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A new, general route to 1-chloro-1-ethynylcyclopropanes *via* chloro(trimethylsilylethynyl)carbene

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A new, general route to 1-chloro-1-ethynylcyclopropanes 6 has been developed *via* cycloaddition of previously unknown chloro(trimethylsilylethynyl)carbene 4b to olefins with formation of the corresponding cyclopropanes 5a–f in 35–65% yield and subsequent removal of the trimethylsilyl group under the action of KF·2H$_2$O in aqueous DMF to give cyclopropanes 6 in up to 80% yield.

We have previously developed a new method for the preparation of 1-chloro-1-alkynylcyclopropanes by cycloaddition of (alk-1-ynyl)halocarbenes **4** [$RC{\equiv}C(X)\ddot{C}$, R = Alk, cyclo-Alk, Ph; X = Cl, Br] to the double bond of olefins.[1] Our attempts to obtain 1-chloro-1-ethynylcyclopropanes **6** *via* cyclopropanation of olefins with chloro(ethynyl)carbene **4a** (R = H, X = Cl), generated from dichloromethylacetylene **3a** ($HC{\equiv}CCHCl_2$) by the action of bases, have not been successful. Under the basic solvolysis conditions employed, dichloride **3a** undergoes γ-elimination of hydrogen chloride to give chlorovinylidenecarbene, which in the presence of alkene results in chlorovinylidenecyclopropanes.[2] In connection with this problem we attempted to prepare cyclopropanes **6** using a so-called ‘silyl protection’ of the terminal triple bond in **3a**. In particular, we have previously successfully used silyl protection to synthesise 1-*H*- and 1,2-*H*-cyclopropene-3-carboxylic or 1-*H*- and 1,2-*H*-cyclopropene-3,3-dicarboxylic acids as well as their esters.[3]

Starting 3,3-dichloro-1-trimethylsilylpropyne **3b**[†] was obtained by oxidation of 3-trimethylsilylprop-2-yn-1-ol **1** with the complex $CrO_3{\cdot}Py{\cdot}HCl$[4] and subsequent chlorination of intermediate aldehyde **2**, used directly without isolation, with PCl_5.

$$\underset{\mathbf{1}}{Me_3SiC{\equiv}CCH_2OH} \xrightarrow{i} \underset{\mathbf{2}}{Me_3SiC{\equiv}CCHO} \xrightarrow{ii} \underset{\mathbf{3b}}{Me_3SiC{\equiv}CCHCl_2}$$

Scheme 1 *Reagents and conditions*: i, CrO_3–Py–HCl, CH_2Cl_2, room temperature, 2 h; ii, PCl_5, pyridine (cat.), CH_2Cl_2, 0 °C, 30 min.

After interaction with freshly prepared and sublimed Bu^tOK in hexane at –10 °C, the dichloride **3b** α-eliminated hydrogen chloride to form chloro(trimethylsilylethynyl)carbene **4b** (R = $SiMe_3$, X = Cl), a new (alk-1-ynyl)halocarbene possessing a reactive substituent at the triple bond. In the presence of alkenes this carbene readily added to the double bond giving (35–65% yield) 1-chloro-1-(trimethylsilylethynyl)cyclopropanes **5a–f**,[‡] promising synthons in organic synthesis.[5,6] As expected, the *endo*(Cl)- and *exo*(Cl)-isomers of cyclopropane **5c** as well as the *cis*- and *trans*-isomers of cyclopropanes **5d–f** were obtained in the reactions with cyclohexene, trimethylethylene, vinyl ethyl ether and styrene, respectively.

Removal of the trimethylsilyl group from the cyclopropanes **5a–f** by treatment with KF·2H$_2$O in DMF at room temperature yielded unsubstituted 1-chloro-1-ethynylcyclopropanes **6a–f**[§] in 70–80% yield. ^{1}H NMR, ^{13}C NMR and IR spectra of cyclopropanes **6a–d** are identical to those given in the literature.[7]

Thus, silyl protection of the terminal triple bond in chloride **3a** allows us to propose a new simple route to the 1-chloro-1-ethynylcyclopropanes **6**, which are versatile polyfunctional synthons.[5,8] These cyclopropanes had previously been obtained by interaction of a three-fold molar excess of BuLi with

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[†] *Characterization data for* **3b**: 51% yield, bp 73–74 °C (20 Torr). ^{1}H NMR (250 MHz, CDCl$_3$) δ: 6.23 (s, 1H, CHCl$_2$), 0.23 (s, 9H, 3CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$) δ: 98.9 (s, ≡*C*CHCl$_2$), 96.09 (Me$_3$SiC≡), 55.07 (d, CHCl$_2$, *J* 185.6 Hz), –0.57 (q, CH$_3$, *J* 119.6 Hz). IR (thin film, ν/cm^{-1}): 2174 (C≡C). MS [electron impact, 70 eV, *m*/*z* (I_{rel},%)]: 180 (0.17), 169/167/165 (3.4/24/3.51) [M–CH$_3$]$^+$, 141 (5.4), 139 (30.8), 138 (8.3), 137 (55.3), 132 (5.2), 130 (15.5), 129 (10.2), 119 (11.2), 117 (51), 115 (80.4), 113 (100), 103 (8.2), 95 (13.1), 93 (29.3), 79 (6.7), 78 (5.5), 67 (10.5), 65 (21.1), 63 (24), 53 (20.3), 52 (22), 51 (8.3), 43 (17).

[‡] All new compounds **5a–f** gave satisfactory analytical and spectral data. For **5a**: 64% yield, mp 76–77 °C (from EtOH) (lit.,[6] 68 °C). ^{1}H NMR (250 MHz, CDCl$_3$) δ: 1.16 (s, 6H, 2CH$_3$), 1.14 (s, 6H, 2CH$_3$), 0.19 (s, 9H, Me$_3$Si). IR (KBr, ν/cm^{-1}): 2164 (C≡C), 1250, 837 (Me$_3$Si). MS [electron impact, 70 eV, *m*/*z* (I_{rel},%)]: 230/228 [M]$^+$ (1/3).

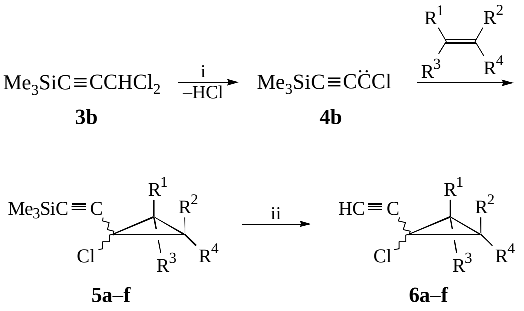
For **5b**: 50% yield, bp 91 °C (42 Torr). ^{1}H NMR (250 MHz, CDCl$_3$) δ: 1.37 (s, 3H, CH$_3$), 1.32 (s, 3H, CH$_3$), 1.18 (d, 1H, *J* 5.9 Hz), 1.08 (d, 1H, *J* 5.9 Hz), 0.204 (s, 9H, Me$_3$Si). IR (KBr, ν/cm^{-1}): 2178 (C≡C). MS [electron impact, 70 eV, *m*/*z* (I_{rel},%)]: 202/200 [M]$^+$ (1/3).

For **5c**: mixture of *endo*(Cl)- and *exo*(Cl)-isomers in the ratio 1:4.5, 43% yield, bp 150 °C (bath temperature, 20 Torr). ^{1}H NMR (90 MHz, CDCl$_3$) δ: 1.55–2.0 (m, 6H, 2CH and 2CH$_2$), 1.1–1.4 (m, 4H, 2CH$_2$), 0.108 and 0.165 (s, 9H, Me$_3$Si for the *endo*-, *exo*-isomers). ^{13}C NMR (50 MHz, C$_6$D$_6$) δ, for the *exo*-isomer: 102.49 (≡C), 94.32 (Me$_3$SiC≡), 38.45 (C–Cl); 27.53 (CH), 20.52 and 19.59 (CH$_2$), –0.37 (Me$_3$Si); for the *endo*-isomer: 108.52 (≡C), 84.59 (Me$_3$SiC≡), 41.68 (C–Cl); 24.31 (CH), 20.76 and 18.69 (CH$_2$), –0.28 (Me$_3$Si). IR (KBr, ν/cm^{-1}): 2168 (C≡C). MS [electron impact, 70 eV, *m*/*z* (I_{rel},%)]: 226/228 [M]$^+$ (1/3).

For **5d**: mixture of *cis*(Cl,H)- and *trans*(Cl,H)-isomers in the ratio 1.13:1, 60% yield, bp 80 °C (8 Torr). ^{1}H NMR (90 MHz, CDCl$_3$) δ: 1.24 and 1.21 (s, 3H, Me), 1.13–1.0 (m, CH and CH$_3$), 1.05 and 1.03 (s, 3H, CH$_3$), 0.1 and 0.09 (s, 9H, Me$_3$Si). ^{13}C NMR (50 MHz, CDCl$_3$) δ, for *cis*-isomer: 105.73 (≡C), 90.54 (Me$_3$SiC≡), 44.83 (C–Cl), 33.91, 23.76 and 17.09 (CH$_3$), 9.78 (CH); –0.02 (Me$_3$Si); for *trans*-isomer: 102.34 (≡C), 86.93 (Me$_3$SiC≡), 44.83 (C–Cl), 31.93, 24.81 and 16.10 (CH$_3$), 27.15 (CH); –0.02 (Me$_3$Si). IR (thin film, ν/cm^{-1}): 2164 (C≡C). MS [electron impact, 70 eV, *m*/*z* (I_{rel},%)]: 216/214 [M]$^+$ (1/3) for *cis*- and *trans*-isomers.

For **5e**: mixture of *cis*(Cl,OEt)- and *trans*(Cl,OEt)-isomers in the ratio 1:2, 35% yield, bp 84 °C (26 Torr). ^{1}H NMR (200 MHz, CDCl$_3$) δ, for *cis*-isomer: 3.6–3.95 (m, 2H, CH$_2$), 3.44 (dd, H, *J* 5.3 and 7.5 Hz), 1.54 (dd, H, *J* 7.5 and 7.5 Hz), 1.35 (dd, H, *J* 5.3 and 7.5 Hz), 1.27 (t, 3H, Me, *J* 7.0 Hz), 0.15 (s, 9H, Me$_3$Si); for *trans*-isomer: 3.6–3.95 (m, 2H, CH$_2$), 3.58 (dd, H, *J* 5.3 and 7.5 Hz), 1.57 (dd, H, *J* 5.0 and 7.4 Hz), 1.48 (dd, H, *J* 7.4 and 7.4 Hz), 1.25 (t, 3H, Me, *J* 7.0 Hz), 0.17 (s, 9H, Me$_3$Si). ^{13}C NMR (50 MHz, CDCl$_3$) δ, for *cis*-isomer: 104.6 (≡C), 87.3 (Me$_3$SiC≡), 67.2 (OCH$_2$), 62.8 (OCH), 31.3 (C–Cl), 26.3 (CH$_2$), 15.0 (CH$_3$), –0.02 (Me$_3$Si); for *trans*-isomer: 101.9 (≡C), 89.5 (Me$_3$SiC≡), 66.8 (OCH$_2$), 65.4 (OCH), 33.2 (C–Cl), 27.3 (CH$_2$), 15.1 (CH$_3$), –0.02 (Me$_3$Si). IR (thin film, ν/cm^{-1}): 2165 (C≡C). MS [electron impact, 70 eV, *m*/*z* (I_{rel},%)]: 218/216 [M]$^+$ (1/3) for *cis*- and *trans*-isomers.

For **5f**: mixture of *cis*(Cl,Ph)- and *trans*(Cl,Ph)-isomers in the ratio 1:2.5, 40% yield. ^{1}H NMR (200 MHz, CDCl$_3$) δ, for *cis*-isomer: 7.35 (m, 5H, Ph), 2.82 (dd, H, PhCH, *J* 8.5 and 9.8 Hz), 1.89 (dd, H, *J* 6.4 and 9.8 Hz), 1.75 (dd, H, *J* 6.4 and 8.5 Hz), 0.26 (s, 9H, Me$_3$Si), for *trans*-isomer: 7.35 (m, 5H, Ph), 2.85 (dd, H, *J* 8.8 and 8.8 Hz), 1.8–1.91 (m, 2H, CH$_2$), 0.04 (s, 9H, Me$_3$Si). ^{13}C NMR (50 MHz, CDCl$_3$) δ, for *cis*-isomer: 134.8 (1-C in Ph), 129.3, 128.1 and 127.4 (CH in Ph); 106.1 (≡C), 86.3 (Me$_3$SiC≡), 35.7 (PhCH), 29.7 (C–Cl), 24.1 (CH$_2$), –0.1 (Me$_3$Si); for *trans*-isomer: 135.6 (1-C in Ph), 128.3, 127.9 and 127.1 (CH in Ph), 102.4 (≡C), 90.7 (Me$_3$SiC≡), 35.8 (PhCH), 33.8 (C–Cl), 25.5 (CH$_2$), –0.4 (Me$_3$Si). IR (thin film, ν/cm^{-1}): 2170 (C≡C). MS [electron impact, 70 eV, *m*/*z* (I_{rel},%)]: 250/248 [M]$^+$ (1/3) for *cis*- and *trans*-isomers.



5,**6a** $R^1 = R^2 = R^3 = R^4 = Me$
b $R^1 = R^3 = Me,\ R^2 = R^4 = H$
c $R^1 + R^2 = (CH_2)_4,\ R^3 = R^4 = H$
d $R^1 = R^2 = R^3 = Me,\ R^4 = H$
e $R^1 = R^2 = R^3 = H,\ R^4 = OEt$
f $R^1 = R^2 = R^3 = H,\ R^4 = Ph$

Scheme 2 *Reagents and conditions*: i, Bu^{t}OK, hexane, –10 °C to 20 °C, 75 min (35–65%); ii, KF·2H$_2$O, DMF, room temperature, 90 min (70–80%).

chloro(trichloroethenyl)cyclopropanes,[7] prepared by lengthy thermolysis of tetrachlorocyclopropene (12–72 h at 150–180 °C in a special apparatus[9]) in the presence of alkenes. However, the high temperature and long duration of these processes limited any practical application of this process.

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[§] *Characterization data for* **6e**: mixture of *cis*(Cl,OEt)- and *trans*-(Cl,OEt)-isomers in the ratio 1:2, 70% yield. ^{1}H NMR (200 MHz, CDCl$_3$) δ, for *cis*-isomer: 3.6–4.0 (m, 2H, CH$_2$), 3.44 (dd, H, *J* 5.3 and 7.4 Hz), 2.42 (s, H, ≡CH), 1.54 (dd, H, *J* 7.4 and 7.4 Hz), 1.35 (dd, H, *J* 5.3 and 7.4 Hz), 1.26 (t, 3H, Me, *J* 7.0 Hz), for *trans*-isomer: 3.6–3.95 (m, 2H, CH$_2$), 3.58 (dd, H, *J* 5.1 and 7.3 Hz), 2.51 (s, H, ≡CH), 1.56 (dd, H, *J* 5.1 and 7.3 Hz), 1.48 (dd, H, *J* 7.3 and 7.3 Hz), 1.25 (t, 3H, Me, *J* 7.0 Hz). ^{13}C NMR (50 MHz, CDCl$_3$) δ, for *cis*-isomer: 83.5 (≡C), 70.8 (HC≡), 67.3 (OCH$_2$), 62.5 (OCH), 31.3 (C–Cl), 25.7 (CH$_2$), 15.0 (CH$_3$); for *trans*-isomer: 80.8 (≡C), 72.9 (HC≡), 67.1 (OCH$_2$), 65.0 (OCH), 32.5 (C–Cl), 26.8 (CH$_2$), 15.1 (CH$_3$). MS [electron impact, 70 eV, m/z (I_{rel},%)]: 146/144 [M]$^+$ (1/3) for *cis*- and *trans*-isomers.

For **6f**: mixture of *cis*(Cl,Ph)- and *trans*(Cl,Ph)-isomers in the ratio 1:2.5, 70% yield. ^{1}H NMR (200 MHz, CDCl$_3$) δ, for *cis*-isomer: 7.35 (m, 5H, Ph), 2.83 (dd, H, PhCH, *J* 8.4 and 9.8 Hz), 2.5 (s, H, ≡CH), 1.90 (dd, H, *J* 6.4 and 9.8 Hz), 1.76 (dd, H, *J* 6.4 and 8.5 Hz); for *trans*-isomer: 7.35 (m, 5H, Ph), 2.86 (dd, H, *J* 8.8 and 8.8 Hz), 2.4 (s, H, ≡CH), 1.8–1.91 (m, 2H, CH$_2$). ^{13}C NMR (50 MHz, CDCl$_3$) δ, for *cis*-isomer: 134.6 (1-C in Ph), 127.9, 127.5 and 127.4 (CH in Ph); 85.1 (≡C), 69.9 (HC≡), 33.7 (PhCH), 29.7 (C–Cl), 24.1 (CH$_2$); for *trans*-isomer: 135.6 (1-C in Ph), 129.3, 128.9 and 128.0 (CH in Ph), 81.0 (≡C), 74.1 (HC≡), 35.8 (PhCH), 35.0 (C–Cl), 24.8 (CH$_2$). MS [electron impact, 70 eV, m/z (I_{rel},%)]: 178/176 [M]$^+$ (1/3) for *cis*- and *trans*-isomers.