

HYDROGEN TRANSFER FROM FORMYL COMPOUNDS TO
 α,β -UNSATURATED KETONES CATALYZED BY Ru, Rh AND Ir COMPLEXES

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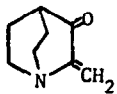
In a previous communication¹ we reported that $\text{RuCl}_2(\text{PPh}_3)_3$ catalyzed the hydrogen transfer from carbinols to α,β -unsaturated ketones: $\text{>C=C-O} + \text{RCH}_2\text{OH} \rightarrow \text{>CH-CH-O} + \text{RCHO}$. We find now that the aldehydes, so formed, are by themselves active hydrogen donors, capable of replacing the above carbinols in the catalytic reaction.

When, e.g., a mixture of 2.08 g benzalacetophenone, 7.8 g α -naphthaldehyde and 96 mg $\text{RuCl}_2(\text{PPh}_3)_3$ (1) is refluxed (preferably under nitrogen) for 2.5 hr, the (distilled) reaction mixture proved (by vpc analysis) to contain 60% phenyl β -phenethyl ketone. $\text{RhCl}(\text{PPh}_3)_3$ (2) and $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (3) may be used instead of 1, but give lower yields. *N*-Methylformamide (at 180°) and formic acid (at 97°) donate their formyl hydrogen atoms in the same way to unsaturated ketones - formic acid in especially good yields.

The results obtained are summarized in Table I.

The catalysis with aromatic aldehydes is formulated as $\text{>C=C} + 2\text{ArCHO} \rightarrow \text{>CH-CH} + \text{ArAr} + 2\text{CO}$. It differs, thus, from the known catalytic decarbonylation reaction of aldehydes², being coupled with an intermolecular hydrogen transfer. The biaryl formed (*p*-tolualdehyde, e.g., gives mainly 4,4'-bitolyl) does not account for all the dehydrocarbonylated aldehyde as polyaryls and various macromolecules are obtained as well.

TABLE I. Examples of Transfer-Hydrogenation of α,β -Unsaturated Ketones by 1, 2 and 3^(a)

Exp.	Hydrogen donor	Hydrogen acceptor	Catalyst	Temp, °C	Time, hr	Yield of saturated ketone, %
1	α -C ₁₀ H ₇ CHO	C ₆ H ₅ CH=CHCOC ₆ H ₅	<u>1</u>	285	2.5	60
2	α -C ₁₀ H ₇ CHO	C ₆ H ₅ CH=CHCOC ₆ H ₅	<u>2</u>	285	2.5	21
3	α -C ₁₀ H ₇ CHO	C ₆ H ₅ CH=CHCOC ₆ H ₅	<u>3</u>	285	2.5	34
4	α -C ₁₀ H ₇ CHO	C ₆ H ₅ CH=CHCOC(CH ₃) ₃	<u>1</u> ^(b)	285	2.5	60
5	β -C ₁₀ H ₇ CHO	C ₆ H ₅ CH=CHCOC ₆ H ₅	<u>1</u>	285	2.5	28
6	<i>p</i> -CH ₃ C ₆ H ₄ CHO	C ₆ H ₅ CH=CHCOC ₆ H ₅	<u>1</u>	200	14	50
7	<i>p</i> -CH ₃ C ₆ H ₄ CDO ^(d)	<i>p</i> -CH ₃ OC ₆ H ₄ CH=CHCOC ₆ H ₅	<u>1</u> ^(e)	200	14	68
8	<i>p</i> -ClC ₆ H ₄ CHO ^(e)	C ₆ H ₅ CH=CHCOC ₆ H ₅	<u>1</u>	210	14	31
9	HCONHCH ₃	C ₆ H ₅ CH=CHCOCH ₃	<u>1</u>	180	2.5	25
10	HOBNHCH ₃	C ₆ H ₅ CH=CHCOC ₆ H ₅	<u>1</u>	180	2.5	30
11	HCOOH	C ₆ H ₅ CH=CHCOCH ₃	<u>1</u>	97	24	90
12	HCOOH	C ₆ H ₅ CH=CHCOCH ₃	<u>2</u>	97	24	16
13	HCOOH	C ₆ H ₅ CH=CHCOCH ₃	<u>3</u>	97	24	94
14	HCOOH	C ₆ H ₅ CH=CHCOC ₆ H ₅	<u>3</u> ^(f)	97	24	95
15	HCOOH	C ₆ H ₅ CH=CHCOC(CH ₃) ₃	<u>3</u> ^(f)	97	24	96
16	HCOOH		<u>1</u>	97	24	90

(a) The experiments were on the scale of 1-4 g. The molar ratio of donors: acceptor: catalyst was 1:5:10⁻² in expts. 1-8, and 1:20:5x10⁻³ in expts. 9-16. (b) 2 and 3 gave 20 and 4%, respectively. (c) 2 and 3 yielded 2 and 19%, respectively. (d) The aldehyde obtained in 90% from PhCD₂OD and PhCH=CHCOPh (ref. 1). (e) *p*-BrC₆H₄CHO gave essentially the same results. (f) 1 gave 58-60% after 24 hr.

The main side reaction, which is particularly pronounced in the presence of 2 and 3, is the well known catalytic decarbonylation of the aldehyde $\text{ArCHO} \rightarrow \text{ArH} + \text{CO}$.² In expts. 1, 2 and 3, e.g., the yields of naphthalene are 20, 66 and 90%, respectively (based on the aldehyde employed). The sterically unhindered β -naphthaldehyde gives naphthalene at such a fast rate that practically no transfer hydrogenation takes place.

At the reflux temperature of the aromatic aldehydes, ketones with active methylene groups undergo condensation reactions. Therefore, benzalacetone, e.g., cannot be reduced by this method. Some condensation of the saturated ketones formed also occurs when heating is continued for a long period. When *p*-chloro- or *p*-bromo-benzaldehyde was used as hydrogen donor, hydrogen halide (which promotes this side reaction) was evolved³. On the other hand, the catalysis by boiling formic acid is neat and the yields are excellent (especially when $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (3) is used as catalyst).

Amongst the unsaturated compounds studied, the conjugated ketones gave the best results, though simple olefins undergo the reaction as well. 4-Phenylbut-1-ene, e.g., is reduced within 24 hr by formic acid to an extent of 7 and 10% in the presence of 1 and 3, respectively (the remaining mixture consists of isomerized phenylbutenes⁴).

Exp. 7 indicates that the transferred hydrogen atoms derive exclusively from the formyl group; it also proves that no significant hydrogen exchange takes place in the geminally deuterated product - $\text{p-CH}_3\text{OC}_6\text{H}_5\text{CHDCHDCOC}_6\text{H}_5$.

In conclusion it is recalled that although the catalytic decomposition reactions of formic acid⁵ and aromatic aldehydes² (by 1, 2 and 3) follow different pathways, both reactions are thought to proceed via metal hydrides⁵⁻⁸. The assumption is strongly supported by the present study. In addition, we succeeded in isolating very labile aroyl-iridium-hydrides from 3 and *p*-bromobenzaldehyde or β -naphthaldehyde⁹. These compounds decompose spontaneously with the evolution of molecular hydrogen.

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