

USE OF MERCURIC ACETATE IN ORGANIC PREPARATIONS

Part II. Some Experiments on its Use as an Oxidising Agent

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BESIDES being used widely as a reagent for mercuration, mercuric acetate has been successfully employed as an oxidising agent.¹ Its action in this respect is said to be similar to that of chromic acid or permanganate and specially suited where a mild oxidising agent is required so that the oxidation may not proceed too far. It is obvious that an excess of the reagent and the sparingly soluble mercurous acetate which is one of the products of reaction, can both be removed easily. It has further been claimed that the sparingly soluble mercurous acetate can be collected and weighed and hence the progress of the reaction followed quantitatively.

Balbiano and his collaborators² found that certain olefines, *e.g.*, anethole, iso-safrole, methyl iso-eugenol, etc., which contain a propenyl group $-\text{CH} : \text{CH} \cdot \text{CH}_3$ react with mercuric acetate in aqueous solution giving rise to glycols of the general formula $-\text{CHOH} \cdot \text{CHOH} \cdot \text{CH}_3$ with the addition of two $-\text{OH}$ groups at the double bond, the mercuric acetate being reduced to mercurous acetate. A similar observation has been made by Sanjiva Rao and Subrahmanyam³ in regard to β -asarone. Safrole and methyl eugenol which contain an allyl group react with mercuric acetate forming a complex compound with the addition of a hydroxy group and an acetoxy mercury group at the double bond ($-\text{CH}_2 \cdot \text{CHOH} \cdot \text{CH}_2 \cdot \text{HgOAc}$).

Gadamer and his co-workers⁴ have successfully employed mercuric acetate for isolating intermediate stages in the oxidation of alkaloids. Papaverine on oxidation yielded papaverinol and papaveraldine and *d*-canadine was converted into berberine. Windaus *et al.*⁵ have employed this reagent in connection with sterols and have been able to obtain dehydro-ergosterol from ergosterol and ergostatrienol—*d* from di-hydro-ergosterol.

From the claims of the previous workers it seemed possible to follow the course of the oxidation reactions, using mercuric acetate, quantitatively by weighing the amount of mercurous acetate formed and it was thus hoped to obtain information regarding their mechanism. In order to test this, the best conditions suitable for the reaction and the behaviour of the reagent

in various solvents had to be studied in detail. Solutions in water, dilute acetic acid or in alcohol have been employed by previous workers. In all cases, it is necessary to add few drops of acetic acid in order to produce a clear solution and to prevent hydrolysis. The following sums up the behaviour of the common solvents. In the cold water, ethyl and methyl alcohols, dry or containing water, by themselves, produce no change. When boiled, however, there was considerable difference in their behaviour. Excepting dry methyl alcohol, all the others produced appreciable amounts of mercurous acetate. Hence this was chosen as the most suitable solvent; but it was soon realised that complications set in during the course of experiments on actual oxidations of well-known substances. Using benzoin and hydroquinone as typical examples, it was observed that mercurous acetate was produced far in excess of what could be expected from the quantities of benzil and quinone formed at the same time. It was therefore suspected that the solvent was taking a share in the reduction of mercuric acetate in the presence of the other more powerful reducing agents. That is, hydroquinone or benzoin acts also as an inducing agent in enabling the oxidation of methyl alcohol with mercuric acetate to take place. This inference was remarkably supported by experiments carried out using small quantities of hydroquinone or benzoin as an inducing agent under two sets of conditions: (i) at the boiling point of the solvent; (ii) at ordinary temperature in the presence of sunlight. Considerable amounts of mercurous acetate were formed thereby showing definitely that the solvents can undergo oxidation to an appreciable extent in the presence of these inducing agents. Hence the yield of mercurous acetate cannot indicate correctly the progress of oxidation of a substance when mercuric acetate is employed.

As a result of a number of experiments carried out in connection with the object mentioned above, convenient methods very suitable in the laboratory for the small-scale production of mercurous acetate in a crystalline and pure condition and of quinhydrone, quinone and benzil have been worked out. A number of substances containing the secondary alcoholic group such as iso-propyl alcohol, diphenyl carbinol, ethyl tartrate, menthol, quinine and cinchonine and cholesterol reduce mercuric acetate and deposit in considerable amounts the mercurous compound. This seems to be of general applicability for all compounds containing the CHOH group. In several cases, the products of oxidation could be identified; iso-propyl alcohol, diphenyl carbinol and cinchonine yielded acetone, benzo-phenone and cinchoninone respectively, though the yields were unsatisfactory. In the other cases, the reactions seemed to be complex and no definite oxidation products could be obtained.

Experimental

Effect of ordinary solvents on mercuric acetate.—In preparing solutions of mercuric acetate in water or alcohol, a few drops of glacial acetic acid were always added in order to prevent the hydrolysis of mercuric acetate. At the ordinary laboratory temperature, the solvents (water, ethyl alcohol, methyl alcohol, etc.) did not produce any appreciable amount of mercurous acetate when the solutions were kept in the dark for a few days. The results that were obtained regarding the action of the solvents on mercuric acetate both at the boiling point of the solvents and at the ordinary temperature exposed to sunlight in a quartz flask are tabulated below. Saturated

TABLE I. *Action of solvents on mercuric acetate at their boiling temperatures*

Solvent	Period of time employed	Yield of mercurous acetate
Water	24 hours	^{g.} 0.1*
Rectified spirit	"	0.8
Absolute alcohol	"	0.3
Anhydrous methyl alcohol ..	"	Nil
Dilute methyl alcohol (90 %) ..	"	0.05

* The yield in the case of water is less probably due to the greater solubility of mercurous acetate in water than in alcohol.

TABLE II. *Action of very small quantities (about 1 m.g.) of inducing agents on anhydrous methyl alcoholic solution*

Boiling or exposure to sunlight	Inducing agent employed	Period of time employed	Yield of mercurous acetate
Boiling ..	Benzoin ..	10 hours	^{g.} 0.17
"	Hydroquinone ..	"	0.50
Exp. to sunlight ..	None ..	"	0.03
"	Benzoin ..	"	0.45
"	Hydroquinone ..	"	1.0

solutions using 5 g. of mercuric acetate in various solvents were used in all the cases mentioned.

Preparation of pure mercurous acetate and benzil.—2 g. of benzoin were dissolved in the minimum amount of anhydrous methyl alcohol and to it was added a solution of mercuric acetate (6 g. in the same solvent 100 c.c.). When allowed to stand at the room temperature, the reaction proceeded very slow. The mixture was therefore heated under reflux, when a colourless crystalline solid began to separate rapidly. At the end of every 6 hours, this solid was filtered and the filtrate again refluxed. This process was repeated till no more of the crystalline solid separated (total time taken 36 hours). The colourless crystalline precipitate obtained was collected together, washed with hot methyl alcohol and dried (yield 4 g., about 80% conversion of the mercuric acetate). It was sparingly soluble in water and alcohol and on heating began to char at 300° C. without previous melting. It dissolved easily in dilute nitric acid and this solution gave a curdy white precipitate with a drop of hydrochloric acid. It turned black in the presence of sodium hydroxide producing mercury. The percentage of mercury in this compound was estimated [Found: Hg, 76.8 per cent.; $\text{Hg}_2(\text{O CO CH}_3)_2$ requires Hg, 77.2 per cent.]. The sample therefore was pure mercurous acetate and the method is convenient for the preparation of pure mercurous acetate from mercuric acetate in the laboratory.

The filtrate from the mercurous acetate was coloured deep yellow. The solvent was distilled off and the yellow residue was washed with hot water to remove the excess of mercuric acetate and unreacted benzoin and finally the product was recrystallised from methylated spirits. Yellow needle-shaped crystals of benzil melting at 95° were thus obtained in a yield of only 40 per cent. (0.8 g.). It formed a diphenyl hydrazone melting at 225° C. A mixed melting point of the substance with benzil established its identity.

The above reaction was conducted more conveniently in hot aqueous medium, when benzil began to separate as a yellow liquid (its m.pt. being 95° C.) along with mercurous acetate. While hot, the aqueous layer was decanted off. The yellow residue remaining behind was purified by extraction with ether and recrystallisation from alcohol. The product was purer than in the previous case since unreacted benzoin was kept in solution in hot water; but there was no improvement in the yield of benzil.

Preparation of quinhydrone.—Hydroquinone (2 g.) dissolved in water (30 c.c.) was added to a similar solution of mercuric acetate (20 g. in 100 c.c.) and thoroughly shaken for a few minutes, when the colourless mixture began to turn brown. It was then repeatedly extracted with small amounts of

ether and the combined ether extract was evaporated. The residue separated as prisms with green metallic lustre (1.3 g.). The product was then purified by washing with small amounts of water, taking it up in ether and evaporating the ether solution. It melted at 171°C . and a mixed melting point determination with a pure sample of quinhydrone established its identity. The mercurous acetate that was obtained as a result of reduction was then filtered from the aqueous *layer* and washed with a small amount of alcohol to remove any adhering quinhydrone.

Preparation of quinone.—The above reaction was carried out by heating the mixture for half an hour at 80°C . on a water-bath and after cooling the mixture to the laboratory temperature, it was extracted with ether in small amounts repeatedly. The combined ether extracts on evaporation gave a yellow crystalline material which after recrystallisation was found to be quinone (yield: 0.7 g.) by its m.pt. (115°C .) and other properties. The aqueous *layer* contained in addition to mercurous acetate some globules of mercury.

When the reaction was carried out at the ordinary temperature but in the presence of sunlight for 3 hours the product of oxidation was quinone. It could be easily obtained by ether extracting the final mixture (yield: 0.5 g.).

Summary

Experiments have been conducted with a view to test if the progress of oxidation by mercuric acetate could be followed by weighing the amount of mercurous acetate precipitated from time to time. This procedure has been found to be not feasible since complications set in owing to the solvent also undergoing oxidation induced by the presence of other substances. It has been found that most compounds containing $-\text{CHOH}$ group produce mercurous acetate in methyl alcoholic solution and the oxidation products could be identified. Convenient methods for the preparation of benzil, quinhydrone, quinone and mercurous acetate in a pure condition in the laboratory are described.

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