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Preliminary communication

TRANSFORMATION OF ORGANIC COMPOUNDS IN THE PRESENCE OF METAL COMPLEXES

I. TRANSFORMATION OF UNSATURATED ALCOHOLS WITH METAL COMPLEX CATALYSTS

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Summary

The transformations of unsaturated alcohols (1-hexen-3-ol, 2-penten-4-ol, 1-penten-4-ol and 2 methylenecyclohexanol) were studied under identical experimental conditions in the presence of various Rh and Ru complexes ($RhCl(PPh_3)_3$, $RhH(PPh_3)_4$, $RhCl_3 \cdot 3H_2O$, $RhCl_3 \cdot 3H_2O + PPh_3$, $Rh(COD)Cl_2$, $Rh(COD)Cl_2 + PPh_3$, $RhCl_2(PPh_3)_3$ and $RuH_2(PPh_3)_4$). Several aspects of both the unsaturated alcohol and the complex exert considerable effects on the extent of the main reactions; isomerization to ketone and double-bond migration.

Metal complex-catalysed transfer hydrogenation has been widely studied [1—5]. It is also well known [6—17] that Rh and Ru complexes in particular catalyse the isomerization of unsaturated alcohols, which can be treated as intramolecular transfer hydrogenation.

Analysis of the literature data reveals that (a) the transformations of isomeric unsaturated alcohols have not been studied under identical experimental conditions in the presence of various Wilkinson catalysts; (b) the isomerization of unsaturated alcohols has not been studied in the presence of Rh complexes formed in situ.

The transformations of diols with a $RhCl_3 \cdot PPh_3$ catalyst system were investigated recently [18, 19]. During consideration of the mechanism of the reaction, unsaturated alcohols were assumed as intermediates. For the reasons listed above, the experiments outlined in Tables 1—4 were carried out on the transformations of unsaturated alcohols.

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Results

The results (Tables 1—4) demonstrate that the direction of transformation is determined mainly by the nature of the metal complex and the structure of the unsaturated alcohol. For α,β-unsaturated alcohols, i.e. with a terminal olefin bond, the main reaction is isomerization to the corresponding ketone (see Scheme 1) (reviews on the mechanism of the isomerization can be found in refs. 3, 20); this is accompanied to a slight extent by intermolecular hydrogenation (Table 1).

When the olefin bond is in other positions, double-bond migration is also

TABLE 1

TRANSFORMATION OF 1-HEXEN-3-OL WITH CATALYSTS[a]

Catalyst	Time (min)	Conversion (%)	Product composition (%)[b]		
			$C_2H_5COC_3H_7$	$C_2H_5CHOHC_3H_7$	$CH{=}OHCOC_3H_7$
$RhCl(PPh_3)_3$	60	51	80	10	10
$RhH(PPh_3)_4$	70	32	80	10	10
$RuCl_2(PPh_3)_3$	40	60	90	5	5
$RuH_2(PPh_3)_4$	5	100	100	—	—
$RhCl_3 \cdot 3H_2O$	50	28	100	—	—
$RhCl_3 \cdot 3H_2O + PPh_3$	50	72	100	—	—
$[Rh(COD)Cl]_2$	50	45	70	15	15
$[Rh(COD)Cl]_2 + PPh_3$	50	55	74	13	13

[a]Conditions: 10 mmol alcohol, 0.01 mmol catalyst, 110°C, [b]By GC.

TABLE 2

TRANSFORMATION OF 2-PENTEN-4-OL WITH CATALYSTS[a]

Catalyst	Conversion (%)	Product composition (%)[b]			
		$CH_3CHOHCH_2CH{=}CH_2$	$CH_3COC_3H_7$	Dienes	Unidentified
$RhCl(PPh_3)_3$[c]	28	30	25	25	20
$RhH(PPh_3)_4$[c]	8	50	25	—	25
$RuCl_2(PPh_3)_3$	44	32	52	16	—
$RuH_2(PPh_3)_4$	16	19	62	—	19
$RhCl_3 \cdot 3H_2O + PPh_3$	45[d]	16	11	53	20

[a]Conditions: 10 mmol alcohol, 0.01 mmol catalyst, 140°C, 1 h, in sealed tube. [b]By GC. [c]Metal precipitation during the reaction. [d]At 115°C, 1 h.

TABLE 3

TRANSFORMATION OF 1-PENTEN-4-OL WITH CATALYSTS[a]

Catalyst	Conversion (%)	Product composition (%)[b]		
		$CH_3CHOHCH{=}CHCH_3$	$CH_3COC_3H_7$	Unidentified
$RhCl(PPh_3)_3$	18	90	6	4
$RhH(PPh_3)_4$	20	90	10	—
$RuCl_2(PPh_3)_3$	91	56	37	7
$RuH_2(PPh_3)_4$	97	36	64	—
$RhCl_3 \cdot 3H_2O + PPh_3$	32	56	14	30

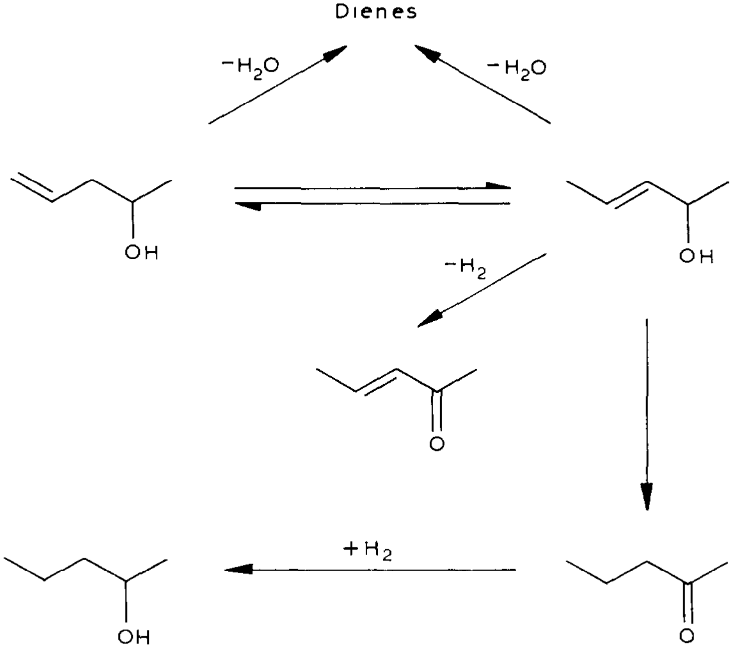
[a]Conditions: 10 mmol alcohol, 0.01 mmol catalyst, 145°C, 1 h, in sealed tube. [b]By GC.

TABLE 4

TRANSFORMATION OF 2-METHYLENECYCLOHEXANOL WITH CATALYSTS[a]

Catalyst	Conversion (%)	Product composition (%)[b]		
		2-Methylcyclohexanone	Cycloheptanone	Unidentified[d]
$RhCl(PPh_3)_3$ [c]	10	58	4	38
$RhH(PPh_3)_4$	26	64	4	32
$RuCl_2(PPh_3)_3$	40	80	4	16
$RuH_2(PPh_3)_4$	62	82	9	9
$RhCl_3 \cdot 3H_2O + PPh_3$	56	58	10	32

[a] Conditions: 10 mmol alcohol, 0.01 mmol catalyst, 175°C, 30 min. [b] By GC. [c] Metal precipitation during the reaction. [d] Probably 1-methylcyclohex-1-en-6-ol mainly.



possible (see Tables 2 and 3 and Scheme 1) (reviews on the mechanism are given in refs. 21, 22). Experiments at higher temperatures (Tables 2—4) showed that side-reactions also occur; these were not studied in detail.

$RuH_2(PPh_3)_4$ proved the most active catalyst in the isomerization to ketones, while the rhodium-containing catalysts also exhibited considerable activity in double-bond migration. Our studies relating to the stereochemistry and mechanisms of the transformations permit detailed analysis and interpretation of the experimental results summarized in Tables 1—4.

Experimental

Experiments were performed in a sealed tube, without solvent under nitrogen (method A), or in a flask fitted with a magnetic stirrer (method B). $RhCCl(PPh_3)_3$, $RuCl_2(PPh_3)_3$ and $RhCl_3 \cdot 3H_2O$ were Strem products, while $Rh(COD)Cl_2$ [23], $RhH(PPh_3)_4$ and $RuH_2(PPh_3)_4$ [24] were prepared by literature methods. PPh_3 and 1-hexen-3-ol were Fluka products, 2-methylenecyclohexanol was made according to ref. 25, and 2-penten-4-ol and 1-penten-4-ol were prepared by Grignard reactions of crotonaldehyde and acetaldehyde, respectively. The product composition was determined by gas chromatography: Fractovap P (Carlo Erba) instrument, 2 m 15% Carbowax 20M/Chromosorb P column, hydrogen carrier gas.

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