

REDUCTIVE COUPLING OF BENZHYDROLS BY HOMOGENEOUS RUTHENIUM CATALYSTS

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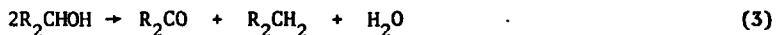
Dichlorotris(triphenylphosphine)ruthenium, $\text{RuCl}_2(\text{PPh}_3)_3$, has been shown to be an excellent catalyst for hydrogen transfer from carbinols to various unsaturated compounds.¹ In the absence of an external hydrogen acceptor the carbinol may suffer dehydration² or dehydrogenation³ and intramolecular hydrogen exchange takes place.^{2a,4}

We now report a new $\text{RuCl}_2(\text{PPh}_3)_3$ -catalyzed hydrogen transfer reaction in which secondary carbinols undergo reductive coupling (eq. 1).⁵



As an example, a mixture of 0.5 mmole benzhydrol, 1.7 mmole water and a pre-prepared solution of 4.4×10^{-3} mmole $\text{RuCl}_2(\text{PPh}_3)_3$ in 0.3 ml α -methylnaphthalene⁶ was heated under N_2 ⁷ in a sealed tube (volume 2 ml) at 190° for 4 hr. Gas chromatography (on 15% DEGS-stab. and on 1% OV-17) of the reaction mixture indicated the formation of 31 mole % (93% yield) 1,1,2,2-tetraphenylethane, 31 mole % (93% yield) benzophenone, 3 mole % dibenzhydrol ether and traces of diphenylmethane.

The two minor products result from two independent Ru(II)-catalyzed reactions shown in eq 2 and 3.



When no water is added to the reaction mixture or its concentration reduced, the rate of reaction 1 decreases and equilibrium 2 is shifted to the right. Under the above

Table I. RuCl₂(PPh₃)₃-Catalyzed Conversion of Benzhydrols into Hydrocarbons and Ketones under Comparable Conditions^a

Exp.	Carbinol	Products (mole %)
1	(C ₆ H ₅) ₂ CHOH	[(C ₆ H ₅) ₂ CH] ₂ (20), (C ₆ H ₅) ₂ CH ₂ (traces), (C ₆ H ₅) ₂ CO (21)
2	(4-CH ₃ C ₆ H ₄) ₂ CHOH	[(4-CH ₃ C ₆ H ₄) ₂ CH] ₂ (23), (4-CH ₃ C ₆ H ₄) ₂ CO (24)
3	(4-CH ₃ OC ₆ H ₄) ₂ CHOH	[(4-CH ₃ OC ₆ H ₄) ₂ CH] ₂ (24), (4-CH ₃ OC ₆ H ₄) ₂ CO (25)
4	(4-ClC ₆ H ₄) ₂ CHOH	[(4-ClC ₆ H ₄) ₂ CH] ₂ (6), (4-ClC ₆ H ₄) ₂ CH ₂ (16), (4-ClC ₆ H ₄) ₂ CO (24)

^a 0.5 mmole carbinol, 10⁻² mmole catalyst, 3 hr at 190° under N₂

conditions, but in the absence of H₂O, the yields of tetraphenylethane, benzophenone and dibenzhydryl ether were, after 3 hr 26, 24 and 6 mole % respectively, (15% unchanged carbinol was recovered).

Benzhydrols with electron releasing groups react similarly to the unsaturated compounds (Table I). Electron withdrawing substituents on the phenyl rings cause the disproportionation reaction 3 to be dominant in the catalysis. The slight excess of ketone formed in some experiments results from slow dehydrogenation of the secondary carbinol (eq 4).



This dehydrogenation becomes the main reaction when DMSO is used instead of α -methylnaphthalene as solvent.⁸

The catalytic activity of the ruthenium complex in reaction 1 depends on the electronic nature of the phosphine ligands. Electron withdrawing substituents X in RuCl₂[P(4-X-C₆H₄)₃]₃ increase the rate and vice versa electron donating groups. In experiments with 0.5 mmole benzhydrol and 3.86 x 10⁻⁴ mmole catalyst in 0.3 ml α -methylnaphthalene the corresponding initial rates of tetraphenylethane formation for X = Cl, H, CH₃ and OCH₃ were 12.0, 10.7, 10.0 and 9.7 mole l⁻¹ min⁻¹ x 10⁻⁴. (Hammett ρ +0.2).

The reductive coupling seems to be limited to secondary carbinols that form relatively stable carbonium ions with great ease, and that do not tend to undergo catalytic dehydration. (Diphenyl methyl carbinol e.g. dehydrates quantitatively to 1,1-diphenylethylene). Aliphatic carbinols may act as external hydrogen donors, even though they do not dimerize, and may cause tetraphenylethane formation in larger yields than 33 mole %. Typically, the addition of 0.43 mmole sec-butanol to a mixture of 0.5 mmole benzhydrol and 1.2×10^{-4} mmole $\text{RuCl}_2(\text{PPh}_3)_3$ (24 hr at 185°) gave 36 mole % 1,1,2,2-tetraphenylethane, 58 mole % ethyl methyl ketone, 13% diphenylmethane and only 5% benzophenone.

Preliminary mechanistic studies revealed that reactions 1,2, 3 and 4 as well as $\text{RuCl}_2(\text{PPh}_3)_3$ -catalyzed decomposition of the ether⁹ are not free radical processes but are related to the same catalytic cycle in which the benzhydrol adduct of $\text{RuCl}_2(\text{PPh}_3)_2$ solv., $\text{HRuCl}_2(\text{OCHPh}_2)(\text{PPh}_3)_2$,^{2a} is the key intermediate. It is noteworthy that tetraphenylethylene is not a precursor of 1,1,2,2-tetraphenylethane and does not undergo transfer-hydrogenation under our experimental conditions.

We have studied the utility of a number of platinum metal compounds for the various transformations of benzhydrol at 200° and found $\text{RuCl}_2(\text{PR}_3)_3$ to be the only series of effective catalysts for the reductive coupling. $\text{PdCl}_2(\text{PPh}_3)_2$ and $\text{PtCl}_2(\text{PPh}_3)_2$ promote practically only ether formation and $\text{RhCl}(\text{PPh}_3)_3$ gives a molar ratio of 1:2 of dibenzhydrol ether and 1,1,2,2-tetraphenylethane.

A study of the scope, kinetics and detailed mechanisms of the various transformations of benzhydrol is now in hand.

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3. K. Ohkubo, K. Hirata, K. Yoshinaga and M. Okada, Chem. Lett., 183 (1976).
4. S.L. Regen, J. Org. Chem., **39**, 260 (1974).
5. E.E. van Tamelen and M.A. Schwartz, J. Am. Chem. Soc., **87**, 3277 (1965) reported a non-catalytic reductive coupling of alcohols by Ti(II) compounds.
6. Typically, a homogeneous solution of $\text{RuCl}_2(\text{PPh}_3)_3$ was obtained by heating the catalyst and the solvent (freshly vacuum distilled over Na and degassed) under reduced pressure in a sealed ampule at 190° for 4 hr. A small amount of undissolved material was removed by filtration under N_2 . Longer heating periods reduces the catalyst activity. E.g., a 1.5×10^{-2} M solution that has been heated for 4 hr promotes reductive coupling 2.7 times faster than one that has been heated for 24 hr.
7. In the presence of O_2 the main product is dibenzhydryl ether.
8. Cf., the dehydrogenation of isopropanol by rhodium-tin chloride complexes. H.B. Charman, J. Chem. Soc. B, 584 (1970).
9. The dibenzhydryl ether formed in the process is slowly consumed when heated in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ and further amounts of tetraphenylethane and benzophenone accumulate.