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REACTION OF BENZILMONOHYDRAZONE WITH S_4N_4. A CORRECTION

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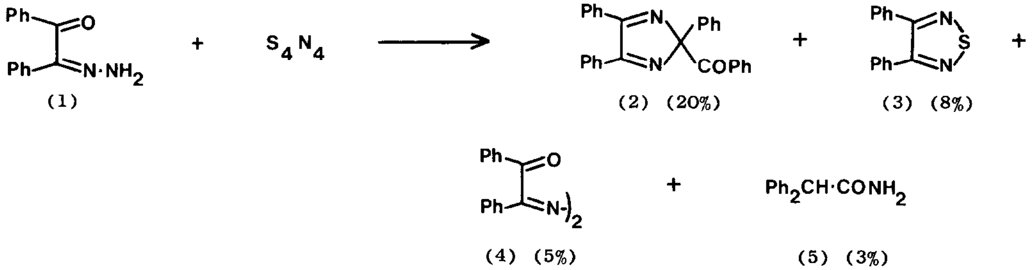
ABSTRACT: Reaction of benzilmonohydrazone (1) with S_4N_4 gives the azine (6) and not the 2-H-imidazole (2); this invalidates the claim that (2) is not the intermediate in the formation of N-benzoyltriphenylimidazole from benzil and ammonia. S_4N_4 converts diphenylketene into thiobenzophenone.

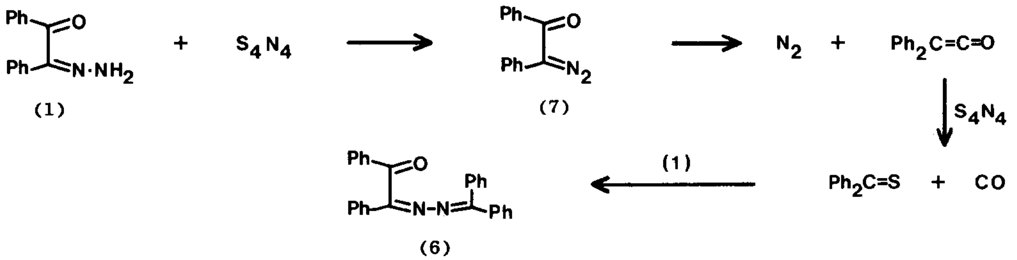
It has been claimed that when S_4N_4 (1 mol) and benzilmonohydrazone (1) (2 mol) are heated in boiling toluene for 24 hours the following products are formed and isolated in the yields shown.[1]


(1)
(2) (20%)
(3) (8%)
(4) (5%)
(5) (3%)

Products (3) to (5) seemed entirely reasonable but we were surprised at the thermal stability of the 2H-imidazole (2) which would be expected to undergo a rapid [1,5]benzoyl shift to nitrogen to give 1-benzoyl-2,4,5-triphenylimidazole, as indeed it is proposed to do in the standard preparation of 2,4,5-triphenylimidazole from benzil and ammonia.[2] Aware of this, Tashiro and Mataka subjected their product (2) to the conditions of the benzil-ammonia reaction, heating it under reflux with ammonium acetate in acetic acid for 1 hour.[1] Since no change was observed they concluded that the 2H-imidazole (2) is not an intermediate in the Weiss reaction[2] and that his reaction pathway is incorrect.

Although the assignment of structure (2) was apparently firmly based on analysis, spectroscopy, including ^{13}C NMR, and chemical degradation, we decided to repeat the reaction of S_4N_4 with hydrazone (1). We obtained the same four products in similar yields and we confirm structures (3) to (5). However product "(2)" was found to be the mixed azine (6) of benzil and benzophenone, by analysis and mass spectrometry ($C_{27}H_{20}N_2O$, not $C_{28}H_{20}N_2O$ as claimed[1]), by inspection of the spectral data, and by independent synthesis. Thus the Japanese results have no bearing on the benzil-ammonia reaction.

We propose the following mechanism for the formation of azine (6) from benzilmonohydrazone and S_4N_4:



There is precedent[3] for dehydrogenation of hydrazones by S_4N_4, and loss of nitrogen from diazoketone (7) with rearrangement to diphenylketene is well known. Involvement of diphenylketene was first suggested by isolation of the small amount of diphenylacetamide (5), ammonia presumably being generated by reduction of S_4N_4. This was confirmed by conducting the reaction under an atmosphere of dry ammonia gas, when diphenylacetamide was isolated as the major product (60%) to the exclusion of the mixed azine (6).

Conversion of diphenylketene into thiobenzophenone and carbon monoxide, under the reaction conditions, was established by independent experiment, as was the final reaction of thiobenzophenone and hydrazone (1) to give the observed product (6). Incidentally, benzophenone does not react with hydrazone (1) under the same, neutral, conditions. The novel transformation of diphenylketene (2 mol) with S_4N_4 (1 mol) proceeds at room temperature, virtually quantitatively.

A possible alternative mechanism, involving cycloaddition of diphenylketene to the diazo group of (7) and extrusion of carbon monoxide to give (6) was disproved by a control experiment. Diazoketone (7) and diphenylketene do not react in the cold; on addition of S_4N_4 the colour darkens and carbon monoxide is evolved, but azine (6) is not formed.

REFERENCES

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2. M. Weiss, J. Amer. Chem. Soc., 1952, **74**, 5193.
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