HETEROCYCLES, Vol. 4, No. 7, 1976

REACTIONS OF N_4S_4 WITH BENZIL MONO- AND BISHYDRAZONE[1)]

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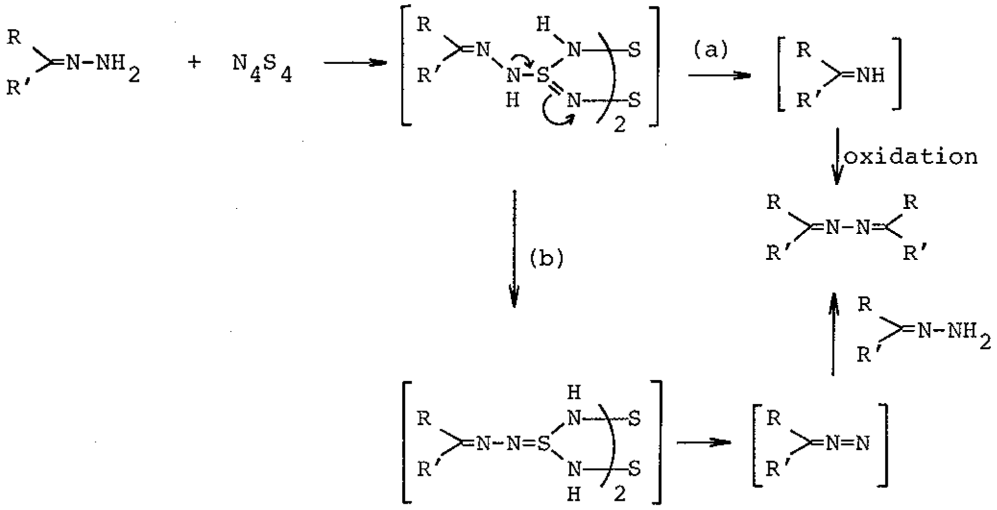
The reactions of N_4S_4 with benzil mono- (1) and bishydrazone (2) were carried out in refluxing toluene. In the reaction with 1, 2-benzoyl-2,4,5-triphenylisoimidazole (3), which was assumed to be the intermediate for the lophine formation in the reaction of benzil with ammonia, was isolated together with 3,4-diphenyl-1,2,5-thiadiazole (4), benzilazine (5) and diphenylacetamide (6), however, the compound (3) was not the intermediate. In the reaction with 2, 4 was isolated in a modest yield with a trace of a novel compound, 5,6-diphenyl-1,3,2,4-dithiadiazine (7).

Recently, we found that N_4S_4 behaves as a N-N bond cleavage reagent in the reaction with 1-methyl-1-phenylhydrazine affording N-methylaniline in 44% yield, while in the reaction with hydrazones affording in excellent yields the corresponding azines which were assumed to be formed via imines or diazo compounds as is shown in scheme 1.[2)]

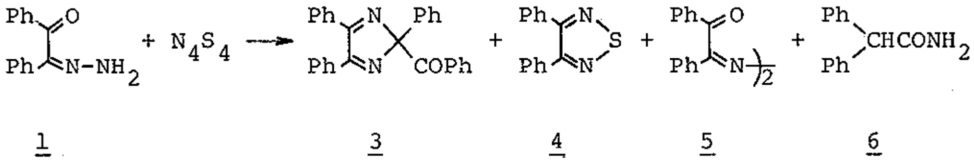
During our study to find the predominant path of the reaction between the imine formation (path a, N-N bond cleavage) and the diazo formation (path b), the reactions of N_4S_4 with benzil mono- (1) and bishydrazone (2) were carried out and we now report the



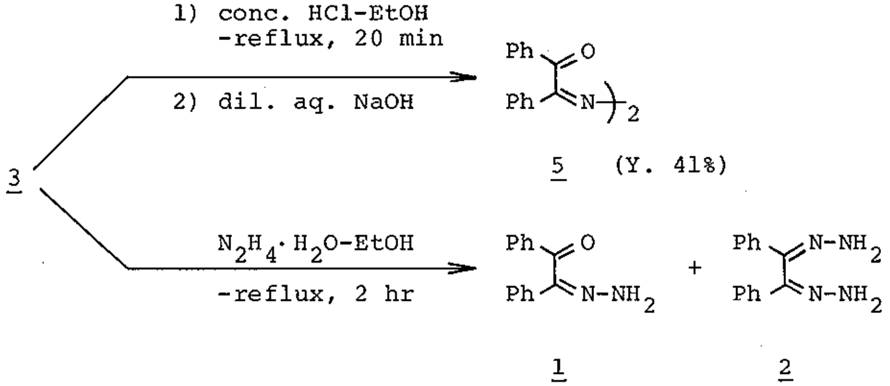
Scheme 1

results together with the isolation of 2-benzoyl-2,4,5-triphenylisoimidazole (3), which was assumed to be the intermediate in the reaction of benzil with ammonia.3)

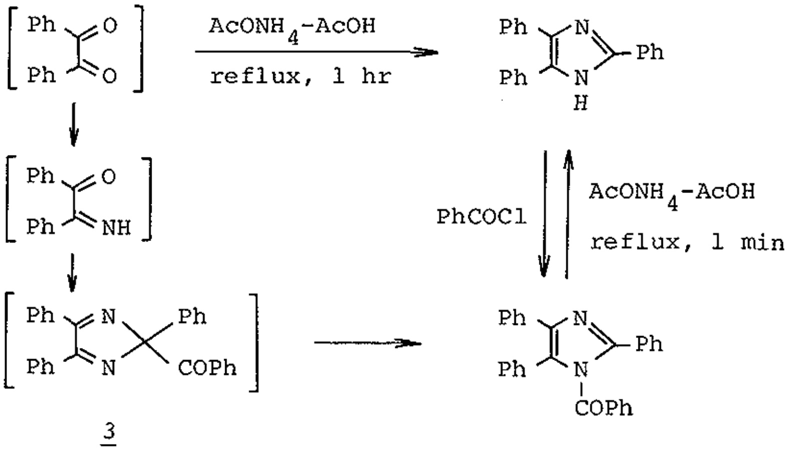
When a mixture of 10 mmole of 1 and 5 mmole of N_4S_4 was allowed to reflux for 24 hr in toluene (20 ml) and the reaction mixture was columnchromatographed on alumina using benzene as an eluent, 2-benzoyl-2,4,5-triphenylisoimidazole (3)4), 3,4-diphenyl-1,2,5-thiadiazole (4), benzilazine (5) and diphenylacetamide (6) were isolated in 20, 8.4, 4.8 and 3.3% yields5) respectively together with sulfur and intractable tar. Compounds 4 - 6 were identified by comparison of ir spectra with authentic ones.



The compound (3), mp 135-6°C of yellow prisms, gave satisfactory elemental analysis and spectral data, especially cmr being very helpful for confirming the presence of C-carbonyl carbon atom; cmr (in $CDCl_3$) δ ppm 163.7 (>$\underline{C}$=N-) and δ 198.2 (>C-$\underline{C}$=O). Hydrolysis and hydrazinolysis also support the isoimidazole structure for 3.



3 was postulated by Weiss[3)] as an intermediate leading to N-benzoyl lophine in the reaction of benzil with ammonia and was suggested to be easily hydrolyzed to lophine under reaction conditions as shown in scheme 2.



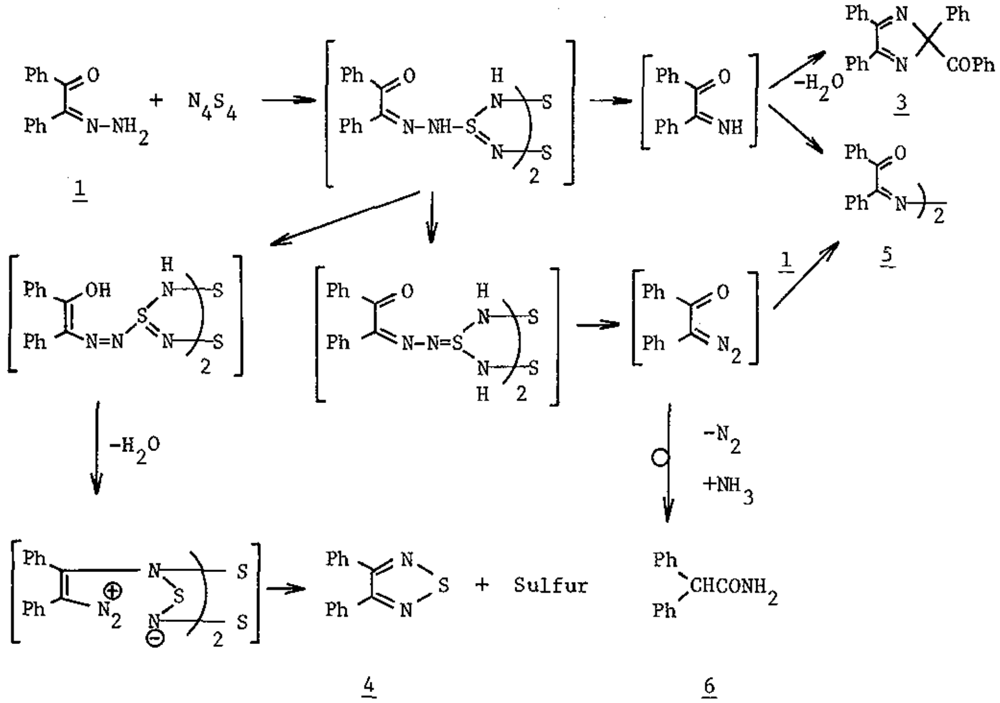
Scheme 2

Thus, 3 was treated under the reaction conditions of Weiss for 1 hr, however 3 was recovered without any change. Therefore,

$$3 \quad \cancel{\xrightarrow[\text{reflux, 1 hr}]{\text{AcONH}_4\text{-AcOH}}}$$

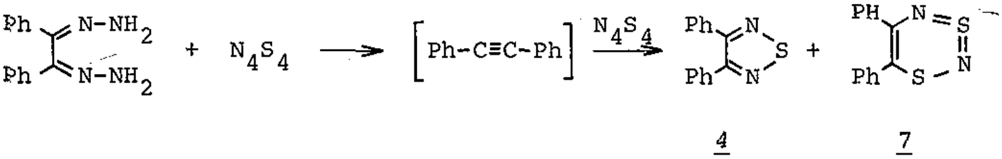
we now conclude that 3 is not an intermediate leading to N-benzoyl lophine in the reaction of benzil with ammonia. Scheme 3 shown below explains the formation of 3 - 6 and N_4S_4 could be considered to play a role in the N-N bond cleavage of hydrazone 1, leading to the major product 3.

Benzil bishydrazone 2 (5 mmole) was treated with N_4S_4 (2.5 mmole) in refluxing toluene (20 ml) for 6 hr and the column chromatography of the reaction mixture afforded 4 in 16% yield with a trace amount of orange needles (7) of mp 79-80.5°C, which



Scheme 3

was deduced to be 5,6-diphenyl-1,3,2,4-dithiadiazine from elemental analysis and uv spectrum which showed the characteristic absorption of -N=S=N- at 457 nm with log ε = 3.42 in ethanol. Since tolane was found to give 4 with a trace amount of 7 6), it seems reasonable to assume the intermediate formation of tolane. This is further supported by the fact that the yield of 4 was raised to 22% when an equimolecular amount of 2 and N_4S_4 was reacted.



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2 M. Tashiro and S. Mataka, Abstract Part 2, The 34th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1976, p. 793.

3 M. Weiss, J. Amer. Chem. Soc., 1952, 74, 5193.

4 3 was separated as the mixture with triphenyl-s-triazine which was formed by the reaction of N_4S_4 with toluene and could be purified by fractional recrystallization from ethanol.

5 Yields were based upon 1.

6 M. Tashiro, S. Mataka and K. Takahashi, Abstract Part 2, The 33rd Annual Meeting of the Chemical Society of Japan, Fukuoka, Oct. 1975, p. 537.

Received, 19th April, 1976