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Chlorovinylidenecarbene: Generation from 3,3-Dichloropropyne by Base Solvolysis (under Phase-transfer Catalysis Conditions) and Reaction with Alkenes

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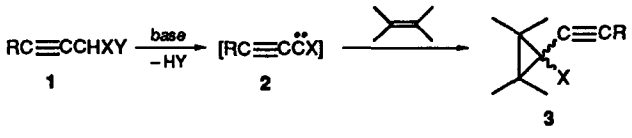
The chlorovinylidenecarbene **6** has been generated from 3,3-dichloropropyne **1a** *via* γ-elimination of hydrogen chloride on treatment with powdered KOH under phase-transfer catalysis conditions and has been trapped by alkenes, to form chlorovinylidenecyclopropanes **7** in 20–45% yields.

Base solvolysis of the substituted dihalomethylacetylenes **1** results in α-elimination of hydrogen halide and formation of the corresponding alkynylhalocarbenes **2**, which were trapped by alkenes forming 1-haloalkyn-1-ylcyclopropanes **3**.[1]

We have discovered that on a similar interaction of 3,3-dichloropropyne **1a**,† the first member of the family of dihalides **1**, with powdered KOH at 20 °C for 45–80 min in CH_2Cl_2 in the presence of a catalytic amount of benzyltriethylammonium chloride (BTEAC) and a five-fold molar excess of alkene, new chlorovinylidenecyclopropanes **7** were obtained in 20–45% yields.‡ Allene **9** (yields 5–10%) and a trace amount of



1 **2** **3**

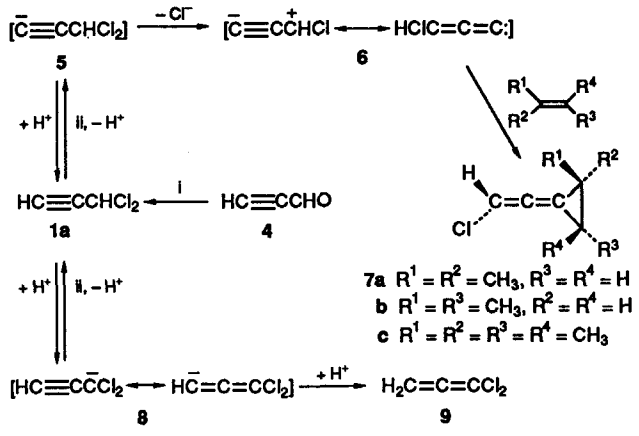
R = Alk, cyclo-Alk, Ph; X, Y = Cl or Br

† **1a** was prepared by chlorination of propargyl aldehyde **4** with PCl_5. Spectral data for **1a**: ^{1}H NMR (60 MHz, CCl_4) δ 3.02 (d, 1H, HC≡, *J* 2.0 Hz), 6.20 (d, 1H, $CHCl_2$, *J* 2.0 Hz); IR ν_{max}/cm^{-1} 2135 (C≡C), 3300 (H–C≡); *m/z* 75/73 [M – Cl]$^+$ (38/100), 72 [M – HCl]$^+$ (18), 47 (25), 38 (55), 37 (66), 36 (32), 35 (29).

‡ All new compounds **7a–c** gave satisfactory analytical and spectral data. For **7a**: b.p. 60–61 °C at 38 mmHg; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.3 (c, 3H, CH_3^1), 1.34 (c, 3H, CH_3^2), 1.56 (dd, 1H, H^4, *J* 9.2, 2.3 Hz), 1.63 (dd, 1H, H^3, *J* 9.2, 2.3 Hz), 6.12 (t, 1H, HClC=, *J* 2.3 Hz); IR ν_{max}/cm^{-1} 1956, 2000 (C=C=C); *m/z* 130/128 [M]$^+$ (5/17).

For **7b**: b.p. 52–54 °C at 30 mmHg; ^{1}H NMR (60 MHz, CCl_4) δ 1.19 (d, 3H, CH_3^1, *J* 5.0 Hz), 1.24 (3H, CH_3^3, *J* 5.0 Hz), 1.3–1.8 (m, 2H, 2×CH in cyclo-C_3H_2), 5.93 (t, 1H, HClC=, *J* 2.2 Hz); IR ν_{max}/cm^{-1} 1965, 2010 (C=C=C); *m/z* 130/128 [M]$^+$.

For **7c**: b.p. 66–68 °C at 24 mmHg; ^{1}H NMR (90 MHz, CCl_3) δ 1.3 (s, 6H, CH_3^1 and CH_3^4), 1.35 (s, 6H, CH_3^2 and CH_3^3), 6.03 (s, 1H, HClC=); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.89 ($2CH_3$), 21.04 ($2CH_3$), 30.59 (CMe_2 in cyclo-C_3), 89.48 (ClHC=), 108.28 (C= in cyclo-C_3), 183.93 (=C=); IR ν_{max}/cm^{-1} 1992 (C=C=C); *m/z* 158/156 [M]$^+$ (3/10).

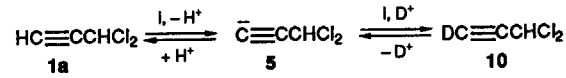


Scheme 1 *Reagents and conditions*: i, PCl_5, pyridine (cat.), CH_2Cl_2, −20°C, 30 min (40%); ii, KOH, BTEAC (cat.), −20°C, 45–80 min (20–45%)

an unidentified isomer of cyclopropane **7** were also found in the reaction mixture using H^1 NMR and GCMS (Scheme 1).

The formation of chlorovinylidenecyclopropanes **7** with hardly any 1-chloro-1-ethynylcyclopropanes **3** (R=H; X=Cl) points to the fact that in the basic solvolysis conditions indicated above, the chlorovinylidenecarbene **6** is generated from dihalide **1a** rather than the chloro(ethynyl)carbene **2** (R=H; X=Cl).

On treatment of the solution of dichloride **1a** in CCl_4 with a 20% solution of NaOD in D_2O in the presence of excess CH_3OD at 20°C for 5 min, the reaction mixture contained only 1-[$^2H_1$]-3,3-dichloropropyne **10**§ and starting **1a**, *i.e.* rapid H–D exchange took place solely for the hydrogen atom at the triple bond (Scheme 2).



Scheme 2 *Reagents and conditions*: i, NaOD, CH_3COD, CCl_4, ~20°C, 5 min

The evidence obtained indicates that, analogous to 3-haloalk-1-ynes,[2,3] rapid equilibrium formation of the acetylenic anion **5** originally occurs on base solvolysis of dichloride **1a** by hydroxides of alkaline metals. Then the anion **5** slowly loses the chloride anion (rate-determining step) resulting in carbene **6**, which adds to a double bond of the alkene present to give cyclopropanes **7**. The hydrogen atom of the dichloromethyl group is more slowly eliminated than the acetylene proton and then this anion **8** is quickly protonated to allene **9** (Scheme 1).

References

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§ Spectral data for **10**: ^{1}H NMR (60 MHz, CCl_4) δ 6.20 (c, 1H, $CHCl_2$); IR ν_{max}/cm^{-1} 1998, (C=C); 2602 (D–C≡); *m/z* 76/74 $[M-Cl]^+$ (32/100), 73 $[M-HCl]^+$ (23), 47 (15), 39 (25).