

Preliminary communication

TRANSFER HYDROGENATION BETWEEN ALCOHOLS AND α,β UNSATURATED KETONES WITH $\text{RhH}(\text{PPh}_3)_4$ AS CATALYST. EVIDENCE FOR REGIOSPECIFICITY AND AN UNUSUAL RATE-LIMITING STEP

D. BEAUPERE, P. BAUER*, L. NADJO et R. UZAN

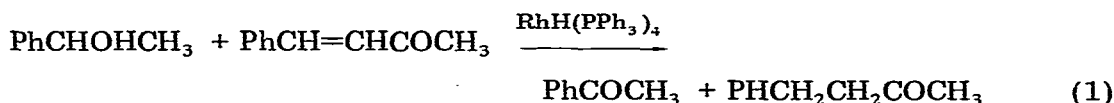
Laboratoire de Chimie Organique Physique, Université d'Amiens (France)

(Received June 22nd, 1982)

Summary

In the hydrogen transfer between an alcohol and an α,β -unsaturated ketone with $\text{RhH}(\text{PPh}_3)_4$ as catalyst under mild conditions the breaking of the O—H bond is, unusually, the rate-determining step, and the hydroxylic hydrogen is selectively transferred to the α -carbon of the ketone.

We recently showed that $\text{RhH}(\text{PPh}_3)_4$ is the most efficient catalyst for hydrogen transfer between an alcohol and an unsaturated ketone (eq. 1) and re-



ported several features relevant to the mechanism [1–3]. The reaction can be carried out at room temperature [1]. The catalyst-alcohol complex, frequently postulated, has been detected and the equilibrium constant for its formation determined by IR spectroscopy [2]. The existence of the ketone catalyst complex is deduced from the influence of the order of mixing of the reactants on the initial rate of the hydrogen transfer [3].

We now report new results for the reduction of unsaturated ketones by various deuterated alcohols. Benzalacetone is quantitatively reduced to 4-phenylbutan-1-one by the labelled alcohols PhCDOHCH_3 and $\text{CH}_3\text{CH}_2\text{OD}$. Using the C_6D_6 solvent effect [4], the ^1H NMR signals from the two methylene groups of the resulting saturated ketones can be assigned and the peak multiplicities and intensities lead to the results summarized in Table 1.

*ITODYS, Université de Paris.

TABLE 1

HYDROGENATION PRODUCTS OBTAINED BY HYDROGEN TRANSFER TO BENZALACETONE (A) FROM LABELLED ALCOHOLS (D) IN THE PRESENCE OF $\text{RhH}(\text{PPh}_3)_4(\text{C})^a$

Alcohol (D)	Products
PhCDOHCH_3	$\text{PhCHDCH}_2\text{COCH}_3$
$\text{CH}_3\text{CH}_2\text{OD}$	$\text{PhCH}_2\text{CHDCOCH}_3$

^a $[\text{C}] = 0.01 \text{ M}$, $[\text{A}] = [\text{D}] = 0.25 \text{ M}$ in C_6D_6 at 50°C . The same products are obtained in the absence of solvent.

TABLE 2

ISOTOPIC EFFECT k ON THE INITIAL RATE OF HYDROGENATION OF CYCLOHEXENONE (A) BY LABELLED ALCOHOLS (D) IN THE PRESENCE OF $\text{RhH}(\text{PPh}_3)_4(\text{C})^a$

Alcohol (D)	$r_i (10^{-4} \text{ M}^{-1} \text{ min}^{-1})$	$k = r_{\text{IH}}/r_{\text{ID}}$
PhCHOHCH_3	75	—
PhCDOHCH_3	60	1.25
PhCDODCH_3	26	2.96

^a $[\text{A}] = [\text{D}] = 0.25 \text{ M}$, $[\text{C}] = 0.01 \text{ M}$ in toluene at 40°C .

TABLE 3

ISOTOPIC EFFECT k FOR THE INITIAL RATE OF HYDROGENATION OF SUBSTITUTED BENZALACETONE (A) BY LABELLED ALCOHOLS (D) IN THE PRESENCE OF $\text{RhH}(\text{PPh}_3)_4(\text{C})$ IN TOLUENE AT 50°C^a

A	D	$r_i (10^{-4} \text{ M}^{-1} \text{ min}^{-1})$	$k = r_{\text{IH}}/r_{\text{ID}}$
PhCH=CHCOCH_3	PhCHOHCH_3	39	—
PhCH=CHCOCH_3	PhCDOHCH_3	32.5	1.20
PhCH=CHCOCH_3	PhCDODCH_3	15	2.60
PhCH=CHCOCH_3	PhCHOHCH_3	23	—
PhCH=CHCOCH_3	PhCDODCH_3	9	2.55
$4\text{NO}_2\text{PhCH=CHCOCH}_3$	PhCHOHCH_3	31	—
$4\text{NO}_2\text{PhCH=CHCOCH}_3$	PhCDODCH_3	13	2.40
$4\text{NMe}_2\text{PhCH=CHCOCH}_3$	PhCHOHCH_3	12.5	—
$4\text{NMe}_2\text{PhCH=CHCOCH}_3$	PhCDODCH_3	5	2.50

^a $[\text{A}] = [\text{D}] = 0.25 \text{ M}$, $[\text{C}] = 0.01 \text{ M}$. ^b $[\text{A}] = 0.05 \text{ M}$, $[\text{D}] = 0.25 \text{ M}$, $[\text{C}] = 0.01 \text{ M}$.

We confirmed that under the mild conditions used PhCDOHCH_3 does not give PhCHODCH_3 by isotopic exchange. Thus the results show unambiguously that the H (or D atom) initially attached to the carbon bearing the hydroxyl group ends up specifically on the β carbon of the α,β -unsaturated ketone.

This is the first demonstration of such a regiospecificity, which, while proposed, could not be proved because of the severe experimental conditions normally used [5]. The observations strongly favour a concerted transfer between alcohol and ketone and rule out a mechanism in which the catalyst initially dehydrogenates the alcohol [6].

Kinetic isotope effects have been measured for the reactions. Only the overall isotope effect was determined for reduction of alkenes by 2-propanol- d_8 with $\text{RhH}(\text{PPh}_3)_4$ [6]. We have measured the initial rate of the reduction of cyclohexenone (Table 2) and three benzalacetones (Table 3) by 1-phenylethanol and its deuterated derivatives, and in all cases kinetic isotope effects greater than unity were observed. With PhCDOHCH_3 , the magnitude of the effect is approximatively 1.20 for both cyclohexenone and benzalacetone. With

PhCDODCH_3 as hydrogen donor the isotope effect increases to 2.96 and 2.55 respectively, for cyclohexenone and benzalacetone. These results imply unambiguously that the rate-limiting step is the breaking of the O—H bond. This remarkable observation is confirmed by the very weak substituent effect in the reduction of cyclohexenone or benzalacetone by several benzylic alcohols. Furthermore, the observed substituent effect for three benzalacetones (Table 3) is consistent with the addition of a hydride ion, which implies that the heterolytic breaking of the C—H bond precedes the breaking of the O—H bond.

Further studies of the mechanism of the hydrogen transfer are in progress.

References

- 1 D. Beaupère, P. Bauer and R. Uzan, *Can. J. Chem.*, 57 (1979) 218.
- 2 D. Beaupère, P. Bauer, L. Nadjo and R. Uzan, *J. Organometal. Chem.*, 231 (1982) C49.
- 3 D. Beaupère, L. Nadjo, R. Uzan and P. Bauer, *J. Mol. Catal.*, 14 (1982) 129.
- 4 S. Danyluk, *Can. J. Chem.*, 41 (1963) 387.
- 5 Y. Sasson and J. Blum, *J. Org. Chem.*, 40 (1975) 1887.
- 6 H. Imai, T. Nishiguchi and K. Fukuzumi, *J. Org. Chem.*, 39 (1974) 1622.