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HOMOGENEOUS TRANSFER HYDROGENOLYSIS OF CARBON TETRACHLORIDE BY CARBINOLS CATALYZED BY DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM (II)

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

$$\text{M-H} + \text{CCl}_4 \longrightarrow \text{M-Cl} + \text{CHCl}_3 \qquad [1]$$

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 hydride[2]. 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 $\text{RuHCl(PR}_3)_3$ results from treatment of $\text{RuCl}_2(\text{PR}_3)_3$ with ethanol as shown in equation [2][4].

$$RuCl_2(PR_3)_3 + CH_3CH_2OH \longrightarrow RuHCl(PR_3)_3 + CH_3CHO + HCl \qquad [2]$$

We now wish to report the combination of reactions [1] and [2], i.e. the transfer hydrogenolysis of ($\underset{\sim}{1}$) by carbinols catalyzed by $RuCl_2(PPh_3)_3$, ($\underset{\sim}{2}$). The reaction can be written:

$$R_1R_2CHOH + CCl_4 \longrightarrow R_1R_2CO + CHCl_3 + HCl \qquad [3]$$

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

$$2R_1R_2CHOH + CCl_4 \longrightarrow R_1R_2CO + CHCl_3 + R_1R_2CHCl + H_2O \qquad [4]$$

When a mixture of ($\underset{\sim}{1}$) (1.60g, 1.04×10^{-2} mole), 2-propanol (3.08g, 5.12×10^{-2} mole) and ($\underset{\sim}{2}$) (30mg, 3.12×10^{-5} mole) was heated, under nitrogen[5] 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 conditions[6]. 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 ($\underset{\sim}{2}$) to generate an inactive carbonylcomplex[7] or possibly due to a poisoning effect of free HCl[8]. The HCl in these cases cannot be efficiently removed, via a substitution reaction with the alcohol, as in the previous examples[8]. 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 ($\underset{\sim}{2}$) saturated with dry HCl was unchanged after 50 hrs. at 150°.

As expected, tertiary alcohols (eg. tertiary butanol) were not active as hydrogen donors. Formic acid, a common hydrogen donor[9], 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 cycle[10]. A detailed study of the scope and mechanism of this reaction is now underway.

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References and Notes

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