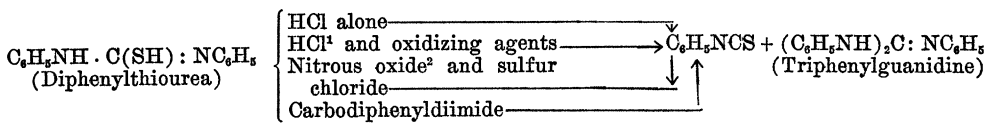
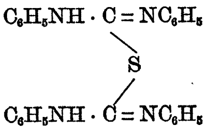
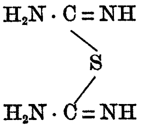
A NEW CONCEPTION OF THE FORMATION OF ARYLGUANIDINES AND ARYLISOTHIOCYANATES FROM ARYLTHIOUREAS*

THE fact that the four chemical reactions expressed below all lead to the same end products, namely isothiocyanates and guanidines, indicates that there is a fundamental relationship in the reaction mechanism of these characteristic transformations. From the data which are now available, it seems very clear to the writer that the present experimental evidence is in support of the conclusion that these thiourea combinations interact, in all these four reactions, in their pseudo or thiol form. If such a conclusion be accepted, it is then possible to introduce a further and more significant conception that leads to a new formulation of these changes and which enables one to obtain a clearer insight into the true mechanism of these type reactions. If now, the pseudothiourea molecule is accepted as the reactive unit, then each one of these four changes can easily be formulated in accordance with a definite and common reaction-mechanism by simply assuming the formation of a common intermediate compound corresponding in structure to a diimidoacid-anhydride combination, as is represented by formula I. The mother substance of this hypothetical aromatic compound is expressed by formula II and its oxygen analogue by formula III.

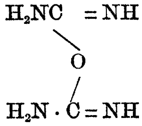




I

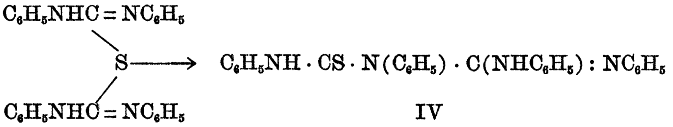


II



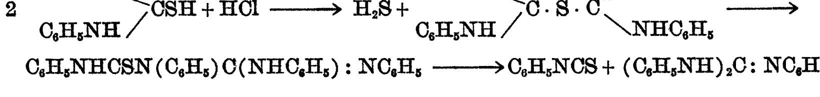
III

A compound having the anhydride constitution represented by formula I would not be stable. Such a molecular construction represents a very labile system and from the evidence which has been produced from previous researches in this laboratory on organic compounds of this type,[3] it would be predicted that a diimidoacid-anhydride of this constitution would easily undergo a molecular rearrangement at ordinary temperature and be transformed into the corresponding thiourea combination represented by formula IV. Such a combination would be unstable in the presence of acids and easily undergo hydrolysis with formation of an isothiocyanate and a triarylguanidine. In fact, it now seems very probable that Weith,[4] in his early work on aromatic thioureas, was actually dealing with both of these molecular constructions in his experiment demonstrating the behavior of carbodiphenyldiimide towards diphenylthiourea, and that his final products—phenylisothiocyanate and triphenylguanidine—resulted from acid hydrolysis of the thiourea IV.



IV

According to the above interpretation of these reactions, the complete hydrolysis of diphenylthiourea with hydrochloric acid in the presence or absence of an oxidizing agent would be expressed as follows:



$$C_6H_5NHCSN(C_6H_5)C(NHC_6H_5) : NC_6H_5 \longrightarrow C_6H_5NCS + (C_6H_5NH)_2C : NC_6H_5$$

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[1] Hofmann, *Ber.*, 2, 458 (1869).

[2] Claus, *Ber.*, 4, 143 (1871); Krall, *Ber.*, 4, 99 (1871).

[3] Wheeler and Johnson, *Amer. Chem. Jour.*, 30, 24 (1903); Jamieson, *J. Amer. Chem. Soc.*, 26, 177 (1904).

[4] *Ber.*, 9, 810 (1876).