

HOMOGENEOUS TRANSFER HYDROGENOLYSIS OF CARBON TETRACHLORIDE BY CARBINOLS

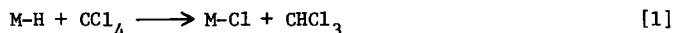
CATALYZED BY DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM (II)

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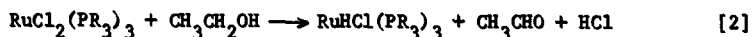
(Received in USA 18 June 1974; received in UK for publication 26 July 1974)

Reductions of carbon tetrachloride (1) to chloroform and other chloromethanes are usually carried out by Group III or Group IV metal hydrides¹. The most common reagents are hydrides of B, Li, Sn, and Ge and the process can be formulated in general as

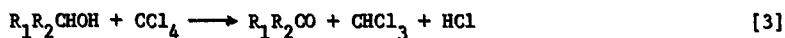


Although they appear to be of less practical value for this reaction, transition metal hydrides are known to behave in a similar manner. The reaction of transition metal hydrides with (1) is often employed to establish the presence of metal hydride². Hydrido complexes of Fe, Co, Pt and Rh in particular as well as some other transition metals have been found to undergo reaction with (1) according to equation [1]^{2,3}. The mechanism of this reaction probably involves oxidative addition of (1) to the hydrido complex followed by reductive elimination of chloroform.

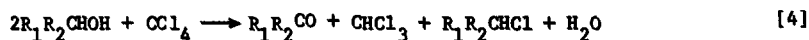
Hydrido complexes of ruthenium and of a number of other transition metals can be prepared by the action of alcohols. For example the formation of $\text{RuHCl}(\text{PR}_3)_3$ results from treatment of $\text{RuCl}_2(\text{PR}_3)_3$ with ethanol as shown in equation [2]⁴.



We now wish to report the combination of reactions [1] and [2], i.e. the transfer hydrogenolysis of (1) by carbinols catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3$, (2). The reaction can be written:



However, since the starting carbinol, especially if it is secondary or benzylic, is easily attacked by the resulting HCl, the general net overall reaction is



When a mixture of (1) (1.60g, 1.04×10^{-2} mole), 2-propanol (3.08g, 5.12×10^{-2} mole) and (2) (30mg, 3.12×10^{-5} mole) was heated, under nitrogen⁵ in a sealed tube to 145° , a clear yellowish-brown solution was obtained. After 2.5 hrs, the mixture was found to contain, (via glc analysis), 1.31 g (98%) chloroform, equivalent mole amounts of acetone, isopropylchloride and water as well as traces of dichloromethane and the remaining 2-propanol.

Experiments with other alcohols have shown that the most active donors, besides 2-propanol, are benzyl alcohol and cyclohexanol which also gave quantitative yields after 2.5 hrs. under similar reaction conditions⁶. Primary aliphatic alcohols, namely ethanol, 1-propanol, 1-hexanol and 1-decanol gave only 30-40% chloroform; methanol yielded only 9% of the products. Reactions with these primary alcohols become very slow after about an hour.

The inhibition could be due to decarbonylation of the aldehyde product by (2) to generate an inactive carbonyl complex⁷ or possibly due to a poisoning effect of free HCl⁸. The HCl in these cases cannot be efficiently removed, via a substitution reaction with the alcohol, as in the previous examples⁸. In experiments with isopropanol, where HCl was present initially, the rate was significantly lower. However, the process is not reversible; a mixture of acetone, chloroform and (2) saturated with dry HCl was

unchanged after 50 hrs. at 150⁰.

As expected, tertiary alcohols (eg. tertiary butanol) were not active as hydrogen donors. Formic acid, a common hydrogen donor⁹, was also found to be inactive.

(1) is the only active chloro substrate we have found. Under the described reaction conditions, chloroform gave only 1.5% of dichloromethane when reacted with benzyl alcohol and less than 1% with cyclohexanol. Benzyl chloride, chlorobenzene and (2-chloroethyl)-benzene were not reduced at all.

Reaction [3] was carried out with 2-propanol and cyclohexanol labelled with deuterium at the α -carbon and/or at the hydroxyl group. These experiments have shown that the hydrogen in the chloroform product originates from the α -carbon of the alcohol while the hydrogen in the HCl product comes from the hydroxylic hydrogen. Thus, the mechanism of reaction [3] as catalyzed by (2), probably involves formation of a ruthenium-hydride complex by the alcohol followed by attack of the hydrido complex on (1) to yield chloroform and to regenerate (2) for the next cycle¹⁰. A detailed study of the scope and mechanism of this reaction is now underway.

Acknowledgement

We thank the National Research Council of Canada and the University of Waterloo for financial support, and Engelhard Industries for the loan of ruthenium.

References and Notes

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6. All these reaction mixtures contained 1.60g carbon tetrachloride and 30 mg (2) in 4 ml of the alcohol at 145°.
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10. The possibility of a radical chain reaction is unlikely since the reaction proceeds normally even in the presence of a radical scavenging agent i.e. hydroquinone.