o-Dithiols in Analysis

Part IV*. Diacetyltoluene-3:4-dithiol, Dibenzoyltoluene-3:4-dithiol and the Zinc Complex of Toluene-3:4-dithiol

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Diacetyltoluene-3:4-dithiol, dibenzoyltoluene-3:4-dithiol and the zinc complex of toluene-3:4-dithiol provide a stable source of toluene-3:4-dithiol. The first two are hydrolysed by alkalis to give toluene-3:4-dithiol, but are stable in acids; diacetyltoluene-3:4-dithiol is hydrolysed slowly by warm aqueous pyridine and almost immediately by ethanolic potassium ethoxide. Diacetyltoluene-3:4-dithiol gives colour reactions with palladium^{II}, rhenium^{VII}, tellurium^{IV} selenium^{IV}, and iridium^{IV} in concentrated hydrochloric acid, the complexes being formed in the order given. Dibenzoyltoluene-3:4-dithiol similarly reacts with palladium^{II} and selenium^{IV}. Reactions for palladium^{II}, rhenium^{VII} and tellurium^{IV} are apparently specific or readily rendered so. The zinc complex of toluene-3:4-dithiol may often be used directly in place of toluene-3:4-dithiol in acid solution. A solution of toluene-3:4-dithiol suitable for analysis may be prepared from the zinc complex by dissolving it either in ethanol containing a small amount of aqueous hydrochloric acid or in aqueous sodium hydroxide solution.

THE keeping qualities of pure toluene-3:4-dithiol (dithiol) are so poor that it is necessary to store it in sealed ampoules. Solutions in organic solvents are unstable and alkaline solutions rapidly deposit the disulphide. In earlier papers[1,2] it was suggested that the

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* For particulars of Parts I, II and III of this series, see reference list, p. 185.

reagent, dissolved in sodium hydroxide solution, should be preserved in an atmosphere of hydrogen or that an excess of thioglycollic acid should be added. Stone[3] suggested a solution containing some thioglycollic acid in 95 per cent. ethanol, but the keeping qualities of this solution still leave much to be desired. Moreover, the presence of thioglycollic acid is often undesirable, especially as it interferes with the reactions described in Part III.[4]

These difficulties can be overcome by generating dithiol, as and when required, from the derivatives described in this paper.

DIACETYLTOLUENE-3:4-DITHIOL AND DIBENZOYLTOLUENE-3:4-DITHIOL

Diacetyltoluene-3:4-dithiol (diacetyldithiol) and dibenzoyltoluene-3:4-dithiol (dibenzoyldithiol) are colourless stable crystalline compounds, hydrolysed by alkalis, but stable to acids. Diacetyldithiol is hydrolysed almost instantly in hot ethanolic potassium ethoxide solution, but dibenzoyldithiol only when heated under reflux for some minutes. Diacetyldithiol is hydrolysed rapidly, even in warm aqueous pyridine, and so elicits the colour reactions in this medium described in Part III.[4] Dibenzoyldithiol gives several of the same colour reactions if a small amount of sodium hydroxide is present.

Diacetyldithiol is readily soluble in most organic solvents. Its solutions in alcohols (methanol, ethanol, *n*-propanol, ethylene glycol), acetone, acetic acid and in solvents liable to peroxidation are somewhat unstable, as the disulphide is precipitated and then a yellow and ultimately a red colour is produced. Solutions can be kept without apparent change for a year in ethyl acetate or ethyl Cellosolve. Dibenzoyldithiol solutions are much more stable; a 0·01 *M* solution in 95 per cent. ethanol is permanent.

Of the two reagents, it would appear that diacetyldithiol is, for purposes of qualitative analysis, the more generally useful and that it is most conveniently stored in the solid state or, if frequently required, as a 1 per cent. solution in ethanol, which will remain stable for 3 to 4 weeks.

PREPARATION OF DITHIOL DERIVATIVES—

Diacetyldithiol—A solution of 1 g of dithiol in 2 to 3 parts by weight of acetic anhydride was heated on a water bath for 30 minutes. The products when poured into water gave the theoretical yield of an oil that did not readily crystallise. Colourless crystals of diacetyldithiol were recrystallised from *cyclo*hexane and had m.p. 48° C. By titration the composition of the product was found to be: $C_7H_6S_2$,* 64·5 per cent.; CH_3CO, 35·2 per cent. (calculated values for $C_{11}H_{12}O_2S_2$ are: $C_7H_6S_2$, 64·3 per cent.; CH_3CO, 35·8 per cent.).

Diacetyl-4-chloro-1:2-dimercaptobenzene—4-Chloro-1:2-dimercaptobenzene, prepared by the method of Mills and Clark,[5] was heated with acetic anhydride on a water bath for 30 minutes. The product was recrystallised from ethanol and had m.p. 68° C. Found on analysis: C, 46·3 per cent.; H, 3·8 per cent. (calculated values for $C_{10}H_9O_2S_2Cl$ are: C, 46·1 per cent.; H, 3·5 per cent.).

Dibenzoyldithiol—Dithiol (1 mole) was dissolved in 5 per cent. aqueous sodium hydroxide solution (2 moles) and shaken with benzoyl chloride (2 moles). Colourless crystals of dibenzoyldithiol were recrystallised from ethanol and had m.p. 92° C. By titration with mercuric chloride the product was found to contain: $C_7H_6S_2$, 41·2 per cent. (calculated value for $C_{21}H_{16}O_2S_2$ is 41·3 per cent.).

PREPARATION OF DITHIOL SOLUTION FROM ITS DERIVATIVES—

A suitable dithiol solution for use in analysis can be prepared as follows—

> Add one drop of water to 0·1 g of potassium hydroxide and heat until it has dissolved. Add 1 ml of 95 per cent. ethanol and 20 to 100 mg of diacetyldithiol. Boil for 10 to 15 seconds and then dilute with ethanol to the concentration required. Alternatively, use 2 to 3 ml of 1 per cent. ethanolic solution and proceed as before. The solution should be used within 1 to 3 hours. If the presence of alkali is undesirable, add 2 *N* hydrochloric acid until a permanent precipitate begins to form.

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* The dithiol contents of the compounds (as a percentage of $C_7H_6S_2$) were determined by dissolving a weighed amount of the compound (10 to 20 mg) in 5 ml of pyridine containing 1 drop of 0·01 *M* cobalt chloride. The brilliant blue solution produced was warmed and titrated with 0·01 *M* mercuric chloride solution from a microburette, the end-point being read to 0·01 ml. With dibenzoyldithiol one drop of 2 *N* sodium hydroxide was added.

REACTIONS OF DITHIOL DERIVATIVES WITH CATIONS—

When ethanolic diacetyldithiol was added to mineral-acid solutions containing the more common heavy metals, the reagent was precipitated unchanged as a white emulsion. In acetic acid or acetate buffer solution, precipitates formed slowly when the solution was boiled. These precipitates generally resembled the precipitates given by dithiol, except that the white cadmium complex slowly turned pink, whereas the dithiol complex remained white under the same conditions. A few preliminary analyses of these precipitates, which could not be purified, appeared to indicate that the lead and cadmium complexes formed in this way retained one acetyl group.

When ethanolic diacetyldithiol was added to 0·002 *M* solutions of palladium^{II}, rhenium^{VII}, tellurium^{IV} and selenium^{IV} in 9 to 10 *N* hydrochloric acid, coloured products were instantly produced, which could all be extracted with ethylene dichloride. The colour reactions of these metals were—

Palladium^{II}—Brick-red complex formed instantly in cold solution (2 to 3 μg per ml could be detected).

Rhenium^{VII}—Intense green colour developed rapidly when the solution was warmed (0·5 μg per ml could be detected).

Tellurium^{IV}—Intense yellow precipitate formed in hot solution with an excess of reagent (5 μg per ml could be detected). In 5 *N* hydrochloric acid a yellow precipitate formed after a few seconds and then rapidly darkened, possibly owing to the presence of free tellurium.

Selenium^{IV}—Evanescent red colour produced that changed to a yellow colour (20 μg per ml would produce the red colour). The colour of the solvent extract was yellowish green.

Iridium^{IV} caused the solution to darken slowly, the solvent extract being brown in colour. The presence of iridium did not interfere with the selenium reaction. In more dilute acid (5 *N*) osmium^{VIII} also gave a black precipitate, but other metallic ions did not give intensely coloured precipitates or colours at acidities above 0·5 *N*.

Dibenzoyldithiol reacted with palladium^{II} under similar conditions to give a brick-red complex, but rhenium^{VII} and tellurium^{IV} did not give colours. Selenium^{IV} did not give a colour immediately, but a red colour developed within 30 to 60 seconds and remained for 1 to 2 minutes. This was not always observed in mixtures containing other elements. Colours were not observed with other cations. Dibenzoyldithiol would, therefore, appear to be specific for palladium^{II}. The reaction was at once obtained with palladium^{II} in a solution containing all the more common cations.

When 2 per cent. ethanolic diacetyldithiol was added dropwise with shaking to 2 to 4 ml of hot solution containing a mixture of metals in 8 *N* hydrochloric acid in the presence of ethylene dichloride, the complexes were formed in the order palladium^{II}, rhenium^{VII} and tellurium^{VI}. By this means, it was possible to "titrate" the elements one by one with no noticeable interference; a sharp change in colour of the aqueous layer indicated that the previous element in the order of formation had been removed from solution. With the quantities investigated no interference was observed and 10 μg per ml of palladium^{II}, rhenium^{VII} and tellurium^{IV} were each detected without difficulty in a 10-fold excess of each of the other two and also of selenium, these elements being present in a solution containing 0·05 to 0·1 per cent. of each of the more common cations. Diacetyldithiol would therefore appear to be a specific or at least highly selective reagent for palladium^{II}, rhenium^{VII} and tellurium^{IV}.

THE ZINC COMPLEX OF DITHIOL

A second approach to the problem was made by investigating the metallic derivatives of the *o*-dithiols, a number of which have been obtained in an analytically pure state. Of those investigated the zinc complex of dithiol (zinc dithiol) appears to be the best for providing a stable source of dithiol. It is a colourless, odourless and water-repellent stable compound from which dithiol is instantly liberated by the action of acids or alkalis.

Zinc dithiol can often be used directly. When added to acid solutions of the heavy metals, the zinc is replaced and the familiar dithiol precipitates are obtained. Zinc dithiol is soluble in cold pyridine and in aqueous sodium hydroxide solution and at once elicits most of the reactions given by dithiol in these media. Hence, in aqueous pyridine, the reactions given by copper, cobalt, iron and nickel were produced at once, that for thallium seemed to be poorly developed, while those for antimony and vanadium were not given. When dithiol was first liberated by means of hydrochloric acid, however, the usual reactions were given.

Zinc dithiol gives cleaner solutions than those produced with diacetyldithiol. It cannot, however, be used in certain reactions (see "Manganese," Part III, p. 181), or when the addition of zinc is undesirable.

PREPARATION—

A solution of 1 g of dithiol in 5 ml of chloroform was added to a hot solution containing 2 g of zinc acetate in 50 ml of water and the resulting solution was shaken. The precipitate formed was filtered off, washed with chloroform and dried at 80° C. The dried precipitate was a white bulky powder, easily charged, and the yield was almost the theoretical. Found on analysis: S, 28·6 per cent.; Zn, 29·9 per cent.; $C_7H_6S_2$, 68·3 per cent. (calculated values for $C_7H_6S_2Zn$ are: S, 29·2 per cent.; Zn, 29·8 per cent.; $C_7H_6S_2$, 70·3 per cent.).

PREPARATION OF DITHIOL SOLUTION FROM ZINC DITHIOL—

A suitable dithiol solution for use in analysis can be prepared from zinc dithiol as follows—

> To 3 to 5 ml of 95 per cent. ethanol add a suitable amount of zinc dithiol and then a few drops of concentrated hydrochloric acid or 5 *N* sulphuric acid and shake the solution. A clear solution is produced within a few seconds in the cold. Alternatively, add a suitable amount of zinc dithiol to 2 *N* sodium hydroxide solution together with one drop of ethanol and shake the solution.

I express my gratitude to Dr. F. G. Mann, F.R.S., and to Mr. P. S. Jewell, for their interest, help and encouragement, and to Hopkin & Williams Ltd., Carnegies of Welwyn Ltd. and the Clayton Aniline Co. Ltd. for gifts of chemicals.

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NOTE—References 1, 2 and 4 constitute Parts I, II and III, respectively, of this series.

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June 25*th*, 1956