# One-Step Preparation of α-Chloro-α,β-unsaturated Carbonyl Compounds by the Reaction of Silyl Enol Ethers with $TiCl_4$–$LiAlH_4$–$CCl_4$

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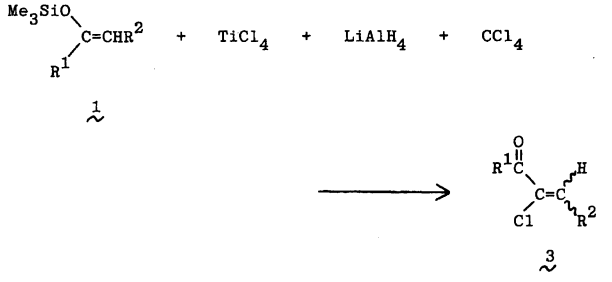
**Synopsis.** Reaction of silyl enol ethers in a system composed of $TiCl_4$, $LiAlH_4$, and $CCl_4$, which generates dichlorocarbene, produced α-chloro-α,β-unsaturated carbonyl compounds in an one-step process.

The reaction of dihalocarbenes with carbonyl equivalent olefins such as silyl enol ethers,[1—3] enol ethers,[4—6] enol acetate,[7,8] and enamines,[9,10] gives cyclopropane derivatives that are next converted to carbon-chain homologated α-halo-α,β-unsaturated carbonyl compounds by thermal, acid, or base treatment. These transformations require a two-step procedure that includes isolation of the cyclopropanes. In this investigation, we found a method by which carbon-chain homologated α-chloro-α,β-unsaturated carbonyl compounds are directly formed in one step from silyl enol ethers.

The addition of 1-trimethylsiloxy-1-cyclohexene (**1a**) and $CCl_4$ to a suspension of $TiCl_4$ and $LiAlH_4$ in THF furnished 2-chloro-2-cyclohepten-1-one (**3a**). Various silyl enol ethers **1** were reacted under the same conditions to form **3** (Scheme 1). The results are shown in Table 1. The reaction with **1c**, which has two bulky substituents (*t*-butyl and trimethylsiloxy) afforded cyclopropane **2c** (54%) as the major product together with the desired product **3c** (34%). When ketene silyl acetals from esters were the substrates, the situation became more complicated. The ketene silyl acetal from methyl phenylacetate, **1i**, gave the desired product **3i**, although the yield was low, but the ketene silyl acetal from ethyl hexanoate, **1j**, did not form a carbon-chain homologated product but product **4**, which has a dichloromethyl group as a pendant (Scheme 2).

$TiCl_4$ and $LiAlH_4$ form reduced titanium, which then reacts with $CCl_4$ to generate dichlorocarbene.[11,12] Thus, our method probably involves the intermediary formation of dichlorocyclopropyl silyl ethers **2** by the reaction of silyl enol ethers **1** with dichlorocarbene generated in this reaction system. The sequential conversion of **2** to **3** under our reaction conditions may be effected by the action of $AlCl_3$ or $TiCl_2$ generated in situ that is a Lewis acid, for which two possible pathways including attack upon an oxygen or chlorine atom[13] as shown in paths a and b of Scheme 3, respectively, may be envisaged. If path b were operative, reaction of the allylsilane **5** instead of **1** in this system could be expected to afford diene **7** (Scheme 4). In fact, dichlorocyclopropane **6** was obtained as the sole product and it was not converted to **7**. Thus, it is likely that **3** is formed via path a under these reaction conditions. The production of **2c** from **1c** also may be evidence for path a. Coordination of the metal chloride on the oxygen atom of **2c** in path a may be disturbed because of steric congestion with the bulky *t*-butyl group, but approach to the chlorine atom in path b is not hindered in this way.

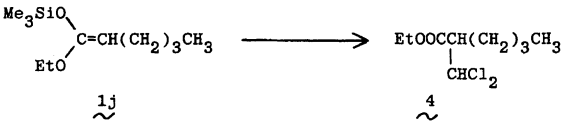



Scheme 1.

Table 1. Preparation of α-Chloro-α,β-unsaturated Carbonyl Compounds **3** from Silyl Enol Ethers **1**

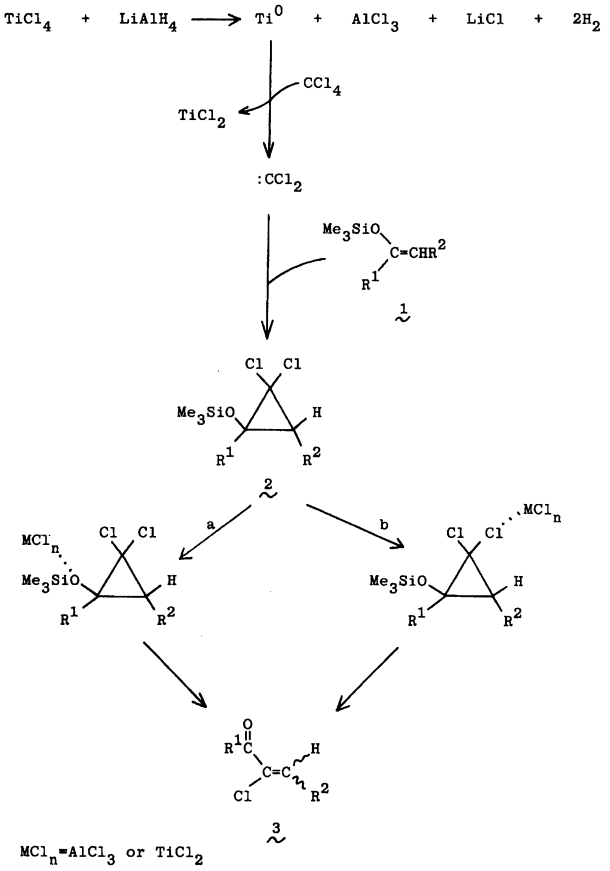
| | 1 | | 3 | |
|---|---|---|---|---|
| | $R^1$ | $R^2$ | Stereochemistry | Yield/% |
| **a** | $-(CH_2)_4-$ | | *E* | 71[a] |
| **b** | $-(CH_2)_3-$ | | *E* | 70[c] |
| **c** | $C(Me)_3$ | H | | 34[a,b] |
| **d** | Et | Me | *Z* | 52[d] |
| **e** | Pr | Et | *Z* | 63[c] |
| **f** | H | $C_5H_{11}$ | *Z* | 61[a] |
| **g** | Ph | H | | 75[a] |
| **h** | Ph | Et | *Z* | 62[d] |
| **i** | OMe | Ph | *Z* | 10[a] |

a) Yields were determined by GC. b) The cyclopropane **2c** (54%) was a major product. c) Yields refer to products isolated by Kugelrohr distillation. d) Yields refer to products isolated by preparative TLC.

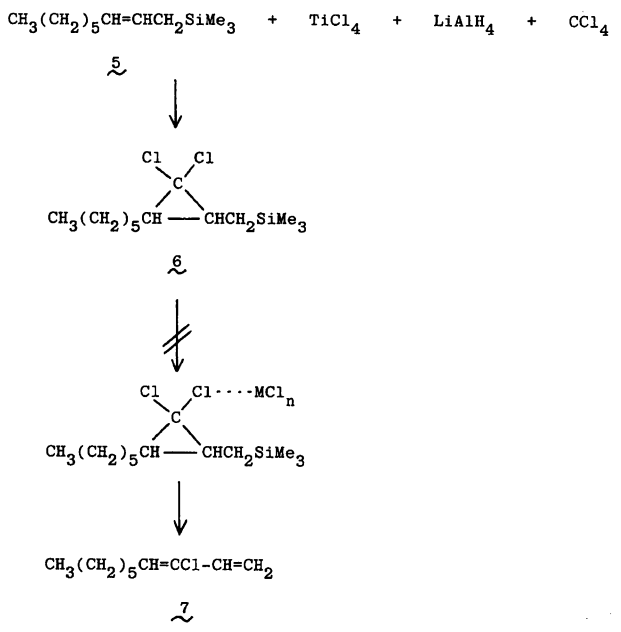



Scheme 2.

The reaction of ketene silyl acetal **1j** afforded 2-dichloromethyl ester **4**, which seems to be formed via the bond cleavage of the intermediate cyclopropane at a different position than cleavage of the cyclopropanes from silyl enol ethers **1a**—**h** and ketene silyl acetal **1i**. The reason for the unusual bond cleavage of **2j** is not known. It might be due to direct attack by the




Scheme 3.




Scheme 4.

metal chloride of the cyclopropane ring, not the oxygen atom, of **2j** to bring about bond cleavage, as suggested by the electrophilic attack by $TiCl_4$ of the ring of the cyclopropanone silyl acetal to form the titanium homonolate.[14]

## Experimental

IR spectra were recorded on a Hitachi EPI-G3 spectrometer with samples as neat oils. $^1H$ and $^{13}C$ NMR spectra were recorded with a JEOL FX60 spectrometer for $CDCl_3/CCl_4$ solutions with $SiMe_4$ as the internal standard. Mass spectra were obtained at 70 eV with a Hitachi M-80B instrument.

**Materials.** Silyl enol ethers **1a**—**h**, ketene silyl acetals **1i**, **j**, and allylsilane **5** were prepared by the methods of House et al.,[15] Ainsworth et al.,[16] and Fleming and Paterson,[17] respectively.

**Treatment of 1 with a System Composed of $TiCl_4$, $LiAlH_4$, and $CCl_4$.** $TiCl_4$ (5.69 g, 30 mmol) was added at a rate that allowed the temperature to remain below 5 °C to THF (40 $cm^3$) being stirred under a nitrogen atmosphere. Then a solution of $LiAlH_4$ (1.14 g, 30 mmol) in THF (25 $cm^3$) was added at a rate that allowed the temperature to remain below 15 °C, and the dark-brown mixture was allowed to warm to 19 °C over a period of 40 min. The flask was cooled again in a salt-ice bath. When the temperature had fallen to 0 °C, **1** (10 mmol) and then $CCl_4$ (4.29 g, 30 mmol) in THF (15 $cm^3$) were added in this order at a rate that allowed the temperature to remain at 0 °C. After being stirred at 0 °C for 30 min, the reaction mixture was poured into 150 $cm^3$ of cold 6.7% hydrochloric acid in water. The upper organic layer was separated from the aqueous layer. The aqueous layer was extracted with dichloromethane (1×40 $cm^3$, 2×30 $cm^3$). The combined organic layers were washed with 10% aqueous sodium carbonate (25 $cm^3$) and dried over anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, the residue was separated by GC, preparative TLC, or Kugelrohr distillation.

**2-Chloro-2-cyclohepten-1-one (3a):** IR 1685 (C=O), 1606 (C=C) $cm^{-1}$; $^1H$ NMR $\delta$=7.29 (t, 1H, $J$=6.9 Hz, CH=C), 2.94—2.46 (m, 4H, $CH_2CO$ and $CH_2CH$=C), 2.07—1.74 (m, 4H, $CH_2CH_2$); $^{13}C$ NMR $\delta$=141.61, 41.23, 27.43, 24.75, 20.86; MS $m/z$ 146 ($M^+$+2; 23), 144 ($M^+$; 77), 81 (100). HR-MS, Found: $m/z$ 144.0330 ($M^+$). Calcd for $C_7H_9OCl$: M, 144.0341.

**2-Chloro-2-cyclohexen-1-one (3b):** IR 1695 (C=O), 1608 (C=C) $cm^{-1}$; $^1H$ NMR $\delta$=7.37 (t, 1H, $J$=6.0 Hz, CH=C), 2.80—2.00 (m, 6H, $CH_2CH_2CH_2$); $^{13}C$ NMR $\delta$=144.87, 38.20, 26.80, 22.51; MS $m/z$ 132 ($M^+$+2; 27), 130 ($M^+$; 93), 39 (100). HR-MS, Found: $m/z$ 130.0183 ($M^+$). Calcd for $C_6H_7OCl$: M, 160.0184.

**1-*t*-Butyl-2,2-dichloro-1-trimethylsiloxycyclopropane (2c):** $^1H$ NMR $\delta$=1.83 (d, 1H, $J$=8.6 Hz, $CH_2$), 1.73 (d, 1H, $J$=8.6 Hz, $CH_2$), 1.17 (s, 9H, $CCH_3$), 0.19 (s, 9H, $SiCH_3$); $^{13}C$ NMR $\delta$=29.63, 27.78, 1.90; MS $m/z$ 256 ($M^+$+2; 1,5), 254 ($M^+$; 2.5), 73 (100). HR-MS, Found: $m/z$ 219.0992 ($M^+$−Cl). Calcd for $C_{10}H_{20}OSiCl$: M−Cl, 219.0971.

**2- Chloro- 4, 4- dimethyl- 1- penten- 3- one (3c):** $^1H$ NMR $\delta$=6.10 (d, 1H, $J$=1.7 Hz, $CH_2$=C), 5.83 (d, 1H, $J$=1.7 Hz, $CH_2$=C), 1.29 (s, 9H, $CH_3C$); MS $m/z$ 148 ($M^+$+2; 2.3), 146 ($M^+$; 8.0), 41 (100). HR-MS, Found: $m/z$ 146.0477 ($M^+$). Calcd for $C_7H_{11}OCl$: M, 146.0497.

**(*Z*)-3-Chloro-2-hexen-4-one (3d):** IR 1690 (C=O), 1617 (C=C) $cm^{-1}$; $^1H$ NMR $\delta$=7.14 (q, 1H, $J$=7.2 Hz, CH=C), 2.81 (q, 2H, $J$=7.4 Hz, $CH_2$), 2.00 (d, 3H, $J$=7.2 Hz, $CH_3CH$=C), 1.14 (t, 3H, $J$=7.4 Hz, $CH_3CH_2$); $^{13}C$ NMR $\delta$=133.52, 31.82, 14.72, 7.94; MS $m/z$ 134 ($M^+$+2; 36), 132

($M^+$; 100). HR-MS, Found: $m/z$ 132.0336 ($M^+$). Calcd for $C_6H_9OCl$: M, 132.0340.

**(*Z*)-4-Chloro-3-octen-5-one (3e):** IR 1714 (C=O), 1618 (C=C) $cm^{-1}$; $^1H$ NMR $\delta$=7.15 (t, 1H, $J$=7.7 Hz, CH=C), 2.80 (t, 2H, $J$=7.7 Hz, $CH_2CO$), 2.46 (app quint, 2H, $J$=7.7 Hz, $CH_2CH$=C), 2.07—1.40 (m, 2H, $CH_2CH_2$), 1.16 (t, 3H, $J$=7.2 Hz, $CH_3CH_3CH_2$), 1.00 (t, 3H, $J$=7.2 Hz, $CH_3CH_2CH$=C); $^{13}C$ NMR $\delta$=139.85, 40.35, 22.51, 17.30, 13.60, 12.13; MS $m/z$ 162 ($M^+$+2; 32), 160 ($M^+$; 100). HR-MS, Found: $m/z$ 160.0655 ($M^+$). Calcd for $C_8H_{13}OCl$: M, 160.0654.

**(*Z*)-2-Chloro-2-octen-1-one (3f):** IR 1705 (C=O), 1628 (C=C) $cm^{-1}$; $^1H$ NMR $\delta$=9.52 (s, 1H, HCO), 6.93 (t, 1H, $J$=7.2 Hz, CH=C), 2.74—2.32 (m, 2H, $CH_2CH$=C), 1.87—1.20 (m, 6H, $CH_2CH_2$), 0.91 (t, 3H, $J$=6.0 Hz, $CH_3$); $^{13}C$ NMR $\delta$=183.80, 149.15, 31.29, 29.04, 27.27, 22.20, 13.79; MS $m/z$ 162 ($M^+$+2; 0.2), 160 ($M^+$; 0.6), 41 (100). HR-MS, Found: $m/z$ 160.0673 ($M^+$). Calcd for $C_8H_{13}OCl$: M, 160.064.

**2-Chloro-1-phenyl-2-propen-1-one (3g):** IR 3033 (Ph), 1670 (C=O), 1590 (C=C) $cm^{-1}$; $^1H$ NMR $\delta$=8.10—7.53 (m, 5H, Ph), 6.33 (d, 1H, $J$=1.7 Hz, $CH_2$=C), 6.16 (d, 1H, $J$=1.7 Hz, $CH_2$=C); $^{13}C$ NMR $\delta$=132.45, 129.28, 127.96, 124.17; MS $m/z$ 168 ($M^+$+2; 8), 166 ($M^+$; 22), 105 (100). HR-MS, Found: $m/z$ 166.0173 ($M^+$). Calcd for $C_9H_7OCl$: M, 166.0184.

**(*Z*)-2-Chloro-1-phenyl-2-penten-1-one (3h):** IR 3028 (Ph), 1670 (C=O), 1598 (C=C) $cm^{-1}$; $^1H$ NMR $\delta$=8.26—7.58 (m, 5H, Ph), 6.92 (t, 1H, $J$=7.7 Hz, CH=C), 2.63 (app quit, 2H, $J$=7.7 Hz, $CH_2$), 1.21 (t, 3H, $J$=7.7 Hz, $CH_3$); $^{13}C$ NMR $\delta$=144.24, 131.81, 129.09, 127.87, 22.85, 12.18; MS $m/z$ 196 ($M^+$+2; 35), 194 ($M^+$; 100); HR-MS, Found: $m/z$ 194.0485 ($M^+$). Calcd for $C_{11}H_{11}OCl$: M, 194.0497.

**(*Z*)-Methyl 2-chlorocinnamate (3i):** IR 3030 (Ph), 1733 (COO), 1614 (C=C) $cm^{-1}$; $^1H$ NMR $\delta$=7.67 (s, 1H, CH=C), 7.61 (br s, 5H, Ph), 3.91 (s, 3H, $CH_3$); $^{13}C$ NMR $\delta$=136.59, 128.50, 128.20, 127.96, 52.24; MS $m/z$ 198 ($M^+$+2; 27), 196 ($M^+$; 95), 161 (100). HR-MS, Found: $m/z$ 196.0263 ($M^+$). Calcd for $C_{10}H_9O_2Cl$: M, 196.0237.

**Ethyl 2-Dichloromethylhexanoate (4):** IR 1739 (COO) $cm^{-1}$; $^1H$ NMR $\delta$=6.10 (d, 1H, $J$=8.6 Hz, $CHCl_2$), 4.39 (q, 2H, $J$=7.7 Hz, $CH_2O$), 3.23—2.84 (m, 1H, CHCO), 1.97—1.20 (m, 6H, $CH_2CH_2CH_2$), 1.37 (t, 3H, $J$=7.7 Hz, $CH_3CH_2O$), 0.97 (t, 3H, $J$=5.1 Hz, $CH_3$); $^{13}C$ NMR $\delta$=75.09, 63.15, 62.18, 59.55, 31.43, 24.75, 16.62, 16.23; CI-MS $m/z$ 229 ($M^+$+2+H; 63), 227 ($M^+$+H; 100). HR-MS, Found: $m/z$ 135.0206 ($M^+-Cl-C_4H_8$). Calcd for $C_5H_8O_2Cl$: $M-Cl-C_4H_8$, 135.0212.

**Treatment of 5 with a System Composed of $TiCl_4$, $LiAlH_4$, and $CCl_4$.** 1-Trimethylsilyl-2-nonen (**5**) (1.98 g, 10 mmol) was treated in a reaction system composed of $TiCl_4$ (5.9 g, 30 mmol), $LiAlH_4$ (1.14 g, 30 mmol), and $CCl_4$ (4.29 g, 30 mmol) as for **1**. From the residue after work-up, dichlorocyclopropane **6** was isolated by preparative GC as a colorless liquid: $^1H$ NMR $\delta$=1.80—1.15 (m, 12H), 0.95 (t, 3H, $J$=4.3 Hz, $CH_3CH_2$), 0.73—0.50 (m, 2H, $CH_2Si$), 0.11 (s, 9H, $CH_3Si$); $^{13}C$ NMR $\delta$=33.09, 31.53, 29.34, 28.99, 28.41, 24.80, 22.46, 13.99, 11.35, −1.46; MS $m/z$ 282 ($M^+$+2; 0.11), 280 ($M^+$; 0.19), 73 (100). HR-MS, Found: $m/z$ 172.0991 ($M^+-Cl-SiMe_3$). Calcd for $C_{10}H_{17}Cl$: $M-Cl-SiMe_3$, 172.1017.

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