A Facile Chloroformyloxylation Reaction of Olefins by Using the *N,N*-Dimethylformamide/Hydrogen Chloride/*m*-Chloroperbenzoic Acid System

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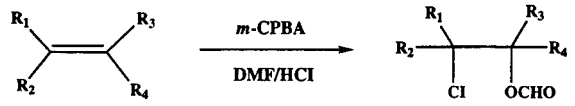
Chloroformyloxylation of olefins is synthetically useful in order to obtain bifuctionalities with regioselectivity.[1,2] Chloroformyloxylation can be achieved by the Vilsmeier reagent from epoxides,[3] or by positive chlorine source and *N,N*-dimethylformamide (DMF) from olefins.[1,2] We achieved the chloroformyloxylation of olefins by using the DMF/HCl/oxone system[2] which was proved to be one of the useful source[4] of positive chlorine ion (Cl^+). The chloroformyloxylation using oxone was heterogeneous and needed around 1 h to complete the reactions. When *m*-CPBA was used as an oxidant instead of oxone, we found the reaction was finished in a minute. Practically we could not detect any trace of olefins left in the reaction mixture by GC analysis after adding *m*-CPBA to the mixture. The results are summarized in Table 1.



I II

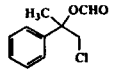
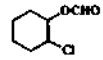
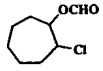
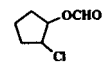
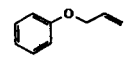
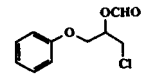
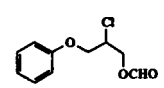
As soon as *m*-CPBA was added to a mixture of olefin I in DMF/HCl solution, the reaction mixture became pale yellow, and the color disappeared immediately. The reaction mixture was then poured into ice-water, extracted with ether and ethyl acetate, and the *m*-chlorobenzoic acid could be removed easily by washing twice with 5% sodium bicarbonate. The organic layer was concentrated to afford an almost pure chloroformyloxylated product **II** in excellent yields. We have monitored the reactions by GC to compare the *m*-CPBA system with the oxone system, and found that the *m*-CPBA system showed cleaner reactions than the oxone system. The mechanism of the reaction can be explained by the same way as that in the previous report.[2] According to the reaction mechanism, the products from the chloroformyloxylation must have trans configurations.[1c] In case of styrene (Entry 1), we could obtain only one regioisomer, which was identified to be 2-chloro-1-formyloxy-1-phenylethane by the analysis of ^1H-^{13}C heteroCOSY spectrum. The protons of chloromethyl at 3.77 ppm corresponded to the peak at 43 ppm in ^{13}C NMR, while the methine proton at 6.07 ppm corresponded to the peak at 74 ppm in ^{13}C NMR. In case of allyl phenol (Entry 6), a mixture of two regioisomers (1-chloro-2-formyloxy-3-phenoxy-propane and 2-chloro-1-formyloxy-3-phenoxy-propane) was obtained in a 57:43 ratio, which was determined by ^1H NMR. When double bonds conjugated with carbonyl groups were used as substrates under the same reaction conditions, α-chloro-α,β-unsaturated ketones were obtained previously.[5]

In conclusion, the DMF/HCl/*m*-CPBA reaction system is believed to be one of the most useful method for the chloroformyloxylation of olefins, considering its convenience, short reaction time, and good yields.

Experimental Section

General Procedure of Chloroformyloxylation. To a solution of olefin (3 mmol) in DMF (10 mL) was added DMF/HCl solution (1.8 mL, 3.6 mmol, 2 M HCl_{gas} in DMF) by a syringe, and *m*-CPBA (3.3 mmol, 50% Aldrich) was added to the reaction mixture in one portion. After stirring for 5 min, the reaction mixture was poured into an ice-water mixture, extracted with ether (100 mL) and ethyl acetate (100 mL). The combined organic layers were washed with 5% sodium bicarbonate (50 mL × 2) in order to remove *m*-chlorobenzoic acid. The organic layer was washed with brine, dried over magnesium sulfate, and concentrated to af-

Table 1. Chloroformyloxylations of Olefins by Using DMF/HCl/*m*-CPBA System

Entry	Olefin	Product	Yield[a] (%)
1			94
2			86
3			91
4			89
5			84
6			49[b]
			37[b]

[a] Isolated yields. [b] Combined yield was 86%, and the ratio was determined by ^1H NMR without separation of isomers.

ford a crude product. The crude product was purified by silica gel column chromatography (EtOAc/n-hexane, 1/10).

2-Chloro-1-formyloxy-1-phenylethane (Entry 1). ^{1}H NMR ($CDCl_3$) δ 3.77 (m, 2H), 6.07 (dd, *J*=5.05, 7.82 Hz, 1H), 7.35-7.50 (m, 5H), 8.12 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 43, 74, 127, 129, 129.5, 134, 160. IR (cm^{-1}) 1718, 1290, 1240, 1146, 1070. MS m/z (relative intensity) (EI, 70 eV) 184 (8.9, M^+), 183 (33.4), 148 (36.1), 145 (15.5), 107 (86.3), 84 (100), 77 (68).

2-Chloro-1-formyloxy-1-methyl-1-phenylethane (Entry 2). ^{1}H NMR ($CDCl_3$) δ 1.98 (s, 3H), 3.83 (d, *J*= 12.6 Hz, 1H), 3.99 (d, *J*=12.6 Hz, 1H), 7.25-7.57 (m, 5H), 8.08 (s, 1H). IR (cm^{-1}) 1718, 1485, 1440, 1380, 1159, 1055. MS m/z (relative intensity) (EI, 70 eV) 200 (0.7), 198 (2.9, M^+), 162 (1), 153 (17), 152 (25), 149 (25), 121 (73), 117 (26), 115 (30), 103 (32), 77 (28), 43 (100).

1-Chloro-2-formyloxycyclohexane (Entry 3). ^{1}H NMR ($CDCl_3$) δ 1.15-2.45 (m, 8H), 3.80-4.10 (m, 1H), 4.85-5.05 (m, 1H), 8.15 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 22.8, 24.0, 30.4, 34.3, 59.9, 75.3, 159.8. IR (cm^{-1}) 2950, 2895, 1725, 1455, 1177. MS m/z (relative intensity) (EI, 70 eV) 163 (3, M^++1), 134 (2), 86 (87), 84 (100), 81 (100), 80 (100), 57 (100).

1-Chloro-2-formyloxycycloheptane (Entry 4). ^{1}H NMR ($CDCl^3$) δ 1.40-2.35 (m, 10H), 4.00-4.20 (m, 1H), 5.05-5.20 (m, 1H), 8.10 (s, 1H). IR (cm^{-1}) 2850, 1720, 1445, 1161, 965, 873. MS m/z (relative intensity) (EI, 70 eV) 177 (3, M^++1), 147 (1), 95 (100), 86 (100), 84 (100), 68 (65).

1-Chloro-2-formyloxycyclopentane (Entry 5). ^{1}H NMR ($CDCl_3$) δ 1.60-2.40 (m, 6H), 4.15-4.30 (m, 1H), 5.20-5.30 (m, 1H), 8.02 (s, 1H). IR (cm^{-1}) 2980, 1685, 1422, 1309, 1255, 898, 755. MS m/z (relative intensity) (EI, 70 eV) 149 (16, M^++1), 141 (44), 140 (27), 139 (100), 138 (60), 111 (48), 84 (38).

1-Chloro-2-formyloxy-3-phenoxy-propane and 2-chloro-1-formyloxy-3-phenoxy-propane (Entry 6). ^{1}H NMR ($CDCl_3$) δ 3.78 (dd, *J*=5.57, 11.83 Hz, 0.57H), 3.82 (dd, *J*=5.16, 11.82 Hz, 0.57H), 4.13-4.19 (m, 2H), 4.35 (qui, *J*=6.43 Hz, 0.43H), 4.47 (dd, *J*=5.80, 11.83 Hz, 0.43H), 4.56 (dd, *J*=4.70, 11.83 Hz, 0.43H), 5.43 (qui, *J*=5.13 Hz, 0.57H), 6.88-7.33 (m, 5H), 8.05 (s, 0.43 H), 8.08 (s, 0.57 H).

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Selective Reduction of Ketones in the Presence of Aldehydes

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Selective reduction of ketones in the presence of aldehydes have been carried out successfully with sodium borohydride and catalytic amounts of lanthanide chlorides such as $CeCl_3$ or $ErCl_3$ in alcoholic solvents,[1-3] and with lithium tri-*t*-butoxyaluminohydride in ether solvents after preferential transformation of aldehydes into aldimines with *t*-butylamine.[4] When lanthanide salts are present, cyclohexanone was reduced in the presence of hexanal with excellent selectivity (100:2). However, the selectivity between other common aldehydes and ketones were generally not good. For example, 5-nonanone was reduced in the presence of benzaldehyde with only fair selectivity (84:17).[1] Recently we observed that 4-nitrobenzaldehyde readily forms acetal in methanol, in contrast to the sluggish formation of ketals from ketones. This prompted us to explore the possibility of selective reduction of ketones in the presence of aldehydes by preferential formation of acetals from aldehydes in the presence of ketones. First we studied the acetal and ketal formation of an equimolar mixture of benzaldehyde and 2-heptanone in the presence of catalytic amounts of HCl in methanol and methanol-ethanol mixtures. The results are summarized in Table 1. As shown in Table 1, the results in methanol-ethanol (6:1) were very promising for the selective reduction of ketones in the presence of aldehydes. We first attempted to use sodium borohydride for the ketone reduction, however sodium borohydride decomposed rapidly in the presence of catalytic amounts of HCl, and thus the reduction of ketone was not completed. Since borohydride exchange resin (BER) decomposes slowly in weakly acidic condition,[5] and has the advantage of simple work up,[5,6] BER was believed to be suitable for the selective reduction. We report here the selective reduction