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OXONIUM SALTS AS HYDRIDE ION ABSTRACTING AGENTS IN ORGANOMETALLIC SYSTEMS

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SUMMARY

Cycloheptatrienetricarbonylchromium is oxidised to the tropyliumtricarbonylchromium cation in high yield when triethyloxonium tetrafluoroborate is used as a hydride ion acceptor. The advantages of this reagent over those used previously are discussed.

INTRODUCTION

The formal one-electron oxidation of an organic molecule bonded to a transition metal as a result of abstraction of hydride ion, H^-, from the compound has been a subject of considerable interest in organometallic chemistry for many years[1].

The reagent most commonly used for such oxidation reactions is the triphenylmethyl (trityl) carbonium ion, Ph_3C^+, usually with a tetrafluroborate counter ion[1-3]. The process takes advantage of the high electrophilicity of the cation which is converted to triphenylmethane in the course of the reaction.

The major disadvantages of the use of trityl salts are the high cost of the starting material, trityl carbinol[3], and the need of fluoroboric acid, which is corrosive.

Prior to an investigation of the reactions of certain nucleophiles with organometallic cations, we sought an alternative reagent for this hydride abstraction reaction which would be of equal generality. The primary aim was to find a reagent which was readily prepared from cheap starting materials. We wish to report one example of many in which triethyloxonium tetrafluoroborate has been used as a hydride abstracting agent.

RESULTS

Trialkyloxonium salts, originally described by Meerwein[4], are strong electrophiles and have found increasingly wide application as alkylating agents[5]. These salts, especially the simplest members, Me_3O^+ and Et_3O^+ are very easily synthesised as tetrafluoroborates[6].

When mixed with an organometallic compound such as cycloheptatrienetricarbonylchromium[7], (I), in a suitable solvent such as methylene chloride, triethyloxonium tetrafluoroborate, (II), causes a smooth oxidation reaction to occur, as a result of which tropyliumtricarbonylchromium tetrafluoroborate[8], (III), is formed in high purity and good yield. The oxonium salt is converted into ethane and diethyl ether according to the equation

$$\underset{(I)}{C_7H_8Cr(CO)_3} + \underset{(II)}{(C_2H_5)_3O^+BF_4^-} \rightarrow \underset{(III)}{C_7H_7Cr(CO)_3} + (C_2H_5)_2O + C_2H_6$$

The tropylium complex, (III), obtained in this way is identical with that obtained using trityl tetrafluoroborate[8]. In the case of trityl salts the hydride abstraction reaction is very rapid, but with oxonium salts the reaction is slower and more readily controlled. The triethyloxonium salts are preferred to the methyl analogues because of their greater solubility in less polar solvents.

Oxonium salts as hydride abstracting agents possess two main advantages over trityl salts. First, the reagent is easily prepared, in large quantities if the need arises, from simple, cheap materials. Second, the ether and the paraffin produced in the reaction are very volatile, thereby facilitating the isolation of oxidation products such as (III), in certain otherwise difficult cases such as the homotropyliumtricarbonyl complexes of the Group VI metals[9].

EXPERIMENTAL

All manipulations were performed in a nitrogen atmosphere and all solvents were carefully dried and purged with nitrogen before use. Cycloheptatrienetricarbonylchromium[7] was prepared by King's method[10] from $(MeCN)_3Cr(CO)_3$[11] and pure C_7H_8 (Koch-Light) in acetonitrile, and isolated as deep red crystals, m.p. 127° (lit.[7] 128–130°). Triethyloxonium tetrafluoroborate was prepared[6] from $Et_2O \cdot BF_3$ and epichlorohydrin in diethyl ether and the purity of the product was determined by hydrolysis and subsequent titration with standard alkali.

Preparation of tropyliumtricarbonylchromium tetrafluoroborate

Triethyloxonium tetrafluoroborate (3.76 g, 20 mmole) dissolved in methylene chloride was added slowly at room temperature to a stirred solution of cycloheptatrienetricarbonylchromium (4.56 g, 20 mmole) in the same solvent. A red crystalline solid precipitated from the solution as the reaction proceeded. When the precipitation was complete, as shown by the change in colour of the solution (deep red to pale orange/yellow), the liquor was removed leaving pure tropyliumtricarbonylchromium tetrafluoroborate (5.72 g, 18.3 mmole, 91%). This product, when treated with sodium borohydride was reconverted to cycloheptatrienetricarbonylchromium (analysis, mixed m.p. and IR spectrum). Treatment of the cycloheptatriene complex with trityl tetrafluroborate in methylene chloride gave a sample of tropyliumtricarbonylchromium tetrafluoroborate which was identical to that described above.

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