

## Ruthenium-catalysed Oxidation of Benzyl Alcohols to Benzaldehydes by Carbon Tetrachloride under Phase-transfer Conditions

Yoel Sasson,\* Harold Wiener, and Subhi Bashir

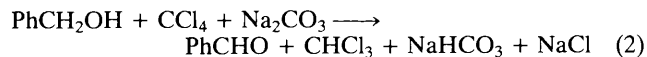
Casali Institute of Applied Chemistry, School of Applied Science and Technology, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

Benzyl alcohols are oxidized selectively to the corresponding benzaldehydes *via* mild transfer hydrogenolysis of carbon tetrachloride to chloroform in the presence of base; the reaction is catalysed by a combination of ruthenium trichloride and a quaternary ammonium salt.

Oxidation of alcohols, in particular benzylic alcohols, to aldehydes by various reagents proceeds concomitantly with the undesirable oxidation of the product aldehyde to carboxylic acid. This occurs even with very mild oxidants like hydrogen peroxide, sodium hypochlorite, or molecular oxygen.<sup>1</sup> One solution to this problem is to perform the reaction in the absence of an oxidant, *i.e.* by dehydrogenation, usually in the presence of a copper catalyst.<sup>2</sup> These reactions however, require relatively high temperatures for both thermodynamic and kinetic reasons. Typically, dehydrogenation of ethanol to acetaldehyde is carried out in the gas phase at 300 °C. Under these conditions benzyl alcohols and related compounds suffer major decomposition reactions.

Another possibility is the application of a hydrogen transfer reaction according to equation (1),<sup>3</sup> where R<sup>1</sup> and R<sup>2</sup> are hydrogen, alkyl, aryl, or aralkyl and A is a hydrogen acceptor. Typical acceptors are unsaturated systems such as olefins, acetylenes, ketones, and nitro or halogen compounds. Although a catalyst is usually required in these reactions, some acceptors are so reactive that they function in the absence of a catalyst.

We have reported the ruthenium-catalysed transfer hydrogenolysis of carbon tetrachloride to chloroform by propan-2-ol.<sup>4</sup> Other polyhalogeno derivatives have also been reduced selectively in a similar manner.<sup>5</sup> We now report the application of carbon tetrachloride as a hydrogen acceptor in the selective oxidation of benzyl alcohols to benzaldehydes [equation (2)].



In our former procedure<sup>4</sup> no carbonate was added to the system and the hydrochloric acid released not only reacted with the starting alcohol but also reduced the catalytic activity. Upon addition of the base the activation energy of the reaction was significantly lowered until reasonable rates were obtained even at 77 °C (*cf.* 160–180 °C in the absence of base<sup>4,5</sup>). In addition, the formation of benzyl chloride is avoided and the yield of benzaldehyde is close to quantitative.

In a typical procedure benzyl alcohol (0.8 g, 0.1 mol), sodium carbonate (10.6 g, 0.1 mol), carbon tetrachloride (54.0 g, 0.35 mol), and dichlorotris(triphenylphosphine)-ruthenium (0.1 g, 1 mmol) were refluxed (80 °C) for 12 h with stirring. G.l.c. analysis of the organic phase indicated 40% conversion of benzyl alcohol into benzaldehyde with 95% selectivity. Benzyl chloride (*ca.* 5 mol %) was also identified in the mixture, indicating that the removal of hydrogen chloride from the organic phase and its neutralization is not instantaneous as expected but rather a step which contributes to the overall rate process. Assuming that a phase-transfer catalyst

would have a positive effect on the transport of the acid from the organic phase to the solid carbonate<sup>6</sup> we added several quaternary ammonium salts to the system. Although in almost every case the rate of the reaction was increased, the most effective additive was didecylidimethylammonium bromide (DDAB). Upon addition of 5 mmol of DDAB the reaction was completed within 4 h and the selectivity was improved to 98–100%.

Since DDAB, like other lipophilic quaternary salts, is known to extract various metal salts from aqueous solution into organic solvents, we attempted to simplify the catalytic system by introducing ruthenium chloride trihydrate as metal catalyst. This salt is totally insoluble in carbon tetrachloride; however upon addition of an equivalent amount of DDAB a clear brown solution is obtained. To our surprise this catalytic system was even more active than the ruthenium phosphine complex combined with the quaternary salt.

In the improved procedure benzyl alcohol (0.1 mol), sodium carbonate (0.1 mol), ruthenium chloride trihydrate (1 mmol) and DDAB (2 mmol) were refluxed for 3 h. After removal of sodium chloride and sodium carbonate by filtration and evaporation of the chloroform and carbon tetrachloride, benzaldehyde was distilled out under vacuum (20 mmHg) (yield 93%; purity 99.5%).

The reaction was applicable to various substituted benzyl alcohols, *e.g.* 4-methyl-, 2-methyl-, 4-methoxy-, 2-methoxy-, and 4-ethyl-. With all these substrates quantitative yields of the corresponding aldehydes were obtained. However, ring-halogenated benzyl alcohols suffer from a hydrogenolytic side reaction which removes the halogen atom from the ring.<sup>7</sup>

A preliminary kinetic study of this system agrees with a first-order rate equation with a rate constant of 0.006 min<sup>-1</sup> at 77 °C for the benzyl alcohol.

The dependence of the observed first-order rate constant on the concentration of the combined RuCl<sub>3</sub>-DDAB catalyst was linear. Altering the ratio of the phase-transfer catalyst to the metal catalyst, on the other hand, resulted in unexpected behaviour. In the absence of DDAB no reaction was observed. On increasing the DDAB: Ru molar ratio the rate increased up to a ratio of 2.0:1 where a maximum rate was measured. Surprisingly, at higher ratios the rate of reaction (2) fell sharply. This phenomenon apparently indicates that DDAB forms more than one complex with ruthenium and that some of these complexes are catalytically inactive.

Other phase-transfer catalysts were inferior to DDAB in this process. Thus under the conditions where DDAB gave complete conversion of benzyl alcohol, the same molar amounts of other quaternary ammonium bromide salts all gave lower conversions as follows: tetramethyl 55%, tetrapropyl 70%, tetrabutyl 50%, tetrahexyl 60%, tetraoctyl 45%. The more lipophilic catalysts like the tetraoctyl or tetrahexyl derivatives, which were separately very effective in extraction of ruthenium trichloride from solid or aqueous solution into an organic phase, performed quite poorly in the overall process

(2). On the other hand salts which were inferior in the extraction of the metal catalyst, *e.g.* the tetrapropyl derivative, showed relatively high activity in the catalytic transfer hydrogenolysis. This suggests that the major role of the quaternary salt in this system is not the extraction of the metal catalyst but rather the transport of hydrochloric acid from the organic phase to the solid base.

We are grateful to Abic Ltd. for the donation of DDAB.

Received, 6th May 1987; Com. 615

### References

- 1 R. A. Sheldon and J. K. Kochi, 'Metal Catalyzed Oxidation of Organic Compounds,' Academic Press, New York, 1981.
- 2 K. Heyns and H. Paulsen, *Angew. Chem.*, 1957, **69**, 600.
- 3 R. A. W. Johnstone, A. H. Wilky, and I. D. Entwistle, *Chem. Rev.*, 1985, **88**, 129.
- 4 Y. Sasson and G. L. Rempel, *Tetrahedron Lett.*, 1974, 3221.
- 5 Y. Sasson and G. L. Rempel, *Synthesis*, 1975, 448.
- 6 M. Halpern, H. A. Zahalka, Y. Sasson, and M. Rabinovitz, *J. Org. Chem.*, 1985, **50**, 5088.
- 7 A. Zoran, Y. Sasson, and J. Blum, *J. Mol. Catal.*, 1984, **27**, 347.