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RUTHENIUM CATALYZED DECARBONYLATION OF ALKYL FORMATES

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Summary : Alkyl formates are efficiently decarbonylated to alcohols in the presence of $Ru_3(CO)_{12}$-$P(C_4H_9)_3$ at 180°C.

The chemistry of alkyl formates is gaining increasing interest owing to recent developments in homogeneous catalysis[1,2]. Methyl formate is the most common starting material for the production of formic acid and its derivatives as well as a promising building block in C_1 chemistry[3,4]. The homogeneous decarbonylation phenomenon has been investigated recently[5-7]. The catalysts are based on rhodium and iridium. However, the reaction was found to be a tedious procedure and the alcohol yields were vary variable ranging from poor to good depending on the formate in spite of the high temperatures used (200-220°C) and the long reaction times.

We examined recently the forward reaction in the presence of ruthenium catalysts in pyridine solution which were found to be an adequate system for the carbonylation of n-alcohols to the corresponding formates[8]. Interestingly, ruthenium complex catalytic systems were also utilized in the hydroesterification of olefins with formates[9]. The results of both investigations indicate a seemingly antagonistic effect of ruthenium (carbonylation *vs* decarbonylation) and prompted us to contemplate the behavior of alkyl formates in the presence of triruthenium dodecacarbonyl. To our knowledge, ruthenium catalysts have not been considered for the decarbonylation of formates hitherto.

$$HCOOR \longrightarrow CO + ROH$$

When n-butyl formate was heated with $Ru_3(CO)_{12}$ and $P(nC_4H_9)_3$ at 180°C for 8 hours at one atmosphere, in a closed system, n-butanol was formed in 75% yield. The pressure increase in the autoclave at the end of the run was 45 bar. The gas was taken, analyzed and found to have the following composition : CO(95%), CO_2(5%), butane (traces). The liquid phase contained only n-butanol and the unreacted formate. When the phosphine was omitted, the yield was only 39% with poor selectivity. The same procedure was applied to other formates. The results are listed in the Table (no optimization was made).

The results indicate that the ruthenium-phosphine catalytic system is quite appropriate for the decarbonylation of alkyl formates. Conversion is good or excellent, even with bulky alkyl groups (runs 6,7,9,11). The selectivity with respect to the alcohol is variable. In the methyl formate reaction, the yield of methanol is the poorest with only 40%. This yield is increased with increasing chain length and bulkiness of the alkyl part. Higher alkyl formates are in generally selectively decarbonylated to the corresponding alcohol (runs 5,6,8,10,11). In the particular case of benzyl formate (run 12), though

Table. Ruthenium catalyzed decarbonylation of alkyl formates HCOOR[a]

Run	R	Conversion %	Yield of alcohol %
1	CH_3	81	40
2	C_2H_5	74	59
3	nC_3H_7	74	67
4[b]	iC_3H_7	85	68
5	nC_4H_9	79	75
6	iC_4H_9	87	84
7	$CH(CH_3)C_2H_5$	96	83
8	nC_5H_{11}	89	89
9	iC_5H_{11}	97	88
10[b]	nC_7H_{15}	89	86
11[b]	cyclohexyl	66	61
12	$CH_2C_6H_5$	93	41

[a] Formate (25-30 mmol), $Ru_3(CO)_{12}$ (0.2 mmol), $P(C_4H_9)_3$ (0.4 mmol), T(180°C), t(8h), no applied pressure

[b] Formate (20 mmol), $Ru_3(CO)_{12}$ (0.08 mmol), $P(C_4H_9)_3$ (0.16 mmol), t(10h).

conversion is excellent, benzyl alcohol is formed in only 41% yield. In contrast with earlier investigations based on rhodium and iridium catalysis[5,6] toluene and benzaldehyde resulting respectively from decarboxylation of the formate and dehydrogenation of the alcohol are formed in minor amounts.

In conclusion, $Ru_3(CO)_{12}$-tributylphosphine is an appropriate catalytic system for the decarbonylation of formates. The present results are among the most convincing obtained in homogeneous catalysis.

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