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SYNTHESIS OF 2-BUTANONE FROM ETHYLENE AND METHYL FORMATE CATALYSED BY RHODIUM-IODIDE COMPLEXES

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Abstract: *Methyl formate reacts with ethylene and carbon monoxide to give mainly 2-butanone, in the presence of a rhodium catalyst with an ionic iodide as promotor*

In the last years, methyl formate has been the subject of particular attention, owing to the fact that it can be considered as a source of carbon monoxide and methanol[1] according to :

$$HCOOCH_3 \xrightleftharpoons{NaOCH_3} CO + CH_3OH$$

Thus, it is a convenient building block in C_1 chemistry[2].

Among the reactions most studied can be mentioned the direct hydroesterification of alkenes by methyl formate with ruthenium[3] or palladium[4] catalysts which leads to saturated esters :

$$CH_2{=}CH_2 + HCOOCH_3 \xrightarrow[CO]{Ru,Pd} CH_3CH_2COOCH_3$$

In this context, we have examined this reaction and observed a drastic change of selectivity by using rhodium catalysts when associated with an ionic iodide promotor, instead of Ru or Pd under these conditions, methyl ketones become the major products.

We report here the first results on this reaction which, to our knowledge, has never been described, either from methyl formate or from CO-CH_3OH mixtures.

In a typical reaction, a solution of $HCOOCH_3$ in N-methylpyrrolidone (NMP) is allowed to react in an autoclave with a CO/C_2H_4 mixture (1/1, total pressure 80 bar) at 180°C in the presence of $RhCl_3,3H_2O$ and LiI to give mainly methylethylketone and CO_2 according to the following equation :

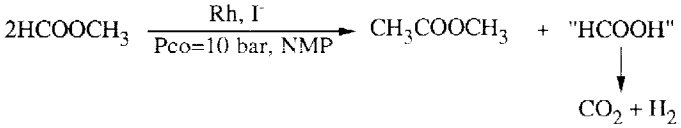
$$HCOOCH_3 + CH_2{=}CH_2 + CO \xrightarrow[P=80\ \text{bar},\ T=180°C]{RhCl_3\text{-}I^-} CH_3CH_2COCH_3 + CO_2$$

Table 1, which lists some typical results obtained under various conditions, shows that the nature of the rhodium salt or complex is not very important but that the halide promotor must solely be ionic iodide $A^+ I^-$ (A^+ = alkali metal ion or $CH_3PPh_3^+$). Indeed, in the presence of CH_3I, well known to be used in carbonylation reactions, methyl acetate and acetic acid become the major products. In the same way with LiBr a large part of HCOOMe is decomposed into $CH_4 + CO_2$.

The nature of the solvent has also a large influence on the reactivity, as other solvents like amides lead mainly to acetic acid ; the best activities and selectivities are only obtained in NMP.

On the other hand, the table shows that by-products always appear, mainly methyl acetate, propionaldehyde, diethylketone and methanol.

Methanol results probably from a partial decarbonylation of $HCOOCH_3$. Methyl acetate is selectively obtained, under these reaction conditions, in the absence of ethylene (cf entry 1), as recently reported[5].



$$2HCOOCH_3 \xrightarrow[Pco=10\ \text{bar, NMP}]{Rh,\ I^-} CH_3COOCH_3 + \text{"HCOOH"} \downarrow CO_2 + H_2$$

The classical hydroformylation of ethylene gives propanal. The hydrogen necessary for its production must therefore be produced from methanol (cf entry 10) or by decomposition of HCOOH ($HCOOH \longrightarrow CO_2 + H_2$).

Table 1 : Reaction of alkyl formates[a] and ethylene catalysed by rhodium-iodide systems[b]

N°	Reaction conditions	Conv. (c) mol (%)	Product Selectivity vs HCO_2R (*vs* C_2H_4)					
			EtCOMe	EtCHO	AcOMe	Et_2CO	$EtCO_2Me$	ROH
1	LiI=3 mmol, NMP=30cm^3 $P_{C_2H_4}$=0bar, Pco=40bar,t=4h	83	0	0	92	0	0	3.5
2	LiI=3 mmol, NMP=30cm^3 $P_{C_2H_4}$=40bar, Pco=40bar,t=4h	89	39*(58)*	13*(19)*	17	12	4	12
3	PPh$_3$MeI=3 mmol, NMP=30 cm^3 $P_{C_2H_4}$=40bar, Pco=40bar,t=4h	65	38*(53)*	17*(23)*	17	14	3.5	7
4	PPh$_3$MeI=3 mmol, NMP=13 cm^3 PPh$_3$=0.15mmol $P_{C_2H_4}$=40bar, Pco=40bar,t=4h	55	50*(61)*	17*(21)*	12	12	3	6
5	CH$_3$I=3 mmol, NMP=30 cm^3 $P_{C_2H_4}$=40bar, Pco=40bar,t=4h	52	0	8.1	81[d]	0	0	2
6	LiI=3 mmol, NMP=0 $P_{C_2H_4}$=40bar, Pco=40bar,t=4h	56	17*(32)*	33*(62)*	38	3	0	9
7	PPh$_3$MeI=3 mmol, NMP=30 cm^3 PPh$_3$=0.15mmol $P_{C_2H_4}$=40bar, Pco=40bar,t=5h	59	48*(61)*	17*(21.6)*	15	10	3.5	6
8	LiI=3 mmol, NMP=30cm^3 $P_{C_2H_4}$=50bar, Pco=10bar,t=3h	88	17*(84.5)*	1.9	57.1	1.2	0.1	21.5
9	LiI=3 mmol, NMP=30cm^3 $P_{C_2H_4}$=10bar, Pco=50bar,t=3h	80	13*(25)*	35*(67)*	21	1.3	2.9	23
10	LiBr=4.1mmol, NMP=30cm^3 $P_{C_2H_4}$=40bar, P_{CO}=40bar,t=4h	80[e]	29	6	28	9.5	15.6	11.1
11	LiI=3 mmol, NMP=30cm^3 MeOH=130mmol $P_{C_2H_4}$=40bar, Pco=40bar,t=4h	25	6.3	73.4	4	14	2	—
12	LiI=4.1 mmol, NMP=30cm^3 $P_{C_2H_4}$=30bar, Pco=30bar,t=4h	84	---	5.3	—	42.2	---	52.5
13	PPh$_3$MeI=3 mmol $P_{C_2H_4}$=30bar, Pco=30bar,t=4h	35	---	9.5	—	74	—	12

a)R=Me entries 1 to 10, R=Et entries 12 and 13

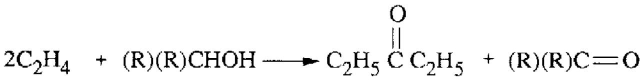
b)$RhCl_3,3H_2O$= 0.114 mmol, except entries 10, 11 and 12 ($RhCl_3,3H_2O$= 0.143mmol) and entry 7 ($[RhCl(CO)_2]_2$ =0.114 mmol) T=180°C except entry 11 (T=210°C) HCO_2R=130 mmol except entries 6 (260 mmol) and 11 (0 mmol)

c) Conversion vs HCO_2R

d) AcOMe=18%, AcOH=63%

e) In these conditions about 60% of HCOOMe is decomposed into CH_4+CO_2, whereas in the others cases this decomposition is less than 5%

Diethyl ketone may be obtained from CH_3OH and C_2H_4 according to a similar reaction described by Sneeden et al[6] in which the alcohol is the hydrogen source.



$$2C_2H_4 + (R)(R)CHOH \longrightarrow C_2H_5\overset{\overset{\displaystyle O}{\|}}{C}C_2H_5 + (R)(R)C{=}O$$

In the case of CH_3OH, formaldehyde should also be formed as by-product but it is further decomposed by temperature It has also to be noticed that in our reaction conditions, the use of CH_3OH instead of $HCOOCH_3$ (entry n°10) gives a much lower reactivity and propanal becomes the main product. This seems to confirm the hydrogen donor character of $HCOOCH_3$.

Finally, we have observed that the activity decreases by increasing the bulkyness of the alkyl formate. In the case of ethyl formate, the selectivity towards diethyl ketone increases but this observation can be linked to the fact that this ketone can be obtained by two ways : the direct reaction of HCOOEt with C_2H_4 or the reaction of ethanol (resulting from decarbonylation of formate) with C_2H_4.

The lack of reactivity of methanol and CO compared to that of methyl formate clearly shows that this compound does not always react as a CO + CH_3OH mixture, but is also able to display its own reactivity, which confers to this molecule a further interest[7].

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