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HOMOGENEOUS CATALYTIC TRANSFER-HYDROGENATION OF α,β-UNSATURATED CARBONYL COMPOUNDS BY DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM (II)

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Dichlorotris(triphenylphosphine)ruthenium (II), $RuCl_2(PPh_3)_3$, is well known for its ability to catalyze hydrogen transfer in several organic reactions[1-10]. We now wish to report the application of this effect to the selective transfer-hydrogenation of α,β-unsaturated carbonyl compounds.

A mixture of 1.46 g (10^{-2} mole) 1-phenyl-1-buten-3-one (benzalacetone), 1.08 g (10^{-2} mole) benzyl alcohol and 19 mg (2×10^{-5} mole) $RuCl_2(PPh_3)_3$ was heated under nitrogen at 200° for 2 hr. By vpc (on a 5 m x 6.4 mm column packed with 10% DEGS on Chrom. W, at 190°) the reaction mixture was found to consist of 1-phenylbutan-3-one (92%) and benzaldehyde (90%). On a larger scale (10 g), the products were isolated, in similar yields, by fractional distillation.

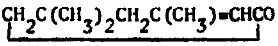
The results of Further experiments are listed in Table I.

The various high-boiling primary alcohols used are of comparable power as hydrogen donors. The initial rates in experiments 1,3 and 5, e.g., are 8.7, 7.6 and 5.7% min^{-1}, respectively. The secondary carbinol employed (exp. 4) is somewhat less efficient (2.4% min^{-1}), and the tertiary dimethylphenylcarbinol proved to be completely inactive. It has however been shown, using $C_6H_5CD_2OH$ and $C_6H_5CH_2OD$, that the hydroxylic hydrogen atom <u>is</u> incorporated in the transfer proven, probably as a result of initial intramolecular hydrogen migration catalyzed by the ruthenium complex.

The catalytic reaction can be carried out in boiling toluene, xylene or mesitylene as solvent, but the reaction rate is reduced by the lower temperature employed.

Hydroaromatics can replace the alcohols as hydrogen donors, but require longer reaction periods and higher temperatures. Tetralin (1.32 g), benzalacetone (1.46 g) and $RuCl_2(PPh_3)_3$ (19 mg), give 76% of the saturated ketone, but only after 48 hr.

TABLE I. Examples of Transfer-Hydrogenation by $RuCl_2(PPh_3)_3$ (a)

Exp.	Hydrogen donor (g)		Hydrogen acceptor (g)		Reaction temp, °C (b)	yield of saturated carbonyl compound after 4 hr, %
1	$PhCH_2OH$	(1.08)	$PhCH=CHCOCH_3$	(1.46)	200	94
2 (c)	$PhCH_2OH$	(1.08)	$PhCH=CHCOCH_3$	(1.46)	160	55
3	$PhCH_2CH_2OH$	(1.22)	$PhCH=CHCOCH_3$	(1.46)	200	94
4	$PhCH(OH)CH_3$	(1.22)	$PhCH=CHCOCH_3$	(1.46)	200	93
5	$CH_3(CH_2)_6CH_2OH$	(1.30)	$PhCH=CHCOCH_3$	(1.46)	190	82
6	$PhCH_2OH$	(1.08)	$PhCH=CHCOPh$	(2.08)	200	98
7	$PhCH_2OH$	(1.08)	 $CH_2C(CH_3)_2CH_2C(CH_3)=CHCO$	(1.38)	200	41
8	$PhCH_2OH$	(1.08)	$PhCH=CHCOC(CH_3)_3$	(1.88)	200	89
9	$PhCH_2OH$	(1.08)	$PhCH=C(CH_3)CHO$	(1.46)	200	61 (d)
10	$PhCH_2OH$	(1.08)	$PhCH=CHCOOC_2H_5$	(1.76)	200	53 (e)

(a) In exp. 2, 57 mg of the catalyst was applied; in all other experiments 19 mg was used.

(b) The temperature refers to the initial stages of the reaction. It dropped in some experiments towards the end of the reaction as products of lower boiling point accumulated. (c) In 10 ml mesitylene. A yield of 92% of 1-phenylbutan-3-one was obtained only after 72 hr. (d) and varying amounts of condensation products.

(e) Yield of pure ethyl 3-phenylpropionate.

Amongst the unsaturated carbonyl compounds studied, ketones give the best results. Aldehydes undergo partial self-condensation, which may be suppressed by dilution with solvents. Unsaturated esters give initially the expected saturated compounds, but suffer trans-esterification with the donor alcohols to a significant extent. In the case of ethyl cinnamate (exp. 10), both benzyl cinnamate and benzyl 3-phenylpropionate are formed, in addition to ethyl 3-phenylpropionate.

Saturated ketones are not reduced under the above reaction conditions.

A priori it is possible that the α,β-unsaturated ketone is attached at the carbonyl group giving an allylic alcohol which is then isomerized to the saturated ketone; however, such a mechanism would not account for the smooth reduction of benzalpinacolone (exp. 8). Furthermore, olefins that do not carry carbonyl groups are also reduced, though slowly, in the presence of, e.g., benzyl alcohol and the ruthenium catalyst. Thus, 4-phenylbut-1-ene gives, in addition to the isomerized olefin[7], 30% of 1-phenylbutane after 72 hr.

Palladium metal which has been found to be a most efficient catalyst in several (heterogeneous) hydrogen transfer reactions[11] gave unsatisfactory results with unsaturated ketones; nor did we succeed in causing transfer-hydrogenation in our system by various rhodium complexes[12] including the generally so versatile $RhCl(PPh_3)_3$.

In conclusion, it is recalled that ruthenium hydrides are formed from alcohols and ruthenium-phosphine complexes[13], and therefore take part in the mechanism. In fact, the unstable $HRuCl(PPh_3)_3$[2-4] catalyzes the reduction of benzalacetone with benzyl alcohol at 200° to an extent of 78% within 10 min (initial rate 18% min^{-1}), as compared with 49% (and 8.7% min^{-1}) by the hydrogen-free $RuCl_2(PPh_3)_3$, under the same conditions.

A study of the scope, kinetics and detailed mechanism of the homogeneous transfer-hydrogenation by $RuCl_2(PPh_3)_3$ is now in hand.

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