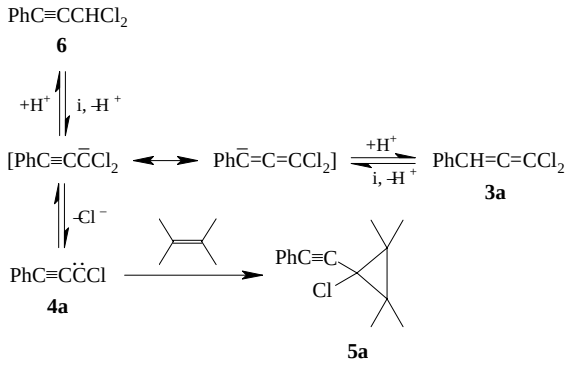
1a R = Ph, X = Y = Cl, Z = Br
1b R = Ph, X = Y = Z = Br
1c R = Bu, X = Y = Cl, Z = Br
1d R = Ph, X = F, Y = Z = Br
1e R = Bu, X = Y = Z = Cl

4a R = Ph, X = Cl
4b R = Ph, X = Br
4c R = Bu, X = Cl
4d R = Ph, X = F

5a R = Ph, R^1 = R^2 = R^3 = R^4 = Me, X = Cl
5b R = Ph, R^1 = R^2 = R^3 = Me, R^4 = H, X = Cl
5c R = Ph, R^1 = R^3 = Me, R^2 = R^4 = H, X = Br
5d R = Bu, R^1 = Ph, R^2 = R^3 = R^4 = H, X = Cl
5e R = Ph, R^1 = R^2 = R^3 = R^4 = Me, X = F
5f R = Bu, R^1 = R^2 = R^3 = R^4 = Me, X = Cl

Scheme 1 *Reagents and conditions*: i, Bu^{t}OK, hexane, 20 °C or KOH/BTEAC, CH_2Cl_2, 20 °C.

(*b*) The carbene species obtained from 3-bromo-1,1,1-trichloro-3-phenylpropane **1a** and from dihalide **6** exhibit the same selectivity toward pairs of competing olefins (each *ca.* 10-fold excess) from a standard set of alkenes (2,3-dimethylbut-2-ene, 2-methylbut-2-ene, *cis*-but-2-ene and



Scheme 2 *Reagents and conditions*: i, Bu^{t}OK, hexane, 20 °C.

[†] All new compounds (**5a**–**b**, **5d**–**e**) gave the expected NMR and mass spectra and satisfactory elemental analyses. ^{1}H and ^{13}C NMR spectra of cyclopropanes **5c** are identical to those described in the literature.[1]

For **5a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.28 (s, 6H, 2Me), 1.31 (s, 6H, 2Me), 7.3–7.5 (m, 5H, Ph); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 18.8 (2Me), 19.7 (2Me), 30.2 (2*C*Me$_2$), 49.7 (CCl), 85.2 and 88.0 (C≡C), 123.0 (C-1 in Ph), 128.25, 128.29, 131.8 (Ph); *m*/*z*: 232, 234 (M$^+$).

For **5b** [*cis* (H,Cl)/*trans* (H,Cl) = 1.4]: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.15–1.5 (m, 10H, 3Me and CH), 7.3–7.55 (m, 5H, Ph); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ *cis* (H,Cl)-**5b**: 10.0 (CH), 17.3, 24.0, 32.1 (3Me), 28.9 (*C*Me$_2$), 45.3 (CCl), 82.8, 86.0 (C≡C), 122.8 (C-1 in Ph); *trans* (H,Cl)-**5b**: 9.4 (CH), 16.3, 25.0, 34.4 (3Me), 27.7 (*C*Me$_2$), 45.2 (CCl), 86.6, 89.9 (C≡C), 122.9 (C-1 in Ph), 128.2, 128.3, 131.7, 131.8 (Ph in both isomers); *m*/*z*: 218, 220 (M$^+$).

For **5d** [*trans* (Ph,Cl)/*cis* (Ph,Cl) = 3.5]: ^{1}H NMR (200 MHz, $CDCl_3$) δ: *trans* (Ph,Cl)-**5d**: 0.81 (t, 3H, *J* 7.5 Hz, CH_3), 1.08–2.0 (m, 6H, 2CH_2 in Bu^n and CH_2 in cyclo-C_3H_3), 2.1 (t, 2H, *J* 8.5 Hz, CH_2C≡), 2.8 (dd, 1H, *J* 10 Hz, *J* 8 Hz, CH in cyclo-C_3H_3), 7.3–7.5 (m, 5H, Ph); *cis* (Ph,Cl)-**5d**: 0.98 (t, 3H, *J* 7.5 Hz, CH_3), 1.08–2.0 (m, 6H, 2CH_2 in Bu^n and CH_2 in cyclo-C_3H_3), 2.29 (t, 2H, *J* 8.5 Hz, CH_2C≡), 2.73 (dd, 1H, *J* 11 Hz, *J* 11 Hz, CH in cyclo-C_3H_3), 7.3–7.5 (m, 5H, Ph); *m*/*z*: 232, 234 (M$^+$).

For **5e**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.21 and 1.22 (2s, 12H, 4Me), 7.3–7.5 (m, 5H, Ph); ^{19}F NMR (188 MHz, $CDCl_3$) δ (CCl_3F): –191.9 (s); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 15.5 (d, 2Me, *J* 8.6 Hz), 19.0 (2Me), 27.7 (d, 2*C*Me$_2$, *J* 11.5 Hz), 80.3 (d, CF, *J* 215 Hz), 83.5 (d, ≡*C*CF, *J* 32.5 Hz); 89.8 (d, Ph*C*≡, *J* 10.2 Hz), 122.6 (d, C-1 in Ph, *J* 3 Hz); 128.2, 128.4, 131.6 (Ph); *m*/*z*: 216 (M$^+$).

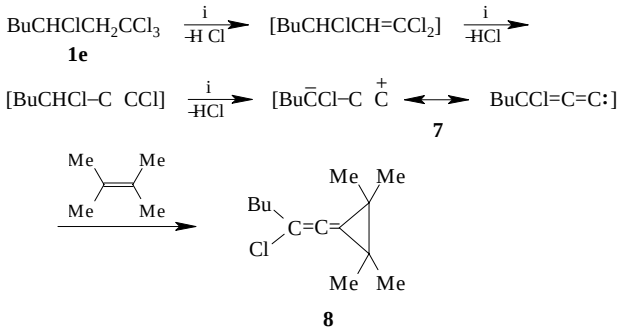
For **5f**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.91 (t, 3H, *J* 7 Hz, CH_3 in Bu); 1.18 (s, 12H, 4Me), 1.2–1.55 (m, 4H, 2CH_2), 2.27 (t, 2H, *J* 7 Hz, CH_2C≡); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 13.7 (Me in Bu), 18.7 (CH_2), 18.8 (2CH_3), 19.7 (2CH_3), 22.0 (CH_2), 29.9 and 31.0 (*C*H$_2$C≡ and 2C in cyclo-C_3), 50.3 (CCl), 78.4 and 86.1 (C≡C); *m*/*z*: 212, 214 (M$^+$).

2-methylpropene as reference). This result points to the fact that carbenes generated from halides **3a** and **6** are identical in nature.

(*c*) In the reaction of halide **1a** with triethylamine 3,3,3-trichloro-1-phenylpropene **2a** is obtained.[3]

$$\underset{\textbf{1a}}{PhCHBrCH_2CCl_3} \xrightarrow{Et_3N} \underset{\textbf{2a}}{PhCH{=}CHCCl_3}$$

It should be noted that the treatment of 1,1,1,3-tetrachloroheptane **1e** with Bu^{t}OK in the presence of tetramethylethylene resulted in a mixture of 1-chloro-1-(hexyn-1-yl)-2,2,3,3-tetramethylcyclopropane **5f** and 1-(butylchlorovinylidene)-2,2,3,3-tetramethylcyclopropane‡ **8** in 50% total yield (ratio **5f**:**8** = 4:1). The fact that cyclopropane **8** is obtained as a by-product which can be detected suggests that butylchlorovinylidenecarbene **7** along with carbene **4c** is generated from tetrachloride **1e.** The formation of carbene **7** may be represented by Scheme 3.



Scheme 3 *Reagents and conditions*: i, Bu^{t}OK, hexane, 20 °C.

In conclusion, some new general means of access to (alk-1-ynyl)halocarbenes **4**, including previously unknown (alk-1-ynyl)fluorocarbenes, are proposed.

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‡ *Spectral data* for **8**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.89 (t, 3H, *J* 7 Hz, CH_3 in Bu), 1.26 (s, 6H, 2Me), 1.29 (s, 6H, 2Me), 1.2–1.55 (m, 4H, $2CH_2$), 2.36 (t, 2H, *J* 7 Hz, CH_2C); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 13.9 (CH_3 in Bu), 21.0, 21.1, 21.8, 29.3, 29.5, 36.9 ($2CMe_2$ in cyclo-C_3, $2CH_3$, $2CH_3$, CH_2–CH_2–CH_2 in Bu), 107.3 and 107.6 (=C in cyclo-C_3 and =CCl), 180.8 (=C=); IR, ν_{max}/cm^{-1}: 2006 (C=C=C); *m*/*z*: 212, 214 (M^+).