SYNTHETIC REAGENTS 4

J. S. PIZEY

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Volume 4

Mercuric Acetate; Periodic Acid and Periodates; Sulfuryl Chloride

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Table of Contents

Author's Preface

A similar plan used for the organisation of the three earlier volumes is repeated here: three reagents are reviewed in sufficient depth to provide a full understanding of their synthetic utility. The three reagents have been chosen for their current importance, their versatility, and their ability to cause major types of reactions.

The important properties of each reagent, together with its preparation, where necessary, are given at the beginning of the respective chapters. The synthetic uses of each reagent are then discussed in extensive surveys which occupy the larger part of each review. Mechanistic ideas have been introduced when it is felt that they will afford a better understanding of the synthetic possibilities or limitations of the reagent.

MERCURIC ACETATE (C. F. Lane) is used for the mercuration of a number of classes of compounds, for amino- and oxy-mercuration, in the preparation of vinylmercurials and in vinyl transfer reactions, as an important oxidant, in certain reactions of organosulphur compounds, and in a number of miscellaneous reactions. PERIODIC ACID (A. J. Fatiadi) effects a large number of very important oxidations, may be used to iodinate numerous classes of compounds, is used in the cleavage of epoxides, as a co-oxidant, and has a number of bio-organic applications. SULPHURYL CHLORIDE (I. Tabushi) is an important ionic and radical chlorinating agent used in a large number of systems.

It is hoped that this book will help chemists to determine the types of reaction the reagent will effect and resolve its selectivity: and that it will also indicate the optimum reaction conditions. This will also enable the chemist to find a method for the synthesis of a large number of specific compounds. The original reference for that method or compound will then (generally) give him the necessary precise synthetic details. Rapid retrieval of information is assisted by a very complete index covering all the types of reactions and all compounds discussed.

CHAPTER 1

Mercuric Acetate

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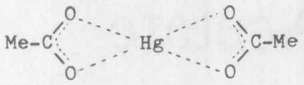
A INTRODUCTION

1. General characteristics of the reagent

Mercuric acetate (Hg2A) has been used as a synthetic reagent for over one hundred years. With thallium(III) acetate and lead tetra-acetate [1] it forms a group of isoelectronic oxidising agents which has been increasingly explored in organic synthesis in recent times and particularly over the past twenty years. Mercuric acetate ($Hg^{2+} + 2e^- \rightarrow Hg^o$, E^o 0.85) [2] is a weaker oxidising agent than lead tetra-acetate ($Pb^{+4} + 2e^- \rightarrow Pb^{2+}$, E^o 1.6–1.75) [3] and this is reflected in its reactions where the metal often remains in the Hg(II) state giving substitutions which afford stable mercurated products. The reagent also exhibits a wide range of interesting oxidations in which the mercury(II) is reduced to mercury(I) or to the metallic mercury(O) state.

Mercuric acetate has been available commercially for many years. It is easily prepared by heating metallic mercury with peracetic acid in acetic acid solution [4]. The peracetic acid may also be generated *in situ* thereby simplifying the overall process [5]. Thus the reagent can be obtained in high yields by careful addition of hydrogen peroxide (50%) (60g.) to a stirring mixture of mercury (150g.), glacial acetic acid (450g.) and nitric acid (7g.) at 40° [5]. A white suspension of HgOAc forms during the stirring (30 min.) at 40°. The mixture is then heated to 80° and stirred (*ca.* 30 min.) to give a clear solution. Cooling and fractional evaporation gives a high or quantitative yield of Hg2A [5]. Mercuric acetate is soluble in hydroxylic solvents such as water (25g. per 100g. solvent at 10°) and ethylene glycol (17.8g. per 100g. at 25°) [6] but it is only sparingly soluble in amines [6,7] (e.g., 0.186g. per 100g. at 25° in ethylene diamine) and hydrocarbon solvents [8]. A solubility product of $10^{-21.5}$ has been reported for Hg2A in acetic anhydride-acetic acid mixtures [9]. Mercuric acetate is undissociated in acetic acid and the K value for the ionization, $Hg(OAc)_2 \rightleftharpoons Hg^{2+} + 2OAc^-$ is 3.75×10^{-9} [10]. Raman spectra of aqueous solutions have

been interpreted in terms of the covalent type structure (**1**) [11a]. In a recent study of the hydrolysis of acetonitrile catalysed by Hg^{2+} ions, Hg2A gave no reaction and IR spectra of the system Hg2A/H_2O/MeCN suggested no dissociation of the Hg2A [11b]. The unit cell of crystalline Hg2A has dimensions of



(**1**)

a, 4.620, b, 20.142, c, 7.158Å and β 107.95° [12]. The z value is 4 (no. of gram formula weights per unit cell) and the space group is $P_{2_1/a}$ [13]. The structure consists of isolated Hg2A molecules with Hg–O bond distance 2.07Å and O–Hg–O angle 176° [13]. Chains are formed in the a direction by two weak Hg–O bonds of 2.73Å and packing of these chains results in a fifth O neighbour for the Hg atom giving a tetragonal pyramid as the co-ordination polyhedron for Hg [13].

Aqueous solutions of Hg2A can be estimated by a standard thiocyanate titration after treatment with nitric acid. In acetic acid solutions Hg2A can be titrated against Cl^- or Br^- salts using indicators such as sodium nitroprusside [14], diphenylcarbazone [14] or dithizone [15]. The reagent can also be titrated to a thymol blue end-point with 0.1M hydrochloric acid in chloroform-propylene glycol (1 : 1 v/v) [16] or in other glycolic solvents [17]. Mercuric acetate is highly toxic. When applied to the rabbit hypothalamus, it evoked brain seizure by blocking sodium transport [18]. Ingestion of Hg2A by rats caused severe kidney damage with as little as 0.5ppm. mercury and the mercury was distributed also to the brain and testes. Storage of mercury in the liver and kidney was ten to twenty times higher for Hg2A ingestion than for other organomercury compounds [19–21]. The major route for subsequent excretion of mercury after Hg2A ingestion was in the urine whereas mercury excretion from phenylmercuric acetate was *via* bile and intestinal tract [22]. Mercuric acetate is also embryopathic and caused delayed growth rate of animal foetuses as well as weight loss, kidney lesions, diarrhoea, tremor and somnolence in the maternal system [23]. A general discussion and literature on the environmental mercury problem is available [24].

Throughout this review the term 'mercuration' means a *substitution* of the group HgOAc for a proton in a molecule. This is distinct and different from terms such as 'oxymercuration', 'aminomercuration' or 'solvomercuration' which imply *addition* of HgOAc together with another functional group, the bonding atom of which is described by the prefix, oxy-, amino-, peroxy-, etc. The term 'acetoxylation' implies the introduction of the elements of an acetoxyl group ($C_2H_3O_2$) to a molecule in any form, not necessarily a compact acetoxyl group. While comparisons of Hg2A with other mercury salts are made throughout this review, for reasons of length it has not been possible to include comparisons with