Fluoride-induced Activation of Molybdenum Hexacarbonyl: Formation of Esters and Lactones from Alkyl Iodides

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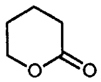
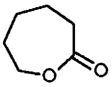
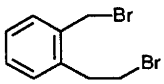
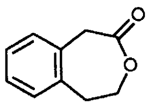
In the presence of fluoride ion, alkyl iodides RI are carbonylated by molybdenum hexacarbonyl to esters RCO_2R, and diiodides lead to good yields of the corresponding lactones.

Although a variety of organometallic complexes in which a transition metal in a low oxidation state is bound to fluorine have been characterized,[1] the synthetic potentialities offered by fluoride-induced reactions of metal carbonyls have been scarcely investigated. Fluoride ion is known to react with metal carbonyls of group 6[2–4] and group 7[5] in solution, or with iron pentacarbonyl in the gas phase,[6] leading to fluoro complexes. The nucleophilic reactivity of fluoride ion with iron, manganese or cobalt carbonyls has been used to generate metal carbonyl anions.[7] We report here a new carbonylation reaction effected by molybdenum hexacarbonyl in the presence of fluoride ion, eqn. (1).

$$RI \xrightarrow{Mo(CO)_6,\ (Bu_4N^+F^-,\ 3H_2O)} RCO_2R \qquad (1)$$

To our knowledge no carbonylation reaction using molybdenum hexacarbonyl or a metal carbonyl of the same group has been reported.[8] Another unusual feature of this reaction is that both R groups of the ester molecule are furnished by an electrophilic reagent, while the oxygen atom appears to come from a water molecule.

Table 1 Synthesis of esters and lactones from alkyl halides, molybdenum hexacarbonyl and fluoride ion

Halide	Method[a]	Ester or lactone[b]	Isolated yield (%)
$n\text{-}C_8H_{17}I$	A	$(n\text{-}C_8H_{17})\text{-}CO_2\text{-}(n\text{-}C_8H_{17})$	91
	C		70
$I(CH_2)_4I$	B		69
	B[c]		70
$I(CH_2)_5I$	B		67
	B		50

[a] Method A: tetrabutylammonium fluoride trihydrate (20 mmol), molybdenum hexacarbonyl (10 mmol), alkyl halide (10 mmol), in tetrahydrofuran (50 ml), reflux 20 h. After cooling the reaction mixture was poured in a saturated $FeCl_3$ solution and extracted with pentane. Method B (lactone synthesis): the diiodide (10 mmol) was slowly added to the refluxing solution containing the other reactants [tetrabutylammonium fluoride trihydrate (40 mmol), molybdenum hexacarbonyl (20 mmol), in THF (100 ml)]. After 20 h reflux the cooled reaction mixture was stirred with diethyl ether (150 ml), filtered from the insoluble material, concentrated and chromatographed on silica. Method C (catalytic in molybdenum): alkyl halide (5 mmol), molybdenum hexacarbonyl (0.5 mmol), methyl formate (25 mmol), tetrabutylammonium fluoride trihydrate (10 mmol), in THF (30 ml), 2 d at 40 °C then 2 d at 60 °C; workup as in method A. [b] The identity of the products was ascertained by comparison of their spectroscopic and analytical data with those of authentic samples. [c] KF + 18-crown-6 (2 equiv. each per diiodide equiv.) was used as fluoride source.

The results are summarized in Table 1. If a diiodoalkane is used as the substrate, the reaction leads to a lactone, which is obtained in a good yield even in the relatively difficult case involving a seven-membered ring closure.[9] The last entry shows that carbonylation occurs selectively on the most reactive site of the dihalide.

Experiments performed without fluoride ion demonstrated the specific role played by the fluoride ion in this reaction: reaction of 1-iodooctane under the same conditions as above but using tetrabutylammonium iodide instead of fluoride led to complete recovery of the starting material; tetrabutylammonium bromide and hydroxide gave only nucleophilic substitution leading respectively to octyl bromide and octanol.

If the carbonylation of 1-iodooctane was performed in dioxane instead of tetrahydrofuran (THF), dioctyl ketone $n\text{-}C_8H_{17}\text{-}CO\text{-}n\text{-}C_8H_{17}$ was obtained as a byproduct (16%) besides octyl nonanoate (84%).

Although commercial trihydrated tetrabutylammonium fluoride appeared as the most convenient source of fluoride, other reagents were also efficient: with tetrabutylammonium hydrogen difluoride[10] or potassium fluoride in the presence of 18-crown-6,[11] octyl nonanoate was obtained with respective yields of 59% and 60%; in the case of valerolactone the latter reagent was as efficient as trihydrated tetrabutylammonium fluoride (Table 1). This indicates that the water molecule required for ester formation can be used at the final hydrolysis stage.

In order to make the reaction catalytic in molybdenum, methyl formate was added to the reaction medium so as to provide the stoichiometric amount of carbon monoxide necessary for ester formation; under these conditions, a good yield of ester was obtained when using 0.1 equiv. of molybdenum hexacarbonyl relatively to 1-iodooctane (Table 1). Methyl formate had been shown to behave as an efficient CO source against dinitrogen complexes of iron[12] and molybdenum.[13] The global transformation resulting in the molybdenum catalysed reaction is shown in eqn. (2).

$$2\,RI + HCO_2Me + H_2O \xrightarrow{Mo(CO)_6,\ F^-} RCO_2R + 2\,HI + MeOH \qquad (2)$$

This reaction could be thought to require only a catalytic amount of fluoride. However, use of 0.1 equiv. of fluoride ion (relative to 1-iodooctane) did not yield a sizeable amount of ester. This is probably due to the stoichiometric release of protons occuring in the reaction, which converts the fluoride ions into less reactive $(HF)_nF^-$ species.[14] In order to make the reaction catalytic in fluoride, we are now trying to add a base which would consume these protons without disturbing the progress of the reaction.

The mechanism of this reaction is currently under investigation. Reaction of molybdenum hexacarbonyl with fluoride ion is known to lead to two possible anionic species whose salts have been isolated and characterized: $Mo(CO)_5F^-$ ion[2] or $Mo_2(CO)_6F_3^{3-}$ ion.[4] Work is in progress to determine if these anionic fluoro complexes are formed in the first stage of ester formation and to isolate or trap subsequent intermediates involved in this reaction.

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References

1 For a review: N. M. Doherty and N. W. Hoffman, *Chem. Rev.*, 1991, **91**, 553.
2 W. Douglas and J. K. Ruff, *J. Organomet. Chem.*, 1974, **65**, 65; E. C. Alyea, A. Malek and J. Malito, *Inorg. Chim. Acta*, 1985, **101**, 147.
3 J. L. Cihonski and R. A. Levenson, *Inorg. Chem.*, 1975, **14**, 1717; R. N. Bagchi, A. M. Bond, R. Colton, D. L. Luscombe and J. E. Moir, *J. Am. Chem. Soc.*, 1986, **108**, 3352.
4 J. F. White and M. F. Farona, *J. Organomet. Chem.*, 1972, **37**, 119.
5 J. L. Cihonski and R. A. Levenson, *Inorg. Chim. Acta*, 1976, **18**, 215.
6 K. R. Lane, L. Sallans and R. R. Squires, *J. Am. Chem. Soc.*, 1985, **107**, 5369.
7 H. Alper and L. C. Damude, *Organometallics*, 1982, **1**, 579.
8 H. M. Colquhoun, D. J. Thompson and M. V. Twigg, *Carbonylation (Direct Synthesis of Carbonyl Compounds)*, Plenum Press, New York, 1991.
9 S. M. Roberts, in *Comprehensive Organic Chemistry*, ed. I. O. Sutherland, Pergamon Press, Oxford, 1979, vol. 2, p. 770.
10 Tetrabutylammonium hydrogendifluoride was prepared according to: D. Landini, H. Molinari, M. Penso and A. Rampoldi, *Synthesis*, 1988, 953. It has been shown to be an efficient nucleophilic fluorinating agent: P. Bosch, F. Camps, E. Chamorro, V. Gasol and A. Guerrero, *Tetrahedron Lett.*, 1987, **28**, 4733.
11 C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, 1974, **96**, 2250; J. Cuomo and R. A. Olofson, *J. Org. Chem.*, 1979, **44**, 1016.
12 H. Felkin, P. W. Lednor, J. M. Normant and R. A. J. Smith, *J. Organomet. Chem.*, 1978, **157**, C64.
13 T. Tatsumi, H. Tominaga, M. Hidai and Y. Uchida, *J. Organomet. Chem.*, 1981, **215**, 67.
14 D. Landini, A. Maia and A. Rampoldi, *J. Org. Chem.*, 1989, **54**, 328; C. Rieux, B. Langlois and R. Gallo, *C. R. Acad. Sci. Paris*, 1990, **310**, 25.