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# 1,2-Acyl Migration from β-Acyl-γ-Trimethylsilyl Carbenium Ion

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*Abstract : $TiCl_4$ induced rearrangement of α-allyl α'-vinyl β-trimethylsilyl ketones* **3c,d,e,g** *leads to rearranged α-allyl α'-vinyl ketones* **4c,d,e** *or 2-vinylcyclopentanone* **9** *resulting of an acyl shift with silyl control.*

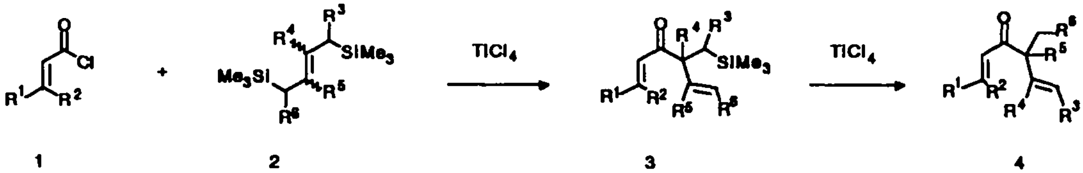
*Résumé : Sous l'influence de $TiCl_4$ et grâce à la présence du groupement triméthylsilyle, les α-allyl α'-vinyl β-trimethylsilyl cétones* **3c,d,e,g** *se réarrangent avec migration du groupement acyle, en α-allyl α-vinyl cétones* **4c,d,e** *ou en vinyl-2 cyclopentanone* **9**.

Due to the poor ability of carbonyl group to stabilize electron deficient carbon atom, acyl migrations are seldom observed. The main results concern the rearrangement of chlorhydrines,[1] α,β-epoxy ketones, esters or thioesters[2] (with inversion of configuration at the migration terminus in nonpolar solvents[3] or in the gas phase at high temperature),[4] the acylation of acetylenic compounds[5,6] or the acid catalyzed rearrangement of α-vinylcyclobutanones.[7] A mechanism has been postulated for carbonyl migration that involves reverse polarization of the carbonyl π-bond.[8]

We would like to report that titanium tetrachloride promoted a carbenium induced 1,2-acyl shift with silyl control of rearranged carbenium ion formation and collapse.

The substrates (**3**) result of the condensation of ethylenic acyl chlorides (**1**) and 1,4-bistrimethylsilyl-2-butenes E and Z (**2**).[9,10] We were attracted to the possibility that allyl vinyl ketones (**3**) might be useful in cyclization reactions.[11]

Treatment of ketones (**3c,d,e**) with 1 equiv. of $TiCl_4$ at -30 °C in $CH_2Cl_2$, gave ketones (**4c,d,e**). The mechanism shown in Scheme II suggests a protonation of the carbon-carbon double bond, an acyl shift giving a β-silyl carbenium ion, a chloride anion addition on the silicon atom and the elimination of chlorotrimethylsilane.[12] The driving force of the acyl shift would be due to the formation of a β-silyl stabilized carbenium ion.[15,16]

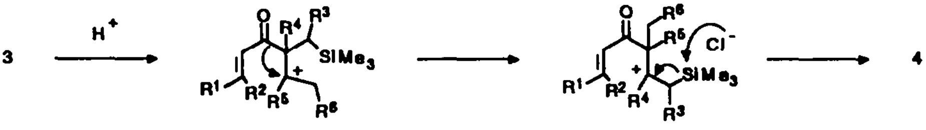


1a : $R^1 = CH_3$ ; $R^2 = H$
1b : $R^1 = R^2 = CH_3$
1c : $R^1 = C_6H_5$ ; $R^2 = H$

2a : $R^3 = R^4 = R^5 = R^6 = H$
2b : $R^5 = CH_3$; $R^3 = R^4 = R^6 = H$
2c : $R^4 = R^5 = CH_3$; $R^3 = R^6 = H$
2d : $R^3 - R^6 = -(CH_2)_4-$ ; $R^4 = R^5 = H$

a : $R^1 = CH_3$ ; $R^2 = R^3 = R^4 = R^5 = R^6 = H$
b : $R^1 = R^2 = CH_3$; $R^3 = R^4 = R^5 = R^6 = H$
c : $R^1 = R^2 = R^5 = CH_3$ ; $R^3 = R^4 = R^6 = H$
d : $R^1 = R^2 = R^4 = R^5 = CH_3$; $R^3 = R^6 = H$
e : $R^1 = CH_3$ ; $R^3 - R^6 = -(CH_2)_4-$ ; $R^2 = R^4 = R^5 = H$
f : $R^1 = R^4 = R^5 = CH_3$ ; $R^2 = R^3 = R^6 = H$
g : $R^1 = R^5 = CH_3$ ; $R^2 = R^3 = R^4 = R^6 = H$

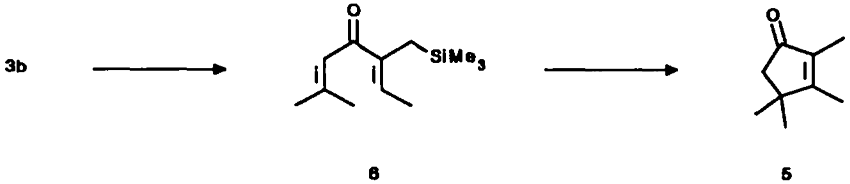
Scheme 1



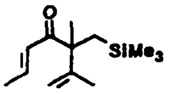
Scheme 2

Except for (**3e**), the transposition was induced by the formation of a tertiary carbenium ion. The new β - silyl stabilized carbenium ion could be secondary ((**3c**) and (**3e**)) or tertiary (**3d**).

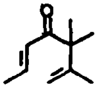
A rearrangement did not take place by treatment of the ketone (**3a**) or (**3b**).[17] The latter quantitatively led to the cyclopentenone (**5**) after heating with $BF_3$-ether (use of $TiCl_4$ led only to (**6**)). The first step of this process was the formation of divinyl ketone (**6**) (possibly isolated) and then Nazarov cyclization.[18]



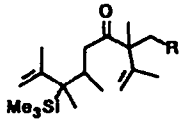
The condensation of crotonyl chloride (**1a**) with (**2c**) was a complex reaction. The primary allyl vinyl ketone (**3f**)(or its rearranged form (**4f**) not isolated) added a second molecule of (**2c**) according to the Sakurai reaction[19] giving (**7**) and (**8**). Both high relative rates of the rearrangement of (**3f**) into (**4f**) and the Sakurai reaction prevented from the isolation of (**3f**) alone.



3f



4f



7 : R = H
8 : R = SiMe3

The condensation of crotonyl chloride (**1a**) with (**2b**) led to another complex mixture at low temperature,but by stirring the reactive mixture at -30 °C for 18 h, the cyclopentanone (**9**) (one isomer) could be isolated. (**9**) could result of a cyclization of the allyl vinyl ketone (**3g**) resulting of the condensation, followed by an acyl shift with loss of the trimethylsilyl group.

3g

9

These results have shown that a 1,2-acyl shift induced by a carbenium ion was possible when the rearranged carbenium ion was stabilized by a β-trimethylsilyl group.

## Experimental Section

**General Methods.** $^1H$ NMR spectra were determined with a Varian EM 360 (60 MHz) or a Varian XL 200 (200 MHz) spectrometer. $^{13}C$ NMR spectra were recorded on a Varian XL 200 (50.309 MHz) with $Me_4Si$ as the internal standard. Attributions were confirmed by *J*-modulated spin echo. Mass spectra were obtained on a Varian MAT 311 mass spectrometer. All reactions were carried out under an argon atmosphere.

**Obtention of the Allyl Vinyl Ketones (3).** A 250 mL two-necked flask equipped of a dropping funnel and a magnetic stirrer was charged with $TiCl_4$ (3.8 g, 20 mmol) and 100 mL of anhydrous $CH_2Cl_2$. After cooling to -30 °C, acyl chloride (**1**) (20 mmol) in 50 mL of anhydrous $CH_2Cl_2$ was added. The solution was cooled to -80 °C and 1,4-bistrimethylsilyl-2-butene (**2**) (22 mmol) in $CH_2Cl_2$ (30 mL) was slowly added. The reaction mixture was stirred at -80 °C and then hydrolyzed by addition into ice. After standard work-up, the crude product was chromatographed on silica gel (ether/pentane, 1/99 ) or distilled.

Condensation of crotonyl chloride (**1a**) and 1,4-bistrimethylsilyl-2-butene (**2a**) gave **3-trimethylsilylmethyl-1,5-heptadien-4-one** (**3a**) after 15 min. at -80 °C (77 % yield). (**3a**) : bp 60 °C/ 1Torr; $^1H$ NMR ($\delta$/$RSiMe_3$)($CCl_4$) $\delta$ 6.80 (1, d.q. $J = 17.0, 6.8$ Hz), 6.10 (1, d. $J = 17.0$ Hz), 5.87-4.90 (3, m.), 3.33 (1, q. $J = 7.5$ Hz), 1.88 (3, d. $J = 6.8$ Hz), 0.87 (2, m.), 0.00 (9, s.); $^{13}C$ NMR $\delta$ 200.1 (s), 142.7 (d), 138.7 (d), 129.7 (d), 116.8 (t), 51.7 (d), 18.5 (t), 18.3 (q), -0.9 (q); IR (film) 1660, 1625, 1250, 910, 860-835, 735 $cm^{-1}$; anal. calcd. for $C_{11}H_{20}Si$ : C 67.34, H 10.20; found : C 67.18, H 10.15.

Condensation of senecioyl chloride (**1b**) and (**2a**) gave **2-methyl-5-trimethylsilylmethyl-2,6-heptadien-4-one** (**3b**) after 30 min. at -80 °C (65 % yield). (**3b**) : bp 65 °C/ 2 Torr; $^1$H NMR ($CDCl_3$) δ 6.08 (1, sept. *J* = 1.3 Hz), 5.69 (1, d.d.d. *J* = 17.1, 9.9, 8.7 Hz), 5.1 (1, d. *J* = 17.1 Hz), 5.04 (1, d. *J* = 9.9 Hz), 3.11 (1, d.d.d. *J* = 8.7, 8.4, 6.2 Hz), 2.10 (3, d. *J* = 1.3 Hz), 1.84 (3, d. *J* = 1.3 Hz), 0.98 (1, 1/2AB, d. *J* = 14.6, 6.2 Hz), 0.71 (1, 1/2, d. *J* = 14.6, 8.4 Hz), -0.05 (9, s.); $^{13}$C NMR δ 201.5 (s), 156.5 (s), 139.3 (d), 122.8 (d), 116.7 (t), 54.7 (d), 28.1 (q), 21.1 (q), 18.6 (t), -006 (q); IR (film) 3080, 1680, 1620, 1250, 860-835 cm$^{-1}$; mass spectrum *m/e* 195 (M$^+$ - Me)(18)(HRMS calcd for $C_{11}H_{19}OSi$ 195.1205, found 195.1213), 83 (100), 73 (60).

Condensation of (**1b**) and 1,4-bistrimethylsilyl-2-methyl-2-butene (**2b**) led to **2,6-dimethyl-5-trimethylsilylmethyl-2,6-heptadien-4-one** (**3c**) after 30 min. at -80 °C (70 % yield). (**3c**) : bp 60 °C/ 1 Torr; $^1$H NMR ($CDCl_3$) δ 6.14 (1, br. s.), 4.90 (1, br. s.), 4.84 (1, br. s.), 3.18 (1, t. *J* = 7.4 Hz), 2.10 (3, br. s.), 1.84 (3, br. s.), 1.59 (3, br. s.), 1.10 (1, 1/2 AB, d. *J* = 15.2, 7.4 Hz), 0.71 (1, 1/2 AB, d.), -0.04 (9. s.); $^{13}$C NMR δ 200.8 (s), 157.5 (s), 145.4 (s), 122.3 (d), 113.7 (t), 57.5 (d), 27.7 (q), 20.7 (q), 19.4 (q), 16.0 (t), -1.18 (q); IR (film) 3085, 1680, 1620, 1245, 870-830 cm$^{-1}$; mass spectrum *m/e* 224 (0.7), 209 (M$^+$ - Me)(25)(HRMS calcd for $C_{13}H_{24}OSi$ 224.1596, found 224.1599), 181 (13), 83 (100), 73 (91).

Condensation of (**1b**) and 1,4-bistrimethylsilyl-2,3-dimethyl-2-butene (**2c**) led to **2,5,6-trimethyl-5-trimethylsilylmethyl-2,6-heptadien-4-one** (**3d**) after 1h at -80 °C (75 % yield). (**3d**) : bp 80 °C/ 2.5 Torr; $^1$H NMR ($CDCl_3$) δ 6.16 (1, br. s.), 5.01 (1, br. s.), 4.94 (1, br. s.), 2.12 (3, br. s.), 1.86 (3, br. s.), 1.60 (3, br. s.), 1.25 (3, s.), 1.09 (2, s.), 0.00 (9, s.); $^{13}$C NMR δ 203.6 (s), 155.4 (s), 149.4 (d), 120.0 (s), 111.6 (t), 55.6 (s), 27.8 (q), 24.0 (t), 22.8 (q), 20.7 (q), 20.4 (q), 0.5 (q); IR (film) 1680, 1620, 1250, 860-830 cm$^{-1}$; mass spectrum *m/e* 238 (1)(HRMS calcd for $C_{14}H_{26}OSi$ 238.1752, found 238.1745), 83 (36), 73 (100).

Condensation of (**1a**) and 1,4-bistrimethylsilyl-2-cyclooctene (**2d**) led to **3-crotonyl-4-trimethylsilylcyclooctene** (**3e**) after 30 min. at -80 °C (70 % yield). (**3e**) : $^1$H NMR (δ/RSiMe$_3$)($CCl_4$) δ 6.90-5.73 (4, m.), 1.9 (3, d. *J* = 6.8 Hz), 0.00 (9, s.); $^{13}$C NMR (two isomers) δ 202.7 and 202.3 (s), 142.1 and 142.4 (d), 132.0, 132.6 and 131.5 (d), 129.0 (d), 46.7 and 46.2 (d), 33.0 and 33.7 (d), 31.7 (t), 31.6 (t), 26.5 (t), 23.2 (t), 22.3 (t), 18.2 (q), -1.5 (q); IR (film) 1665, 1635, 1250, 835 cm$^{-1}$; anal. calc. for $C_{15}H_{26}OSi$ : C 72.00, H 10.40; found : C 72.18, H 10.32.

**Rearrangement of the Allyl Vinyl Ketones (3c-e) into Allyl Vinyl Ketones (4c-e)**. A 25 mL flask equipped of a no-air septum was charged with $TiCl_4$ (0.38 g, 2 mmol) and 15 mL of anhydrous $CH_2Cl_2$. After cooling to -30 °C, ketone (**3**) (2 mmol) in $CH_2Cl_2$ (5 mL) was added. The solution was stirred at -30 °C for 30 h. After standard work-up, (**4**) was obtained in quantitative yield from the crude product by chromatography on silica gel (ether/pentane, 5/95 ).

Rearrangement of (**3c**) gave **Artemesia ketone** (**4c**)$^{20}$ (quantitative yield) : $^1$H NMR δ 6.04 (1, br. s.), 5.83 (1, d. d. *J* = 17.5, 9.5 Hz), 5.10 (1,m.), 4.83 (1, m.), 2.07 (3, br. s.), 1.84 (3, br. s.), 1.15 (6, s.); IR (film) 3090, 1680, 1620, 900 cm$^{-1}$. Rearrangement of (**3d**) led to **2,5,5,6-tetramethyl-2,6-heptadien-4-one** (**4d**) : $^1$H NMR δ 5.97 (1, br. s.), 4.83 (2, br. s.), 2.10 (3, br. s.), 1.84 (3, br. s.), 1.61 (3, br. s.), 1.15 (6, s.); IR (film) 3100, 1685, 1620, 900 cm$^{-1}$; anal. calc. for $C_{11}H_{18}O$ : C 79.51, H 10.84; found : C 79.63, H 10.77.

Rearrangement of (**3e**) led to **3-crotonylcyclooctene** (**4e**) : $^1$H NMR δ 6.68 (1, d.q. *J* = 15.0, 6.4 Hz), 6.0

(1, d. $J$ = 15.0 Hz), 5.55 (2, m.), 1.87 (3, d. $J$ = 6.4 Hz); $^{13}$C NMR $\delta$ 202.7 (s), 142.2 (d), 131.7 (d), 130.3 (d), 127.8 (d), 49.9 (d), 29.3 (t), 27.8 (t), 26.8 (t), 25.7 (t), 24.4 (t), 18.2 (q); IR (film) 1665, 1630, 970, 860-840 cm$^{-1}$; anal. calc. for $C_{12}H_{18}O$ : C 80.89, H 10.11; found : C 80.94, H 10.02.

**Condensation of (1a) with (2c).** The experimental procedure was the same as the one reported for the acylation (1h at -80 °C). The crude product was distilled in three fractions (45-100 °C; 100-140 °C and 140-170 °C/ 0.2 Torr) and then purified by chromatography on silica gel. **(3f)** : $^{1}$H NMR ($\delta$/RSiMe$_3$)(CCl$_4$) d 6.80 (1, d. q. $J$ = 16.0, 6.4 Hz), 6.18 (1, d. $J$ = 16.0 Hz), 4.92 (2, br. s.), 1.83 (3, d. $J$ = 6.4 Hz), 1.57 (3, br. s.), 1.22 (3, s.), 0.83 (2, AB Pattern), 0.00 (9, s.); $^{13}$C NMR $\delta$ 201.8 (s), 148.5 (s), 142.3 (d), 126.2 (d), 112.3 (t), 54.8 (s), 23.7 (t), 22.5 (q), 20.4 (q), 18.1 (q), 0.5 (q); IR (film) 3090, 1680, 1610, 1250, 890, 840 cm$^{-1}$; anal. calc. for $C_{13}H_{24}OSi$ : C 69.64, H 10.71; found : C 69.80, H 10.80. **(7)** : $^{1}$H NMR ($\delta$/RSiMe$_3$) d 4.97 (2, br. s.), 4.77 (2, br. s.), 1.63 (3, br. s.), 1.00-0.7 (12, m.), 0.00 (9, s.); IR (film) 3075, 1700, 1635, 1250, 890, 860-835 cm$^{-1}$; mass spectrum *m/e* 251 (M$^{+}$ - $C_4H_9$)(0.6), 237 (0.5), 225 (1.5), 209 (1.5), 183 (4), 155 (9), 75 (10), 73 (100), 69 (70). **(8)** (two isomers) : $^{1}$H NMR ($\delta$/RSiMe$_3$)(CCl$_4$) $\delta$ 4.93 (2, br. s.), 4.73 (2, br. s.), 1.67 (6, br. s.), 1.57 (9, m.), 0.00 (9, s.); $^{13}$C NMR $\delta$ 213.5 and 213.3 (s), 151.0 (148.4, 148.1 (s), 112.4 and 111.2 (t), 56.4 and 56.36 (s), 43.90 and 43.85 (s), 38.15 and 38.10 (t), 36.7 and 36.3 (d), 26.4 and 26.3 (t), 24.1 and 24.06 (t), 22.9, 22.6, 20.4, 20.35 and 20.0 (q), 15.2 and 15.1 (q), 0.5 (q); IR (film) 3075, 1700, 1635, 1250, 890, 860-835 cm$^{-1}$; mass spectrum *m/e* 283 (0.2)(M$^{+}$ - 97), 225 (0.3), 209 (0.9), 155 (11), 73 (100).

**Cyclisation of (3b). Obtention of 2,3,4,4-tetramethyl-2-cyclopentenone (5).** Boron trifluoride etherate (2.7 g, 19 mmol) was added to a solution of **(3b)**(500 mg, 2.4 mmol) in $CH_2Cl_2$ (15 mL) and refluxed for 30 h. After cooling, the mixture was poured into ice. After decantation, the aqueous fraction was extracted with $CH_2Cl_2$. The combined organic layers were washed with sodium hydrogenocarbonate and then brine, dried ($MgSO_4$), evaporated. The crude product was purified by chromatography on silica gel (305 mg, 92 %). **(5)** : $^{1}$H NMR (CCl$_4$) $\delta$ 2.12 (2, s.), 1.90 (3, s.), 1.60 (3, s.), 1.17 (6, s.); $^{13}$C NMR $\delta$ 208.0 (s), 176.7 (s), 134.8 (s), 50.5 (t), 41.2 (s), 26.9 (q)(2C), 11.8 (q), 8.2 (q); IR (film) 1695, 1645, 1385, 1325 cm$^{-1}$; mass spectrum *m/e* 138 (44)(HRMS calcd for $C_9H_{14}O$ 138.1044, found 138.1045), 123 (100), 95 (64), 67 (31), 55 (22).

**Condensation of (1a) with (2b); Obtention of (9).** The general procedure was used. The reactive mixture was stirred at -80 °C for 1 h and then 18 h at -30 °C. **2,4-Dimethyl-2-vinylcyclopentanone (9)**(56 % yield) : bp 60 °C/ 0.2 Torr; $^{1}$H NMR $\delta$ 5.67 (1, d.d. $J$ = 16.4, 11.0 Hz), 4.93 (1, d. $J$ = 11.0 Hz), 4.78 (1, d. $J$ = 16.0 Hz), 1.17 (3, s.), 0.98 (3, d. $J$ = 5.0 Hz); $^{13}$C NMR $\delta$ 217.9 (s), 141.2 (d), 113.7 (t), 51.1 (t), 44.7 (t), 44.6 (s), 41.4 (d), 24.8 (q), 14.5 (q); IR (film) 3095, 1745, 1640, 1175, 920 cm$^{-1}$; mass spectrum *m/e* 138 (15)(HRMS calcd. for $C_9H_{14}O$ 138.1044, found 138.1035), 96 (18), 81 (12), 73 (17), 68 (100).

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[12] (a) Adventitious protic acid is invariably difficult to remove from such media.[13] But, curiously, no rearrangement was observed by use of anhydrous hydrochloric acid in $CH_2Cl_2$. Only β-chloro ketones resulting from hydrochloric acid addition were obtained. The rearrangement seems due to the presence of both traces of hydrochloric acid and $TiCl_4$ (for another example, see ref. 14) . (b) Ketones **4** were formed as the minor products during the formation of ketones **3**.

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