[Jour. Indian Chem. Soc., Vol. 47, No. 1, 1970]

SHORT COMMUNICATIONS

Study of the Action of α:β-Dibromo Ketones on Thiourea and Substituted Thioureas

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Action of α-haloketones like monochloroacetone[1], α-chloroethyl-methyl ketone[2], α-chlorocyclohexanone[3] and w-bromo acetophenone[4] on thiourea and phenylthiourea has been studied by a large number of workers and the formation of a thiazole derivative has been reported in each case. But the action of $\alpha : \beta$-dihaloketones on thiourea and substituted thioureas has not been studied. The action of $\alpha : \beta$-dibromoethylphenyl ether[5], $\alpha : \beta$-dichlorotetrahydrofuran[6] and $\alpha : \beta$-dibromoethyl ether[7] on thiourea has been studied and the formation of 2-amino-thiazole derivative has been reported in each case. In the present communication, the study of the action of $\alpha : \beta$-dibromo ketones on thiourea and substituted thioureas has been reported.

When benzylideneacetonedibromide is condensed with thiourea, 2-amino-4 β-phenyl ethyl)-thiazole was isolated. The same compound was also isolated when benzylideneacetone was condensed with thiourea in presence of bromine or iodine. The identity of the products was proved not only by the compounds' same melting point but same m.m.p. also. The R_f values of the two compounds on paper chromatograms in acidic, neutral and alkaline solvent systems are same.

The formation of the same compound from the above two different starting materials can be explained on the basis that, benzylideneacetonedibromide at the condensation temperature of the boiling water-bath, undergoes decomposition to the unsaturated ketone and bromine which then condense with thiourea.

The evidence for the formation of 4(β-phenylethyl)-2-amino thiazole comes from the following observations.

(1) The above thiazole undergoes bromination at C_5-position by the brominating agents, which usually brominate the thiazole at C_5-position showing the C_5-position free[8,9].

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(2) The resulted thiazole also undergoes coupling reaction with diazotised sulphanilic acid giving an azo dye having the azo group at the C_5-position. This confirms further that C_5-position is free[10,11,12].

(3) The disappearance of the unsaturation of the side chain at C_4-position is proved by the fact that with bromine-water there is no addition of bromine at the olefinic double bond showing its absence. The evidence for the removal of unsaturation came from the work of Kobayashi[12].

There might be other possibilities of condensation giving compounds 5-(phenyl, bromomethyl)-4-methyl-2-aminothiazole or 5-phenyl-4-acetyl-2-amino thiazole.

These possibilities are ruled out on the ground that both of the above compounds are substituted at C_5-position which is not the case.

The formation of 5-phenyl-4-acetyl-2-amino thiazole is further ruled out on the ground that it contains a CH_3-CO- group at C_4, which is not the case as the compound does not respond to iodoform reaction.

EXPERIMENTAL

1. *Synthesis of benzylidene acetone dibromide* : Benzylidene acetone (2 g.) was dissolved in dry chloroform (30 ml.) and stirred for some time. Bromine (5 g.) dissolved in 35 ml. of chloroform was added dropwise to the above solution and the mixture was stirred for another hour. Chloroform was then evaporated from the mixture at the room temperature and the solid was collected and kept overnight in a vacuum desiccator. It was crystallised finally from absolute alcohol as white needle shaped crystals, m.p. 122–23°, yield 85% (Found : Br, 51·3; $C_{10}H_{10}OBr_2$ requires : Br, 52·28%).

2. *Synthesis of anisylidene acetone dibromide* : Anisylidene acetone (2 g.) was dissolved in 30 ml. of chloroform and remaining procedure was same as above. m.p. 107°, yield, 85% (Found : Br, 46·71; $C_{11}H_{12}O_2Br_2$ requires : Br, 47·62%).

3. *Synthesis of 4-(β-phenyl ethyl)-2-amino thiazole* : A mixture consisting of benzylidene acetone dibromide (3 g.) and thiourea (2 g.) was condensed in absolute alcohol (25 ml.) for 12 hr. in a waterbath using a condenser. The heating was discontinued and alcohol was distilled off. The residue was then boiled with water for sometime. Water was decanted and the product was treated with conc. ammonium hydroxide. The product was finally crystallised from absolute alcohol, m.p. 90–91°, yield, 87% (Found : N, 13·79, S, 15·97; $C_{11}H_{12}N_2S$ requires N, 13·13; S, 15·65%).

4. *Synthesis of 4-β-(p-methoxy phenyl)-ethyl 2-amino thiazole* : A mixture consisting of anisylidene acetone dibromide (3·4 g.), thiourea (2 g.) and absolute alcohol (25 ml.) was heated in a waterbath. The remainimg procedure was same as above, m.p. 97–98°, yield, 88% (Found : N, 10·98; S, 13·01; $C_{12}H_{14}ON_2S$ requires : N, 11·92, S, 13·68%.)

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5. *Synthesis of 4-β-phenyl ethyl 2-phenyl amino thiazole* : Procedure is same as in 3.Phenylthiourea is taken in place of thiourea, m.p. 82–83°, yield, 78% (Found : N, 9·82; S, 11·18; $C_{17}H_{16}N_2S$ requires : N, 10·00; S, 11·43%).

6. *Synthesis of 4-β-(p-methoxy phenyl) ethyl 2-phenylamino thiazole* : Procedure is same as in 4. Phenyl thiourea is used in place of thiourea, m.p. 89°, yield, 75%, (Found N, 8·91; S, 10·13; $C_{18}H_{18}ON_2S$ requires : N, 9·03; S, 10·32%).

7. *Synthesis of 2-phenylimino 3-phenyl 4-β-phenylethyl thiazoline* : Procedure is same as in 3.Thiocarbanilide is taken in place of thiourea, m.p. 101°, yield, 70%, (Found : N, 7·31; S, 8·58; $C_{23}H_{20}N_2S$ requires : N, 7·86; S, 8·99%).

8. *Synthesis of 2-phenylimino, 3-phenyl 4-β-(p-methoxy phenyl) ethyl thiazoline* : Procedure is same as in 4. Thiocarbanilide is used in place of thiourea, m.p. 188°, yield, 65%, (Found : N, 7·51; S, 8·1, $C_{24}H_{22}ON_2S$ requires : N, 7·25; S, 8·29%).

The authors are thankful to the Board of Scientific and Industrial Research, Government of Orissa for a research grant and to the University of Ranchi for granting study leave to one of them (B.C.D.) to work in this laboratory.

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Received June 17, 1969.