

INTERACTION OF HYDROXY ACETOPHENONES AND THEIR DERIVATIVES AND THIONYL CHLORIDE IN PRESENCE OF FINELY DIVIDED COPPER

Part IV. Preparation of 3 : 3'-Diacetyl-4 : 4'-dihydroxy-6 : 6'-
dibenzoyloxy-diphenyl thioether and its derivatives

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2-HYDROXY-4-BENZYLOXY-ACETOPHENONE, thionyl chloride and chloroform were mixed together and copper powder was gradually added to it when the thioether was obtained. This thioether gave 2-hydroxy-4-benzoyloxy-5-bromo-acetophenone¹ when treated with bromine in acetic acid medium and when treated with concentrated nitric acid in acetic acid medium, it gave a mono nitro compound which on debenylation with hydrobromic acid gave 2 : 4-dihydroxy-5-nitro-acetophenone.² This proved that the thioether was 3 : 3'-acetyl-4 : 4'-dihydroxy-6 : 6'-dibenzoyloxy-diphenyl thioether.

Methylation, acetylation and benzylation gave dimethoxy, diacetoxy and dibenzoyloxy derivatives of the thioether. Phenyl-hydrazine gave diphenyl hydrazone of the thioether.

The same ketone gave the same thioether with (i) sulphur mono-chloride and (ii) sulphur dichloride in presence of traces of copper and hence the mechanism of the reaction can be explained in the same way as is done by Hirve, Jadhav and Chakradeo.³

EXPERIMENTAL

3 : 3'-Diacetyl-4 : 4'-dihydroxy-6 : 6'-dibenzoyloxy-diphenyl thioether (I)

2-Hydroxy-4-benzoyloxy-acetophenone (12 g.) and thionyl chloride (20 g.) were mixed together and dry chloroform (20 c.c.) was then added to the mixture. It was surrounded by crushed ice when copper powder (8 g.) was gradually added to it. The reaction mixture was left overnight at room temperature and next day more dry chloroform (20 c.c.) was added and it was heated on a water-bath at 60° for about ten minutes. The solution was filtered and the residue was again extracted with chloroform. A pasty greyish

residue was obtained after the removal of the liquid. Pinkish white solid was obtained after repeatedly washing the mass with acetone. It finally crystallised from acetic acid in white needles, m.p. 202–3°. It gave greenish coloration with alcoholic ferric chloride solution. It was soluble in benzene, carbon tetrachloride, carbon disulphide and alcohol and insoluble in ether and petrol. Found: S, 6.4; $C_{30}H_{26}O_6S$ requires S, 6.2 per cent. This same substance was obtained by the interaction of the ketone (2 g.), sulphur monochloride (1 g.) or sulphur dichloride (1 g.) and copper powder (a few milligrams) in presence of dry chloroform and the reaction was carried out and finished as above. The compound showed no lowering in melting point with the above thioether.

Phenylhydrazone of 3:3'-diacetyl-4:4'-dihydroxy-6:6'-dibenzoyloxy-diphenylthioether

It was prepared by heating acetic acid solutions of the reactants on a boiling water-bath for half an hour. The product separated on cooling. It crystallised from acetic acid, m.p. 239–40°. Found: N, 8.2; $C_{42}H_{38}O_4N_4S$ requires N, 8.1 per cent.

3:3'-Diacetyl-4:4'-dimethoxy-6:6'-dibenzoyloxy-diphenyl thioether

Methylation was carried out by dimethyl sulphate in presence of acetone as usual by heating the mixture on a boiling water-bath for about an hour. It crystallised from alcohol in brown plates, m.p. 128–29°. Found: S, 5.8; $C_{32}H_{30}O_6S$ requires S, 5.9 per cent.

3:3'-Diacetyl-4:4'-dibenzoyloxy-6:6'-dibenzoyloxy-diphenyl thioether

Benzoylation was carried out by heating the reactants in presence of a few drops of pyridine for ten minutes at 170–80°. On mixing the reaction mixture with crushed ice a brown liquid separated. It was extracted with ether and the pasty solid left after the removal of ether was triturated with dilute caustic soda solution and finally crystallised from alcohol, m.p. 107–9°. Found: S, 4.6; $C_{44}H_{34}O_8S$ requires S, 4.4 per cent.

3:3'-Diacetyl-4:4'-diacetoxy-6:6'-dibenzoyloxy-diphenyl thioether

Acetylation was carried out as usual by boiling the substance with acetic anhydride in pyridine solution for three hours. The pasty mass obtained on dilution was repeatedly washed with dilute hydrochloric acid and finally crystallised from acetic acid as dark brown crystals, m.p. 173–75°. Found: S, 5.4; $C_{34}H_{30}O_8S$ requires S, 5.3 per cent.

2-Hydroxy-4-benzyloxy-5-bromo-acetophenone

The thioether (I) (1 g.) was dissolved in boiling acetic acid (10 c.c.). When the solution cooled to 90°, a crystal of iodine was added and 15 per cent. solution of bromine in acetic acid (5 c.c.) was added and the reaction mixture was shaken for eight hours and then left overnight at room temperature. Acetic acid was allowed to evaporate at room temperature. Solid began to separate after one day which was finally crystallised from alcohol and ethylacetate mixture in white needles, m.p. 154–55°. Found: Br, 24·7; $C_{15}H_{13}O_3Br$ requires Br, 24·9 per cent.

2-Hydroxy-4-benzyloxy-5-nitro-acetophenone

The thioether (I) (0·5 g.) was suspended in acetic acid (5 c.c.) and concentrated nitric acid (5 c.c.) was slowly added to it and the mixture left overnight at room temperature. Next day crystals had separated which were filtered and recrystallised from alcohol in white needles, m.p. 140–41°. Found: N, 5·3; $C_{15}H_{13}O_5N$ requires N, 4·9 per cent. When boiled with hydrobromic acid in presence of acetic acid this benzyloxy compound gave 2:4-dihydroxy-5-nitro-acetophenone.

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