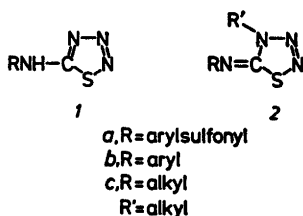


# On the Reaction between Azide Ion and Thiobenzophenone or Thiobenzophenone S-Oxides. Thiatriazolines as Possible Intermediates

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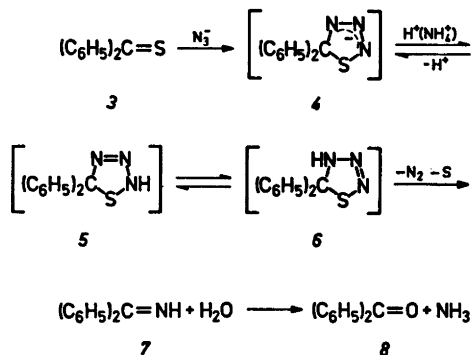
Examples of  $\Delta^2$ -1,2,3,4-thiatriazolines (2) have been described recently. 5-Arylamino- and 5-arylsulfonylaminothiatriazoles (1*b* and 1*a*) are alkylated in position 4 by diazomethane to give 2*b* and 2*a*, respectively<sup>1</sup> and trialkyloxonium tetrafluoroborates similarly alkylate 1*b* and 1*c* in position 4.<sup>2</sup> 4-Alkyl-5-arylsulfonylaminothiatriazolines (2*a*) are obtained from alkyl azides and the reactive arylsulfonyl isothiocyanates<sup>3</sup> and thiatriazolines (2*b*) are probably also formed from alkyl azides and aryl isothiocyanates but the primary products cannot be isolated.<sup>4,5</sup>



We report on the apparent transient formation of thiatriazolines 5 and/or 6 and their anion 4 (Scheme 1) and the corresponding *S*-oxides.

When a blue ethanolic solution of thiobenzophenone (3) is left together with ammonium azide at room temperature decolorization is observed. After 2½ h all colour has vanished, and the resulting solution contains diphenylmethaneimine (7) and benzophenone (8) in almost equal amounts as well as elemental sulfur. In aqueous ethanol, only benzophenone (100%) is formed in agreement with the facile hydrolysis of the imine<sup>6</sup> while in non aqueous solution diphenylmethaneimine is formed in better than 90% yield. The reaction between hydrogen azide and 3 in aqueous ethanol proceeds with formation of benzophenone only but the reaction is much slower than with azide ion. No reaction takes place between hydrogen azide and thiobenzophenone in ether/methylene chloride unless triethylamine is added, which suggests that the azide ion is the reactive species. A general scheme explaining the observed products is depicted below (Scheme 1).

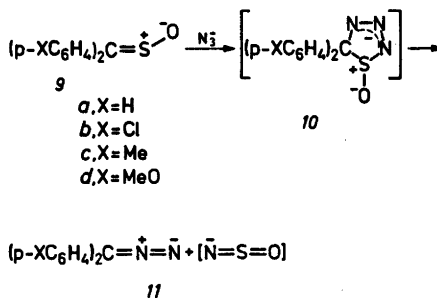
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Scheme 1.

We have not been able to observe directly the formation of the assumed thiatriazoline intermediates either by TLC or through monitoring the reactions with UV spectroscopy.

The almost colourless thiobenzophenone *S*-oxide (9*a*) also reacts with azide ion in ethanol. Under these conditions a red color is slowly developed, identified as due to diphenyldiazomethane (88%). Benzophenone is observed in small amounts, probably owing to reaction of diphenyldiazomethane with oxygen. The formation of diphenyldiazomethane in this reaction may be formulated as shown in Scheme 2.



Scheme 2.

In agreement with nucleophilic attack on the thiocarbonyl group it has qualitatively been found that formation of diaryldiazomethane is accelerated by substitution with electron-attracting groups in the benzene rings. Thus 4,4'-dichlorothiobenzophenone *S*-oxide (9*b*) reacts faster than thiobenzophenone *S*-oxide (9*a*), which again reacts faster than 4,4'-dimethylthiobenzophenone *S*-oxide (9*c*), while no reaction is observed over a long period of time with 4,4'-dimethoxythiobenzophenone *S*-oxide (9*d*).

Reaction with hydrogen azide in aqueous ethanolic solution instead of azide ion gives

rise to the same products, but as in the thio-benzophenone case it proceeds at a much lower rate, resulting in increased amounts of benzophenone at the expense of diphenyldiazomethane. Only a very slow reaction takes place with hydrogen azide in ether/methylene chloride but the red colour of diaryldiazomethane is immediately produced on addition of triethylamine. As in the thiobenzophenone case this strongly suggests that the azide ion is the reactive species.

The formation of diphenyldiazomethane is remarkable since this is the first example of a thiatiazole or thiatiazoline which does not fragment by loss of nitrogen.<sup>7</sup> The anion ( $\bar{N}=\text{S}=\text{O}$ , 11) of thiocarbonylimide ( $\text{HN}=\text{S}=\text{O}$ )<sup>8</sup> which apparently is extruded in these processes could not be isolated. From the solution a salt was obtained, but it contained approximately 50 % oxygen and was not identified.

*Experimental. Reaction of thiobenzophenone (3) with ammonium azide and with hydrogen azide.* All reactions involving 3 were carried out under oxygen-free conditions.

Thiobenzophenone (1 mmol) and ammonium azide (1 mmol) were dissolved in ethanol (20 ml). After 2½ h the blue colour of 3 had disappeared, and the reaction mixture was evaporated to dryness. The residue consisted of almost equal amounts of benzophenone and diphenylmethaneimine according to TLC, IR and UV spectroscopy.

Thiobenzophenone (1 mmol) in ethanol (25 ml) was added to an aqueous solution of hydrogen azide (1 mmol). After 72 h the colour of 3 had disappeared. Analysis as above revealed the formation of benzophenone in better than 90 % yield.

Triethylamine (1 mmol) in methylene chloride (20 ml) was added to a mixture of thiobenzophenone (1 mmol) and hydrogen azide (1 mmol) in ether (10 ml). After 2½ h the colour of 3 had disappeared. Analysis as above revealed the formation of diphenylmethaneimine in better than 90 % yield.

*Reaction of thiobenzophenone S-oxide (9a) with ammonium azide and with hydrogen azide.* Thiobenzophenone S-oxide (18.7 mmol) and ammonium azide (20 mmol) were dissolved in ethanol (200 ml). After 18 h a deep red colour had developed. Addition of water (10 ml) caused precipitation of inorganic material, which was removed by filtration. After addition of more water (500 ml) the aqueous phase was extracted with ether (3 × 75 ml), and the combined ether extracts were dried over  $\text{MgSO}_4$  and evaporated to dryness. The residue was dissolved in light petroleum (b.p. 40–60 °C), filtered, and evaporated to dryness, affording deep red crystals of diphenyldiazomethane with m.p. 26–27 °C (lit. 29–32 °C),<sup>9</sup> yield 88 % based on 9a. The infrared spectrum was identical with that of an authentic sample.

The reaction of an ethanolic solution of 9a ( $10^{-4}$  M) with excess ammonium azide was monitored by UV spectroscopy. The absorption maximum of 9a at 329 nm<sup>10</sup> disappeared simultaneously with the appearance of a new maximum at 287 nm (diphenyldiazomethane). An isobestic point was observed at 312 nm.

Thiobenzophenone S-oxide (9a) (1 mmol) in ethanol (25 ml) was added to an aqueous solution of hydrogen azide. After 24 h the red colour of diphenyldiazomethane had developed, but according to TLC and UV spectroscopy more than 85 % of 9a was still present. After 1 week the now colourless reaction mixture was evaporated to dryness and analyzed by means of TLC and UV spectroscopy. Benzophenone (ca. 50 %) was found together with traces of tetraphenylethylene, while ca. 40 % of sulfine 9a remained. Diphenyldiazomethane was not detected.

Thiobenzophenone S-oxide (9a) (1 mmol) in ethanol (25 ml) was added to an aqueous solution of acetic acid (1 mmol). After 1 week the reaction mixture was analyzed by means of UV spectroscopy. Benzophenone (15 %) was detected together with unreacted sulfine 9a (85 %). This shows that hydrolytic formation of benzophenone directly from 9a is less important.

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