Ruthenium Trichloride-catalysed Hypochlorite Oxidation of Organic Compounds

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Summary Household bleach (sodium hypochlorite) generates ruthenium tetroxide from its lower valence states.

OXIDATION of organic compounds by RuO_4[1] can be achieved by using a catalytic amount of RuO_2[2] or $RuCl_3$,[3] in combination with sodium metaperiodate. Although this procedure is convenient,[4] it has drawbacks: the relatively high cost and high molecular weight of periodate, the effective reagent; the precipitation of voluminous quantities of iodate as the reaction proceeds; and, with certain substrates or intermediates, the ability of periodate to enter an oxidation directly.

It has been stated that an aqueous solution of RuO_4 can "be kept unchanged for years if a few drops of chlorine water are added to it".[5] The implication of this observation is that hypochlorite can regenerate RuO_4 from its lower valence states and, on this premise, the oxidation procedure now reported, $RuCl_3$-catalysed hypochlorite oxidation of organic compounds, has been developed. In this procedure RuO_4 is the actual oxidant, but household bleach, a readily available and inexpensive 5·25% aqueous solution of sodium hypochlorite, is the effective reagent. This hypochlorite solution is stable almost indefinitely at room temperature (the titre of one sample changed from 1·51—1·31N during two years). In a typical procedure, a solution of cyclohexanol (10 mmol, 20 m equiv.) in water (40 ml) containing 0·5 ml of 2% aqueous $RuCl_3$ was titrated at 0° with 1·51N-sodium hypochlorite. Each drop of hypochlorite caused a colour change from black to yellow to black and, after 13·8 ml (20·8 m equiv.) had been added, a reasonably stable (up to 30 min.) yellow end point was reached. Filtration of the mixture through Celite and treatment of the filtrate with an excess of 2,4-dinitrophenylhydrazine reagent afforded cyclohexanone 2,4-dinitrophenylhydrazone in 90—95% yield. No cyclohexanone was formed in a control experiment from which the $RuCl_3$ was omitted.

Titration experiments established that cyclohexene, the cyclohexane-1,2-diols and cyclohexane-1,2-dione consume, respectively, a total of 8·0, 6·2, and 5·8 equiv. of hypochlorite/mol. This stoicheiometry corresponds to oxidation of the olefin and the glycols to adipic acid, and to over-oxidation of the diketone. Preparative experiments with these and other substrates could be conducted in aqueous solution or suspension or, most conveniently, by stirring a methylene chloride solution of the substrate with an aqueous solution containing the catalyst and the desired amount of hypochlorite until the yellow mixture turned green–black. In this way, and with the quantities of hypochlorite indicated by the titration experiments, cyclohexene gave adipic acid (86—95%), the diols gave adipic acid (80—90%), and the diketone gave an 82% yield of carboxylic acids which, by g.c. analysis of the methyl esters, was found to contain adipic acid (28%), glutaric acid (56%), and succinic acid (3%). With half the above quantities of hypochlorite, the olefin yielded adipaldehyde (25—30%) in addition to adipic acid, and the diols yielded 2-hydroxycyclohexanone in addition to adipic acid. These results indicate that the cleavage of a double bond proceeds by the route: olefin → dialdehyde → diacid; and that the cleavage of a glycol proceeds by the route: glycol → α-ketol → diacid. The diketone is apparently not an intermediate in the oxidation of the olefin or the glycols.

The degradation of a benzene ring can be achieved in low yield by the $RuCl_3$–periodate procedure.[3] After 10 days at 60° in CCl_4–H_2O, cyclohexanecarboxylic acid was obtained in 25% yield from phenylcyclohexane; and, after several days at room temperature, *p*-t-butylphenol afforded pivalic acid in 12% yield. With the $RuCl_3$–hypochlorite reagent, the oxidation of β-phenylpropionic acid, in water as the potassium salt, has been found to obey closely the stoicheiometry $RC_6H_5 + 28[O] \rightarrow RCO_2H + 5\ CO_2$. In 3 h at room temperature this substrate was converted into succinic acid (94%) and benzoic acid (6%). The efficiency of this degradation suggests that it may be useful in biosynthetic studies.

If it is assumed that RCOCHO is an intermediate in the oxidation of RPh, and that the structural grouping –CHOH–CO– undergoes carbon–carbon bond cleavage, then the structural grouping $PhC(OH)R^1R^2$ would be expected to yield sequentially $R^1R^2C(OH)COCHO$, followed by the ketone R^1R^2CO. Oxidation of 1-phenylcyclohexanol in CH_2Cl_2–H_2O was performed with 30 equiv./mol of hypochlorite, was complete after stirring overnight at room temperature, and afforded cyclohexanone in 72% yield. Cyclopentanone was obtained similarly in 68% yield from 1-phenylcyclopentanol. Thus, in combination with $RuCl_3$–hypochlorite oxidation, phenylmagnesium bromide can be considered to be a protecting group for ketones.

Preliminary studies indicate that hypochlorite can also be employed in combination with OsO_4, $RhCl_3$, and $IrCl_3$.

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