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# RHODIUM CARBONYL-2-METHOXYETHANOL. AN EFFECTIVE CATALYTIC SYSTEM FOR THE DECARBONYLATION OF FORMATE ESTERS.

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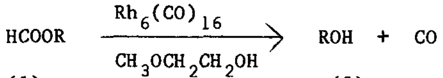
Summary: The decarbonylation of formate esters to alcohols can be attained in good yields using rhodium carbonyl as the catalyst and added 2-methoxyethanol.

Metal catalyzed reactions of formate esters have attracted considerable interest in recent years. Of potential value is the decarbonylation of formate esters to alcohols. For example, methyl formate is an intermediate in $C_1$ chemisty[2,3]. Recently, we described the use of chlorocarbonylbis(triphenylphosphine)iridium(I) [Vaska's complex] as a catalyst for the decarbonylation reaction. Reasonable yields of alcohols result on exposure of a formate ester to a catalytic amount of the iridium(I) complex at 180-240°C and one atmosphere [60-130/1 ratio of formate/catalyst][4]. However, this reaction has two limitations: (i) methyl formate, commercially the most important formate ester, is not effectively decarbonylated to methanol and carbon monoxide; (ii) appreciable quantities of elimination products result when secondary formates [e.g., 2-octyl formate] are used as reactants. We now wish to report that the use of rhodium carbonyl as a catalyst, together with 2-methoxyethanol, overcomes both of these limitations.

When methyl formate [1,R=$CH_3$] was heated with rhodium carbonyl [200/1 ratio of 1/$Rh_6(CO)_{16}$] at 220°C for 22 hours at one atmosphere in an autoclave, methanol was formed in 72% yield. The beneficial effect of 2-methoxyethanol was found previously in the ruthenium carbonyl and phase transfer catalyzed reduction of nitro compounds[5]. When the methyl formate reaction was repeated with added 2-methoxyethanol, nearly the same yield of methanol resulted after only 8 hours. The rhodium carbonyl 2-methoxyethanol system is superior to rhodium carbonyl alone for the decarbonylation of ethyl, n-butyl, and n-octyl formate (Table 1). The results using secondary formates [s-$C_4H_9$, 2-$C_7H_{15}$] as reactants are especially gratifying with decarbonylation occurring in fine yields, accompanied by only small amounts of olefins as by-products. Only in the case of benzyl formate is the rhodium carbonyl-2-methoxyethanol catalytic system of no appreciable advantage when compared with Vaska's complex.



$$HCOOR \xrightarrow[CH_3OCH_2CH_2OH]{Rh_6(CO)_{16}} ROH + CO$$

(1) (2)

This decarbonylation reaction may proceed via oxidative addition of the rhodium cluster, or an in situ generated lower nuclearity rhodium complex (e.g., monomer), to the carbon-hydrogen bond of the formate followed by decarbonylation. Indeed, Milstein[6] has recently isolated a complex from the insertion of rhodium of chlorotris(trimethylphosphine)rhodium(I) into the C-H bond of methyl formate. Decarbonylation of the complex at elevated temperature afforded methanol as the principal product. Such an oxidative addition-decarbonylation-reductive elimination pathway was also proposed for the decarbonylation of formate esters catalyzed by Vaska's complex[4].

TABLE 1. $Rh_6(CO)_{16}$ Catalyzed Decarbonylation of Formate Esters[a]

| HCOOR,R= | 2-Methoxyethanol | T,°C | Reaction time, hr. | Products,%[b] |
|---|---|---|---|---|
| $CH_3$ | No | 220 | 22 | 2,72; 1,16 |
| | Yes | 220 | 8 | 2,69; 1,14 |
| $C_2H_5$ | No | 200 | 48 | 2,42; 1,47; $(C_2H_5)_2O$, 7 |
| | Yes | 220 | 22 | 2,76; 1,20 |
| | Yes | 220 | 60 | 2,94; $(C_2H_5)_2O$,4 |
| n-$C_4H_9$ | No | 210 | 41 | 2,65; 1,20 |
| | Yes | 210 | 30 | 2,94 |
| 2-$C_4H_9$ | Yes | 210 | 24 | 2,67; 1,9; olefins, 4 |
| 2-$C_7H_{15}$ | Yes | 220 | 24 | 2,84; 1,10; olefins, 4 |
| | Yes | 220 | 42 | 2,93; olefin, 4[c] |
| n-$C_8H_{17}$ | Yes | 220 | 42 | 2,88; 1,10[c] |
| $PhCH_2$ | No | 200 | 17 | 2,5; 1,22; $PhCH_3$,44; $(PhCH_2)_2$, 20 |
| | Yes | 200 | 8 | 2,40; $PhCH_3$, 35; PhCHO, 17. |

[a] 200/1 ratio of 1/$Rh_6(CO)_{16}$. [b] gas chromatographic yields. [c] isolated yields.

The following general procedure was used: a mixture of the formate ester [12 mmol] and $Rh_6(CO)_{16}$ [0.06 mmol] in 2-methoxyethanol [3 mL.] was heated in an autoclave (no applied pressure) at 200-220°C (see Table 1 for reaction times). The alcohol was isolated by distillation.

In conclusion, rhodium carbonyl and 2-methoxyethanol can effect the decarbonylation of formate esters by an exceptionally simple procedure. The reaction is applicable to methyl as well as secondary formates.

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## References

1. John Simon Guggenheim Fellow, 1985-86; Killam Research Fellow, 1986-88.
2. W. Keim, Pure Appl. Chem., 58, 825 (1986).
3. T. Ikaraski, Chem. Econ. Eng. Rev., 12, 31 (1980).
4. H.A. Zahalka, H. Alper and Y. Sasson, Organometallics, 5, 2497 (1986).
5. H. Alper and S. Amaratunga, Tetrahedron Lett., 21, 2603 (1980).
6. D. Milstein, J. Am. Chem. Soc., 108, 3525 (1986).

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