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HYDROACYLATION OF OLEFINS

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Summary

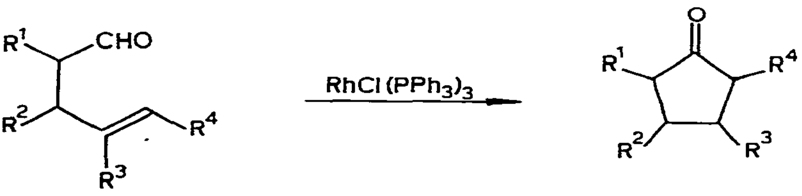
Diethyl ketone, methyl ethyl ketone and dipropyl ketone may be formed, albeit in modest yields, by the ruthenium catalyzed hydroacylation of ethylene and propylene with propionaldehyde, acetaldehyde and butyraldehyde, respectively. The major side reactions consist of aldehyde Cannizzaro and Tishchenko-type transformations as well as aldolizations. Preliminary mechanistic studies have revealed the promoting influence of water in the formation of Ru-carboxylates, $RuH(OCOC_2H_5)L_3$, from propionaldehyde and H_2RuL_4.

Introduction

The formation of dialkyl ketone by-products in the alkoxycarbonylation of olefins with primary alcohols and CO has been interpreted in terms of an intermolecular addition of the corresponding aldehyde to the olefin, eq. 1 [1] (hydroacylation reaction).

$$RCH_2OH \xrightarrow{cat} RCHO \xrightarrow[cat]{C_2H_4} RCOCH_2CH_3 \quad (1)$$

Numerous intramolecular hydroacylation reactions have been reported [e.g. 2 to 5]. Thus various unsaturated aldehydes, particularly those containing the 4-pentenal-1 skeleton [5], undergo smooth cyclisation in the presence of soluble rhodium catalysts to the corresponding cyclic ketone as outlined in eq. 2.



(2)

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However, apart from a brief mention of the synthesis of 2-nonanone, from acetaldehyde and 1-heptene (eq. 3) [7], attempts to bring about the intermolecular addition of aldehydes to olefins seem so far to have been unsuccessful [e.g. 2, 3, 5].

$$\mathrm{CH_3CHO + C_5H_{11}CH{=}CH_2 \xrightarrow[\text{or } Pt(PPh_3)_4]{RhCl(PPh_3)_2} C_7H_{15}COCH_3} \qquad (3)$$

We now report the formation of dialkyl ketones by the ruthenium catalyzed intermolecular addition of an aldehyde to an olefin, albeit in low yields.

Results and discussion

The results summarized in Table 1 (run 1) show that in the absence of solvent the products from the reaction of propionaldehyde and ethylene, in the presence of $\mathrm{RuCl_2L_3}$ consist of diethyl ketone (DEK) together with unreacted aldehyde and its transformation products. Most of the aldehyde apparently undergoes aldolization reactions to give, for example, 2-methyl-2-pentenal-1. The use of a solvent alone (Table 1, run 2) or in conjunction with a modification of the aldehyde/ethylene ratio (run 3) causes a substantial drop in the overall activity of the system. The hydroacylation of propene, with 1-butyraldehyde may also be effected with $\mathrm{Cl_2RuL_3}$, but the use of hexane or toluene as solvent (runs 4 and 5) again leads to low productivities.

n-Propanol and propionic acid could be formed by a ruthenium catalyzed Cannizzaro-type reaction, as described by Maitlis et al. [8], and the propylpropionate by a ruthenium catalyzed Tishchenko-type reaction as observed by Horino et al. [9,10]. In either case hemiacetal (hydrate)-type intermediates formed in the rapid reversible reaction (eq. 4), R′ = H or alkyl, could be involved [cf. 11].

$$\mathrm{RCHO + R'OH \rightleftharpoons RCH}\begin{matrix}\mathrm{OH}\\ \mathrm{OR'}\end{matrix} \qquad (4)$$

The formation of the ketonic products (diethyl ketone, methyl ethyl ketone,

TABLE 1

HYDROACYLATION OF ETHYLENE AND PROPYLENE CATALYZED BY $\mathrm{RuCl_2(PPh_3)_3}$ (autoclave, 300 ml)

Experiment No.	RCHO (mmol)	Olefin	N_2 (bar)	Solvent (ml)	Temp (°C)/ Time (h)	Ketone (mmol)
1 [a]	R = Et (1100)	C_2H_4 10 b	–	–	210/18	Pentanone-3 (23)
2 [b]	R = Me (77)	C_2H_4 24 b	78	Toluene 80	180/8	Butanone-2 (1.7)
3 [b]	R = Me (125)	C_2H_4 12 b	88	Toluene 80	180/8	Butanone-2 (0.5)
4 [b]	R = Pr^n (65)	C_3H_6 260 mmol	90	Toluene 80	220/8	Heptanone-4 (2.6) [c]
5 [b]	R = Pr^n (64)	C_3H_6 240 mmol	100	Hexane [d] 80	220/8	Heptanone-4 (0.3) [c]

[a] Catalyst (0.10 mmol). [b] Catalyst (0.52 mmol). [c] 2-Methylhexanone-3 also present in lesser quantities. [d] Black precipitate formed.

dipropyl ketone (runs 1 to 5)) on the other hand implies acyl-metal intermediates, produced by the "oxidative addition" of the aldehyde to the metal centre, as proposed for the aldehyde decarbonylation reaction [12]. The exact products formed by the interaction of aldehydes and certain ruthenium complexes H_2RuL_4 and $HClRuL_3$ remain a subject of controversy [13,9,14–16]. In order to obtain further information concerning the formation of the ester and ketonic products we studied the reaction of propionaldehyde with H_2RuL_4 and $HClRuL_3$. We confirmed the catalytic formation of propylpropionate, and under our reaction conditions in the case of H_2RuL_4, the only pure organometallic complex isolated was the carboxylate $RuH(O_2CEt)L_3$ [13] (see Experimental). We further noted that in ketonic solvents traces of water greatly favoured the formation of the carboxylato-compound, in accord with aldehyde hydrate intermediates (eq. 4). Further investigations in this area are in progress.

Experimental (with the collaboration of Mr.B. Béguin (CNRS) and Mr. M. Renaud (PCUK))

All reactions were carried out either in glass-lined 300 ml Autoclave Engineers autoclaves equipped with Magnedrive units or in Fischer and Porter type glass pressure vessels equipped with magnetic stirring bars. The organometallic compounds $RuCl_2L_3$ [17], RuH_2L_4 [18], and $RuHClL_3$ [19] were prepared by literature methods, and the aldehydes were carefully distilled under argon before use.

The products were analyzed either directly (gas-phase) or after total distillation (liquid phase) by vapour-phase chromatography (VPC) or by VPC mass spectrometry [20]: gaseous products CO, CO_2, H_2O on Carbosieve B and Porapak Q columns; organic compounds Porapak Q and R columns.

Thus in a typical run the catalyst ($RuCl_2(PPh_3)_3$, 0.10 mmol) and propanal (1100 mmol) contained in the glass-liner were introduced under argon into the autoclave. The olefin (10b) was added subsequently. After 18 h at 210°C the cooled autoclave was vented and the organic material recovered by distillation under vacuum. The products, were quantitatively analyzed by VPC and identified by VPC/MS [20] included pentanone-3 (23 mmol), propylpropionate (75 mmol), propanol-1 (30 mmol) and propionic acid (110 mmol), together with the aldolisation product 2-methyl-2-pentenal (310 mmol). The yields of ketones obtained with other aldehydes and ethylene or propylene are given in Table 1.

$RuHCl(PPh_3)_3$ with propanal

A stirred solution of $RuHCl(PPh_3)_3$ (0.165 mg) in benzene (15 ml) containing freshly distilled propanal (2 ml) was heated under reflux under argon for 7 h. The cooled solution was distilled under vacuum; VPC/MS analysis [20] indicated the presence of n-propylpropionate (0.96 mmol, 60% based on aldehyde) as the major product.

$RuH_2(PPh_3)_4$ and propanol in acetone, cf. [18]

A suspension of $RuH_2(PPh_3)_4$ (0.27 g) in distilled acetone (10 ml) containing propanal (35 μl) was stirred at room temperature under argon for 3.5 h. The yellow precipitate (0.12 g) was isolated by filtration under argon, washed with hexane, dried (h.v.), and identified as $RuH(OCOEt)(PPh_3)_3$ by comparison of its IR spectrum with that of an authentic specimen [21]: ν_{max} 2020 (MH), 1520, 1460 (MOCOR) cm^{-1}; ^{1}H NMR δ −18.75 ppm (q, *J* 27 Hz, M–H coupled to phosphine); 0.41 (t), 1.41 (q) CH_3CH_2: addition of CF_3COOH gave δ 1.15 (t), 2.4 (q) ppm corresponding to CH_3CH_2 in free propionic acid [22].

$RuH_2(PPh_3)_4$ and propanal in methyl ethyl ketone, influence of water

No reaction was observed between RuH_2L_4 (0.33 g) and propanal (25 μl) after stirring at room temperature in methyl ethyl ketone (10 ml dried over molecular sieves) under argon, 4 h: the recovered solid had an IR spectrum (ν_{max} 2080 cm^{-1} M–H) identical with that of the starting material.

$RuH_2(PPh_3)_4$ (0.27 g) was stirred at room temperature under argon for 4 h in the same methyl ethyl ketone (10 ml) containing propanal (20 μl) and water (50 μl). The yellow solid (0.11 g) which was isolated by filtration under argon, washed with hexane and dried (h.v.) was identified as $RuH(OCOEt)(PPh_3)_3$ by comparison (IR and NMR spectra) with an authentic specimen [21].

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