

INTERACTION OF THIONYL CHLORIDE AND ESTERS OF AROMATIC HYDROXY ACIDS AND THEIR DERIVATIVES IN PRESENCE OF FINELY DIVIDED COPPER—IV

Interaction of Methyl- β -Resorcyate and Thionyl Chloride
in Presence of Finely Divided Copper

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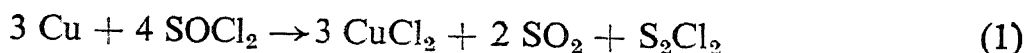
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It was observed by Hirwe, Jadhav and Chakradev¹ that the reaction of thionyl chloride and methyl β -resorcyate in presence of finely divided copper was very vigorous and no definite product could be isolated. It has, however, been now found that diaryl disulphide (dithio-ether) could be isolated when the reaction was carried out at a lower temperature.

The point of linking of the two nuclei in this disulphide was arrived at by treating it with nitric acid in presence of sulphuric acid below -5° when 5-nitro- β -resorcylic acid was obtained, which showed that the two nuclei were linked through sulphur atom which occupied the position para to $-OH$ group and meta to $-COOCH_3$ group. If, however, this nitric acid reaction was carried out at room temperature 3:5-dinitro- β -resorcylic acid was obtained.

The disulphide should have the constitution as $\begin{matrix} R \\ \diagdown \\ S \\ \diagup \\ R \end{matrix} = S$ (where R is the nucleus) and not $R-S-S-R$ as it gave 2:2'-dimethoxy-4:4'-dihydroxy-5:5'-dicarbomethoxy-diphenyl thioether when methylated with dimethyl sulphate in presence of alkali. This thioether gave 2:2'-dimethoxy-4:4'-dihydroxy-5:5'-dicarboxy-diphenyl thioether identical with the one got by Hirwe, Jadhav and Chakradev (*loc. cit.*). If the thioether would be supposed to have the constitution $R-S-S-R$ both sulphur atoms should have been lost simultaneously.

As the same disulphide (dithioether) was formed by the action of sulphur monochloride as well as that of sulphur dichloride, the mechanism of the reaction may be explained by considering that thionyl chloride first decomposes as (1)² or (2)



and then $2 \text{ SCl}_2 \rightarrow \text{S}_2\text{Cl}_2 + \text{Cl}_2$.

As the yield of the disulphide with sulphur dichloride and sulphur monochloride is poor as compared with that obtained with thionyl chloride and copper, copper may be acting as catalyst also in this reaction. Further as the yield with sulphur dichloride is better than with monochloride, chlorine formed by its decomposition may be acting as a catalyst.

Sulphur monochloride has been known to form dithioethers (disulphide) by Naik³ and Naik and Bhat.⁴

The diacetyl and dibenzoyl derivatives of the disulphide were also prepared.

EXPERIMENTAL

2:2'-4:4'-Tetrahydroxy-5:5'-dicarbmethoxy-diphenyl disulphide (I).—Methyl- β -resorcyate (6 g.) and thionyl chloride (25 c.c.) were mixed together and the mixture was surrounded by ice. Finely divided copper (8 g.) was gradually added to it. Fumes of hydrogen chloride and sulphur dioxide were evolved. The reaction mixture was protected from moisture and kept overnight in refrigerator. It was then mixed with dry chloroform and heated on a boiling water-bath for two hours and the hot solution filtered. A pasty mass was obtained after the removal of the liquid, which turned into solid after repeated washings with acetone. The solid was then boiled with carbon disulphide to remove free sulphur and finally crystallised from a mixture of nitrobenzene and acetic acid, m.p. 245–6°. Yield: 4 g. Found: S, 16.1; $C_{16}H_{14}O_8S_2$ requires S, 16.08 per cent.

5-Nitro- β -resorcylic acid.—The disulphide (I) (0.5 g.) was dissolved in sulphuric acid (5 c.c.) and the solution was surrounded by freezing mixture. Nitric acid (con.) (5 c.c.) was gradually added to it, not allowing the temperature to rise above -5° . The reaction mixture was kept in ice after the addition was over and then diluted with water when solid was obtained, which crystallised from hot water. m.p. 215–6°. This showed no lowering in melting point when mixed with a genuine specimen.

3:5-Dinitro- β -resorcylic acid.—The disulphide (I) was dissolved in sulphuric acid (5 c.c.) and nitric acid (con.) (5 c.c.) was added to it when a vigorous reaction commenced which was allowed to proceed for ten minutes. The precipitate obtained on diluting the mixture with water was crystallised from dilute acetic acid. It sintered at 190° and melted completely at 204° (decomposition). It showed no lowering in melting point when mixed with a genuine specimen.

2:2'-Diacetoxy-4:4'-dihydroxy-5:5'-dicarbmethoxy-diphenyl disulphide (II).—It was prepared by acetylating (I) in presence of pyridine. Crystallised from glacial acetic acid, m.p. 213–4° (decomposition). Found: S, 13.4; $C_{20}H_{18}O_{10}S_2$ requires S, 13.3 per cent.

2: 2'-Dibenzoyloxy-4: 4'-dihydroxy-5: 5'-dicarbomethoxy-diphenyl disulphide (III).—It was crystallised from acetic acid. It shrinks at 170° and melts at 191–2° (decomposition). Found: S, 10·3; $C_{30}H_{22}O_{10}S_2$ requires S, 10·6 per cent.

2: 2'-Dimethoxy-4: 4'-dihydroxy-5: 5'-dicarbomethoxy-diphenyl sulphide (IV).—This was obtained when the disulphide (I) (0·5 g.) was heated on a boiling water-bath with dimethyl sulphate (5 c.c.) in presence of 20% solution of potassium hydroxide (40 c.c.). It crystallised from acetic acid in colourless needles which did not melt upto 300°. Found: S, 7·7; $C_{18}H_{18}O_8S$ requires S, 8·1 per cent.

This sulphide (IV) was hydrolysed to 2: 2'-dimethoxy-4: 4'-dihydroxy-5: 5'-dicarboxy-diphenyl sulphide by boiling it for 2 hours with 10 per cent. sodium hydroxide solution. It crystallised from acetic acid, m.p. 224–5°. Found: S, 8·6; $C_{16}H_{14}O_8S$ requires S, 8·7 per cent. Hirwe, Jadhav and Chakradev (*loc. cit.*) gave m.p. 226°.

It showed no lowering in melting point when mixed with the genuine specimen.

The same disulphide (I) was also prepared by allowing sulphur dichloride (5 c.c.) to interact with methyl β -resorcylate (4 g.) in presence of dry ether (20 c.c.) and allowing the reaction to proceed for two days at room temperature. The semi-solid obtained after the removal of ether was stirred with carbon disulphide when grey solid separated. It crystallised from acetic acid, m.p. 245–6°. Yield, 1·7 g. Found: S, 16·03; $C_{16}H_{14}O_8S_2$ requires S, 16·08 per cent.

Sulphur monochloride also gave the same product when the reaction was allowed to proceed at room temperature for two days, but the yield was very poor (0·7 g. only from 4 g. of ester).

SUMMARY

The disulphide was obtained in this reaction and it was found to be unstable towards alkali. Its characteristic derivatives such as di-acetoxy and di-benzoyloxy were prepared.

REFERENCES

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