Molybdenum Pentachloride-Induced Reaction of Cyclopropyl-Substituted Carbonyl Compounds

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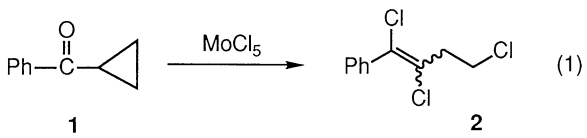
Synopsis. Molybdenum pentachloride induced the ring-opening reactions of cyclopropyl phenyl ketone or propyl 2-(trimethylsilylmethyl)cyclopropanecarboxylate to give 1-phenyl-1,2,4-trichloro-1-butene or *cis*-2-chloro-4-pentanolide, respectively.

Molybdenum pentachloride is an excellent reagent for *cis*-chlorination of olefins.[1] In our previous papers, molybdenum pentachoride has been disclosed to work well as a Lewis acid to cleave a carbon–oxygen bond of acetals in the reaction with vinylsilanes.[2] This characteristic is expected to be useful in the transformations of carbonyl compounds via molybdenum enolates. Ring-opening reactions of small-ring compounds provide a versatile synthetic method.[3] We herein report the molybdenum pentachloride-induced reactions of cyclopropyl-substituted carbonyl compounds.

Cyclopropyl phenyl ketone (**1**) was treated with molybdenum pentachloride in dichloromethane to give 1-phenyl-1,2,4-trichloro-1-butene (**2**). Ring cleavage[4] and chlorination are achieved by this procedure. An increase in the amount of molybdenum pentachloride raised the yield of **2** as shown in Table 1 (Eq. 1).



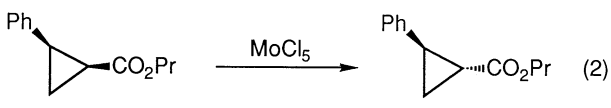
1 2 (1)

Table 1. Synthesis of **2**

$MoCl_5$/equiv	Time/h[a)]	Yield/% **2**
2	45	10
3	45	22
4	24	34

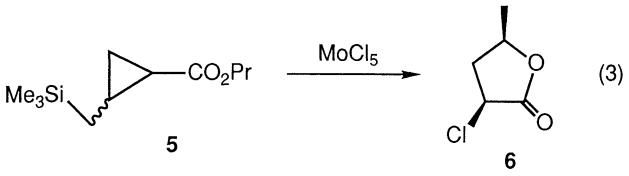
a) Reaction temperature, room temperature.

Propyl *cis*-2-phenylcyclopropanecarboxylate (**3**), however, did not undergo the ring-opening reaction under similar conditions, and was isomerized to the *trans* isomer **4** in 70% yield (Eq. 2). This result indicates that the reactivity of the ester function is lower towards molybdenum pentachloride.



3 4 (2)

On the contrary, it should be noted that the reaction of propyl 2-(trimethylsilylmethyl)cyclopropanecarboxylate (**5**) with molybdenum pentachloride led to desilylation and ring-opening lactonization giving *cis*-2-chloro-4-pentanolide (**6**) stereoselectively in 45% yield (Eq. 3).



5 6 (3)

Such a ring-opening reaction was not observed in the case of propyl 2-butyl-3-(trimethylsilyl)cyclopropanecarboxylate (**7**) even on treatment at 80 °C in DMF. The ester **7** was recovered quantitatively, suggesting that the presence of trimethylsilylmethyl group appears to facilitate ring opening as is the case with 1-[2-(trimethylsilylmethyl)cyclopropylcarbonyl]imidazole.[5]

The reaction scheme is explained by the intervention of an enolate intermediate based on the operation of molybdenum pentachloride as a Lewis acid, which is considered to be supported by the isomerization of **3** to **4**. Desilylative ring cleavage of **5** gives the enolate, which undergoes recyclization and *cis*-chlorination possibly with molybdenum pentachloride.[1] Chlorination seems to take place at the α- and γ-positions of the ketone **1**, being accompanied by the transformation of the ketone function to the corresponding olefinic chloride.

Molybdenum pentachloride is demonstrated to be a versatile Lewis acid with the capability of chlorination.

Experimental

IR and ^{1}H NMR spectra were recorded with Hitachi 270-30 and JEOL JNM-FX90Q spectrometers, respectively. Electron impact mass spectra were recorded with JEOL JMS-DX303 at the Faculty of Engineering, Osaka University.

The cyclopropanecarboxylates **3** and **5** were prepared according to the reported method.[6]

Synthesis of 1,2,4-Trichloro-1-phenyl-1-butene (2). To a solution of molybdenum pentachloride (1.37 g, 5.0 mmol) in dichloromethane (5.0 mL) was dropwise added cyclopropyl phenyl ketone (**1**, 0.183 g, 1.25 mmol) over 30 min at 0 °C. The mixture was warmed to room temperature and was stirred for 24 h. Ether (20 mL) and conc. HCl (2 mL) were added to the resulting mixture, which was extracted with ether (3×20 mL). The combined ethereal solution was washed with 10% aqueous $Na_2S_2O_3$ (10 mL), saturated aqueous NH_4Cl (10 mL), and brine (10 mL), dried ($MgSO_4$), and concentrated. GLC analysis (1.2 m PEG 20M 10% column, 180 °C) of the residue showed the formation of **2** (34%). **2** (*E* and *Z* mixture): IR (neat) 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$ with TMS, 90 MHz) δ=2.82 (t, 1.04H, J=6.9 Hz), 3.21 (t, 0.96H, J=6.9 Hz), 3.71 (t, 1.04H, J=6.9 Hz), 3.81 (t, 0.96H, J=6.9 Hz), 7.3—8.3 (m, 5H); MS m/z 238 (M^++4), 236 (M^++2), 234 (M^+). Anal. ($C_{10}H_9Cl_3$) C, H, Cl.

Synthesis of *cis*-2-Chloro-4-pentanolide (6). To a solution of molybdenum pentachloride (0.137 g, 0.50 mmol) was dropwise added propyl 2-(trimethylsilylmethyl)cyclopropanecarboxylate (**5**, 0.107 g, 0.50 mmol) over 5 min at 0 °C. The mixture was stirred at 0 °C for 5 min and then at room temperature for 20 h. Methanol aqueous solution (50%, 2 mL) was added to the reaction mixture, which was stirred at room temperature for 1 h and was extracted with ether (3×20 mL). The combined ethereal solution was washed with brine, dried (Na_2SO_4), and concentrated. GLC analysis (1.2 m PEG 20M 10% column, 150 °C) of the residue showed the formation of **6** (45% yield). **6:** IR (neat) 1780 cm^{-1}; ^1H NMR ($CDCl_3$ with TMS, 90 MHz) δ=1.46 (d, 3H, J=6.6 Hz), 2.33 (dd, 1H, J=8.5, 6.7 Hz), 2.48 (dd, 1H, J=5.6, 2.9 Hz), 4.43 (dd, 1H, J=6.7, 2.9 Hz), 4.89 (ddq, 1H, J=8.5, 6.6, 5.6 Hz); MS m/z 136 (M^++2), 134 (M^+). Anal. ($C_5H_7O_2Cl$) C, H, Cl.

Isomerization of Propyl *cis*-2-Phenylcyclopropanecarboxylate (3) to the *trans*-Ester 4. The reaction of **3** was carried out in a similar manner as mentioned above. The ester **4** was produced in 70% yield with the recovery (30%) of the starting ester **3**.

References

1) J. S. Filippo, A. F. Sowinski, and L. J. Romano, *J. Am. Chem. Soc.*, **97**, 1599 (1975).

2) T. Hirao, S. Kohno, J. Enda, Y. Ohshiro, and T. Agawa, *Tetrahedron Lett.*, **22**, 3633 (1981); T. Hirao, S. Kohno, Y. Ohshiro, and T. Agawa, *Bull. Chem. Soc. Jpn.*, **56**, 1569 (1983).

3) A. de Meijere, "Topics in Current Chemistry, Small Ring Compounds in Organic Synthesis I-IV," Springer-Verlag, Berlin (1986, 1987, 1988, 1990); D. Tunemoto and K. Kondo, *J. Synth. Org. Chem. Jpn.*, **35**, 1070 (1977).

4) L. Bagnell, A. Meisters, and T. Mole, *Aust. J. Chem.*, **28**, 821 (1975).

5) T. Hirao, D. Misu, and T. Agawa, *J. Chem. Soc., Chem. Commun.*, **1986**, 26.

6) T. Hirao, Y. Harano, Y. Yamada, Y. Hamada, S. Nagata, and T. Agawa, *Bull. Chem. Soc. Jpn.*, **59**, 1341 (1986).