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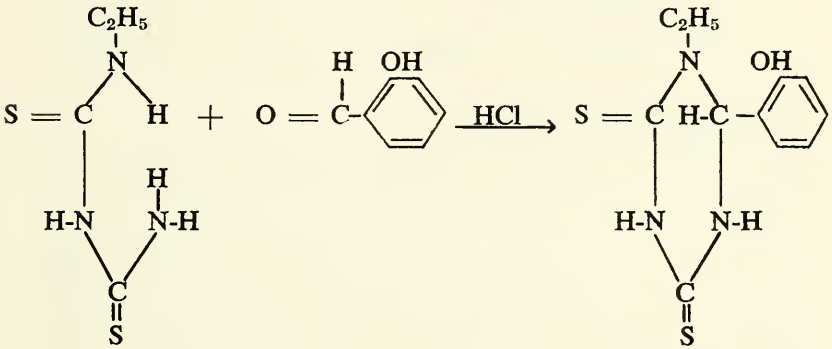
Synthesis of 4:6 Thio 1, 3, 5-triazine Derivatives (I)

by

Kamalakar B. Raut

The present work describes the synthesis of 4:6 thio 1,3,5-triazine derivatives for biological studies, by condensation of 1-ethyl dithiobiuret with different aromatic aldehydes. The reaction takes place as follows:



Ethyl dithiobiuret

Salicylaldehyde

1-ethyl-2-O-hydroxy phenyl 4:6 dithio 1, 3,5-triazine

Experimental

A mixture of ethyl dithiobiuret and salicylic aldehyde [1:1] in ethanol was cooled to 0°C. Dry hydrogen chloride gas was passed through this mixture for thirty minutes. The reaction mixture was poured in 1N sodium hydroxide, warmed to 50° and filtered. The filtrate was acidified with dilute acetic acid and cooled overnight. The solid that precipitated was separated by filtration and crystallized from ethanol or ethyl acetate.

Similarly, other derivatives were prepared.

With ethyl dithiobiuret, the following aldehydes were condensed.

Aldehyde	*M.P. of the Product*
1. Salicylaldehyde	228°C
2. m-hydroxy benzaldehyde	171°C
3. m-chloro benzaldehyde	230°C
4. p-tolu-aldehyde	227°C
5. Veratric aldehyde	226°C
6. 5-Bromovanillin	224°C
7. Vanillin	226°C
8. Anisaldehyde	227°C
9. p-dimethylamino benzaldehyde	222°C

Further work is in progress.

Certain Condensation Reactions with Copper Powder as a Catalyst

by

Kamalakar B. Raut*

In 1904 Ullmann (1) was able to show that copper powder readily eliminates the iodine from aromatic iodo-compounds yielding cuprous iodide and derivatives of diphenyl. A few years later (2) it was shown that the reagent acts catalytically in condensing halogenated benzenes with metallic phenoxides, thus providing a simple method for preparing substituted diphenyl oxides; still later (3) Ullmann showed that the copper reacts catalytically in removing hydrogen halides from aromatic amines and halogenated benzenes, yielding substituted diphenylamines. Thus aniline and p-chloronitrobenzene yield p-nitrodiphenylamine. The yields are quite good when potassium carbonate is added, as this not only neutralizes the hydrogen halide formed during the reaction, but also stabilizes any carboxylic acids by converting them into potassium salts. The method is a general one for preparing arylanthranilic acids (4). With halogen or methoxy-substituted amines the addition of amyl alcohol is advisable. In a similar manner 2-chloro-4-nitrobenzoic acid condenses at 180° with sodium phenoxide yielding 5-nitrodiphenylether-2-carboxylic acid (5). In some cases a mixture of copper and potassium iodide or even cuprous iodide gives good results.

The replacement of halogen in aromatic halides by hydroxyl is readily effected by heating the compound with sodium acetate at 140-150° in the presence of a little copper powder. By this process salicylic acid is readily obtained from o-chlorobenzoic acid, and halogen can be replaced by carboxyl by heating the halogenated benzene with aqueous alcoholic potassium cyanide and cuprous cyanide at 260° (7).

Reactions of aniline with carbon tetrachloride and with chloroform in presence of copper powder are presently being studied. From reactions of aniline and carbon tetrachloride three compounds melting at 167°, 258°, and 267°C have been isolated. From the reaction of aniline and chloroform a compound melting at 209° was isolated. The structural studies of these compounds are under progress and will be reported later. It appears that the four compounds isolated have not been isolated before.

Experimental

Three moles of aniline, carbon tetrachloride, [25.5cc] and copper mesh powder [E. H. Sargent & Company, Chicago, Illinois] mea-

*The investigator is indebted to Jannie Singleton and Laura Grant, both students, at Savannah State College, for their cooperation and assistance.

sured on the tip of a spatula were refluxed for two hours over a steam bath. The refluxing was discontinued when a hard black solid was present. The solid was allowed to cool and subjected to steam distillation using a 10 per cent solution of sodium hydroxide. After the solid had been distilled until a clear liquid began to distill off, the solid left during distillation was filtered from the liquid by use of a buchner funnel, ground, and dried. The dry solid was then extracted with a 7 per cent solution of sulfuric acid. The filtrate was allowed to cool to 10°C, and refiltered. To the filtered solution, cold ammonium hydroxide solution was added slowly to the liquid until the solution was neutralized. The entire solution was refiltered using a suction funnel. The precipitate was dried, and purified through recrystallization. The purified compound was dried and the melting point was taken. It was found to be 167°C.

The solid left after extraction with 7 per cent sulfuric acid was then extracted with alcohol, filtered, allowed to dry, and the melting point taken which was 258°C. Finally, the remaining solid from the above two extractions was dried, and its melting point was taken. It was 267°C.

27.9 ml of aniline, 20.8 ml chloroform, and a little copper powder were refluxed for 10 hours on the water bath. The reaction mixture was made alkaline with 10 per cent solution of sodium hydroxide and steam distilled. The solid which remained behind was washed with 7 per cent sulfuric acid and crystallized from alcohol. White flakes melting at 209°C were obtained.

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