

REACTION OF TETRASULFUR TETRANITRIDE ( $N_4S_4$ ) WITH HYDRAZINES AND HYDRAZONES<sup>1)</sup>

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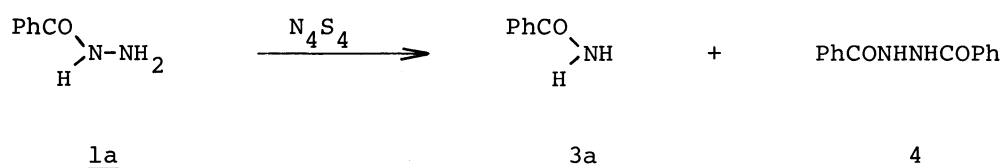
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The reaction of  $N_4S_4$  with benzoyl- (1a) and 1-methyl-1-phenylhydrazine (1b), benzophenone- (2a) and fluorenone hydrazone (2b) was carried out in refluxing benzene (1a and 1b) or toluene (2a and 2b) and  $N_4S_4$  was found to behave as a N-N bond cleaving reagent for 1b, while both a N-N bond cleaving and an oxidizing reagent for 1a and 2. The reaction mechanism was briefly mentioned.

Although  $N_4S_4$  is known to react with nucleophiles such as Grignard reagents<sup>2)</sup>, diazo compounds<sup>3)</sup> and amines<sup>4)</sup>, nothing is known on the reaction with hydrazines except phenylhydrazine<sup>4b)</sup> affording diphenyl di- and trisulfides in good yields.

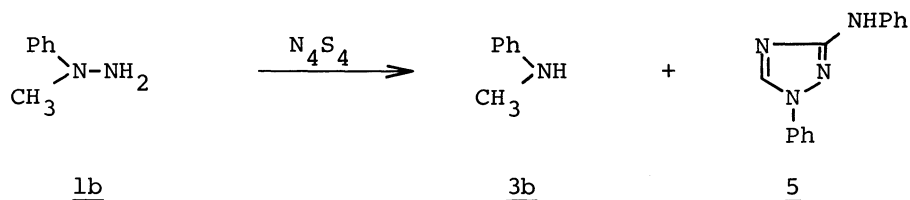
As a part of our study on  $N_4S_4$  as a synthetic reagent, we investigated the reaction with hydrazines (1a, b) and hydrazones (2a, b) and now report our preliminary results in the present paper.

A mixture of benzoylhydrazine (1a, 10.9 mmole) and  $N_4S_4$  (2.7 mmole) in benzene (20 ml) was heated at reflux for 2 hr and working up the reaction mixture gave benzamide (3a), N-N bond cleavage product of 1a, and 1,2-dibenzoylhydrazine (4) in 27 and 28% yields respectively, together with recovered 1a (14%),  $N_4S_4$  and sulfur. Since 1a is known to begin transacylation giving 4 and hydrazine at higher temperature than 180 °C<sup>5)</sup>, it seems to be unreasonable to explain the formation of 4 by transacylation

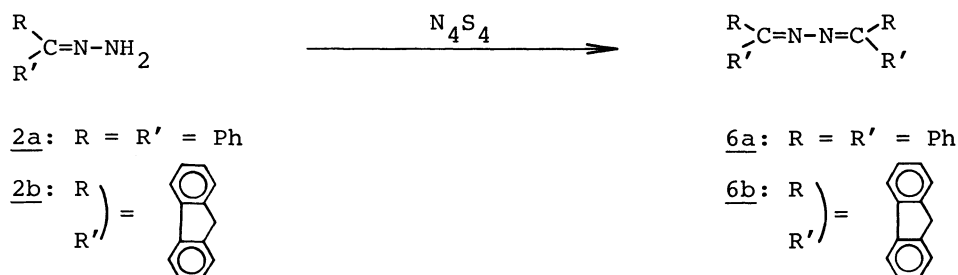


under such a mild reaction conditions mentioned above.

The reaction of  $N_4S_4$  with 1-methyl-1-phenylhydrazine (1b) was conducted in refluxing benzene for 7 hr and the reaction mixture was column chromatographed on alumina using benzene as an eluent affording also the N-N bond cleavage product, N-methylaniline (3b) in 44% yield with a trace amount of 3-anilino-1-phenyl-1,2,4-triazole (5), whose structure was deduced from analysis, spectral data and the comparison of mp  $184-5^\circ\text{C}$  with the reported, mp  $181^\circ\text{C}$ .<sup>6)</sup>

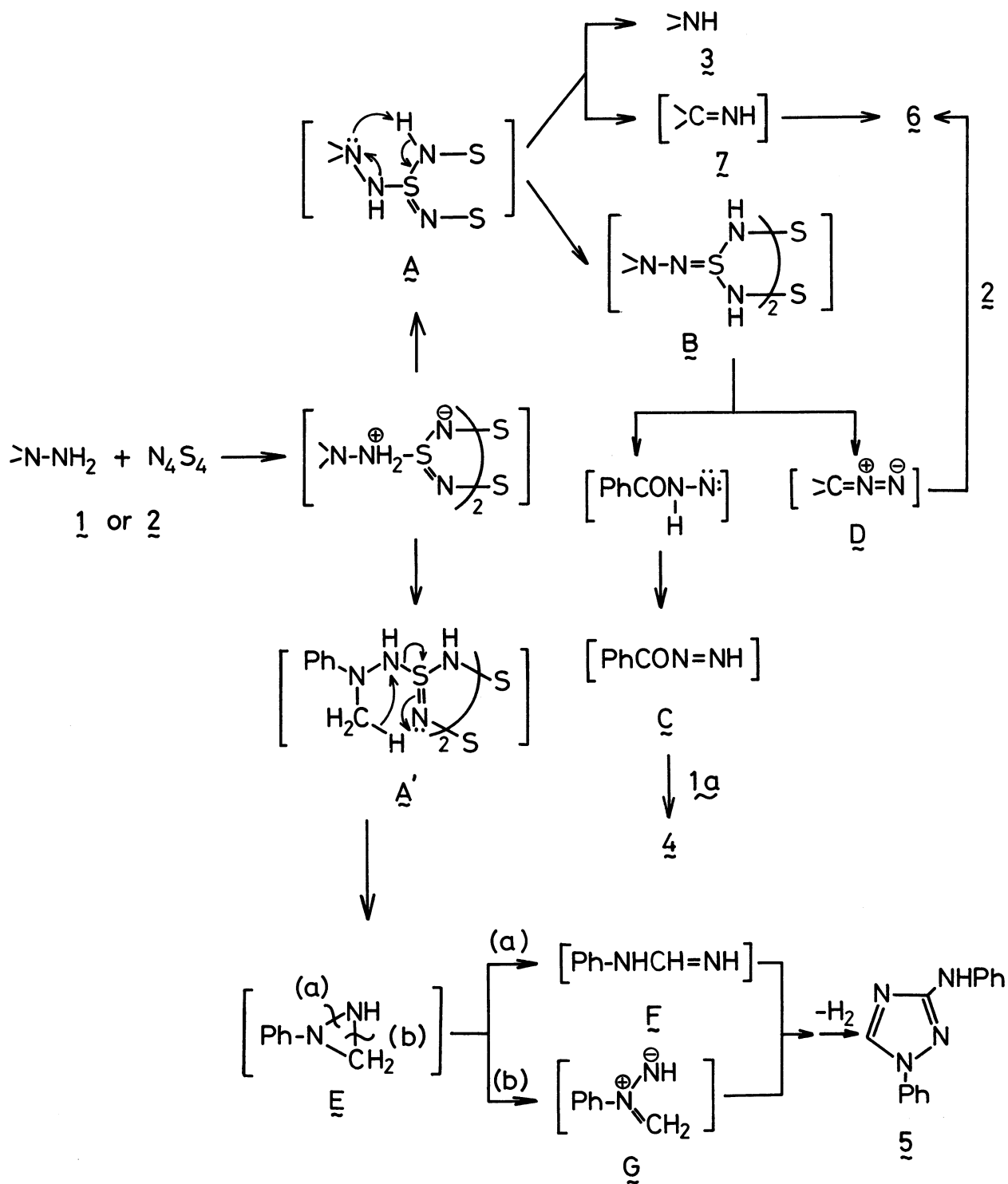


On the other hand, the reaction of 10 mmole of benzophenone- (2a) or fluorenone hydrazone (2b) with 2.5 mmole of  $N_4S_4$  in 20 ml of toluene at reflux for 18 or 24 hr afforded the corresponding azine, 6a and 6b, in 89 and 86% yields respectively and none of the expected N-N bond cleaved product, imine, was obtained.



The formation of compounds 3 - 6 may be reasonably explained by the following mechanism.

Nucleophilic attack of nitrogen atom of 1 or 2 on cationic sulfur atom of  $N_4S_4$  might give A which affords 3 or imine 7 by N-N bond cleavage with hydrogen migration via 5-membered cyclic transition state. Another migration of hydrogen in A may give B which may be cleaved to benzoyldiimine (C) or diazo compounds (D). C might react as yet untouched 1a affording 4.<sup>7)</sup> Although both 7 and D were not detected in the reaction mixture, azine 6 might be considered to be formed via 7 and/or D. 5 may be formed via hydrogen migration from carbon of 1b to nitrogen of  $N_4S_4$  as depicted in A' followed by diazirine (E) formation and ring opening of E, then subsequent recombination of F and G.



## REFERENCES

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