Interaction of Arylthioureas and Aromatic Sulphonyl Chlorides

It was recently shown¹ that the reaction of arylureas and aromatic sulphonyl chlorides in pyridine under restrained conditions does not yield arylsulphonyl arylureas but occurs with simultaneous dehydration, and results in the formation of arylsulphonyl arylcyanamides in good yields. The production of the appropriate substituted melamines was also observed in some cases². In continuation of this work, the interaction of sulphonyl chlorides and arylthioureas has been examined.

The action of benzenesulphonyl chloride on thiourea in alcoholic solution was first studied by Remsen and Turner³, who obtained dithioformamidine dihydrochloride and diphenyl disulphoxide; similar results were obtained by Leitch *et al.*⁴ using *p*-acetamido-benzenesulphonyl chloride. Fromm and Heyder's attempts⁵ to prepare the corresponding aryl-substituted dithioformamidine by the action of sulphonyl chlorides on phenylthiourea resulted in ring-closure, with formation of 2:4-diphenyl-3:5 di-imino-2:3:4:5-tetrahydro-1:2:4-thiadiazole.

In the present investigation, using conditions recently employed with arylureas, the interaction of arylthioureas and aromatic sulphonyl chlorides was found to take a different course. The aromatic thiourea is rapidly desulphurized giving arylecyanamide as one of the main products, and the reaction then proceeds essentially as with arylureas¹. Thus, treatment of 1 mole of arylthiourea with 2.5 moles of sulphonyl chloride in pyridine at moderate temperatures gives a product from which approximately 1 gm. molecule each of arylecyanamide (I) and sulphur are obtained. Some of the cyanamide reacts further with the excess of sulphonyl chloride, as shown by the isolation of arylsulphonyl arylecyanamide (II). Part of the sulphonyl chloride is converted to the disulphoxide (III) during the reaction.

Disregarding, for the time being, the mechanism of the reaction, the net results can be represented by the following overall equation:

As an example, the interaction between phenylthiourea and toluene-*p*-sulphonyl chloride gave phenylecyanamide (65 per cent yield), sulphur (80 per cent, based on the thiourea), toluene-*p*-sulphonyl phenylecyanamide (25 per cent) and di-*p*-toluene disulphoxide (25 per cent). Similar results are obtainable with other arylthioureas.

Further experiments in connexion with this work are in progress, and a detailed account will appear elsewhere in due course.

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¹ Kurzer, *J. Chem. Soc.*, 1034, 3029 (1949).

² Kurzer, *J. Chem. Soc.*, 3033 (1949).

³ Remsen and Turner, *Amer. Chem. J.*, **25**, 190 (1901).

⁴ Leitch, Baker and Brickman, *Canad. J. Res.*, **23 B**, 139 (1945).

⁵ Fromm and Heyder, *Berichte*, **42**, 3804 (1909).

Structure of the Diazonium Ion

ACCORDING to the accepted constitution of the diazonium ion, a nitrogen atom takes the place of three hydrogen atoms in a substituted ammonium ion. It is accordingly conceivable that there may be resonance between the two forms:

By labelling one of the nitrogen atoms, we have shown that such resonance does not, in fact, occur.

Starting with phthalimide containing labelled nitrogen, we synthesized and diazotized labelled aniline and coupled it with β -naphthol. By reduction we split the product to aniline and α -amino- β -naphthol. If resonance of the above kind exists, the labelled nitrogen should be equally divided between the aniline and the amino-naphthol. If, on the other hand, such resonance is absent, the labelled nitrogen should be entirely in the aniline. According to our preliminary results, more than 97 per cent of the labelled nitrogen remains in the aniline. We conclude that there is no resonance.

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The Reaction between β -Carotene and Antimony Trichloride

It has always seemed anomalous that anhydrovitamin A with six conjugated double bonds should give $\lambda_{\max}$ at 620 m μ with the Carr-Price reagent, and that β -carotene with eleven conjugated double

bonds should give $\lambda_{\max}$ at 585 m μ . Further, $\epsilon_{\max}$ for anhydrovitamin A is 170,000, whereas that for β -carotene at 585 m μ is only 22,000¹.

Assuming that the compounds formed in the reaction are unsymmetrical ions, $\lambda_{\max}$ should be a linear function of the number of conjugated double bonds². In the colour test, anhydrovitamin A₁ (with six conjugated double bonds) has $\lambda_{\max} = 623$ m μ ³, whereas anhydrovitamin A₂ (with probably seven conjugated double bonds) has $\lambda_{\max} = 693$ m μ ⁴. Hence for eleven conjugated double bonds one would expect $\lambda_{\max} = 693 + 4(693 - 623) = 973$ m μ . Also, axerophthene (five conjugated double bonds) has $\lambda_{\max} = 577$ m μ ⁵ in the colour test and *iso*-desmethylaxerophthene (four conjugated double bonds) has $\lambda_{\max} = 490$ m μ ⁶. Hence for eleven conjugated double bonds one would expect $\lambda_{\max} = 577 + 6(577 - 490) = 1,099$ m μ . The assumptions here debar quantitative prediction, but they prompt investigation in the region