

Structure of azo coupling products of 5-nitro-2,1-benzisothiazole-3-diazonium hydrogensulphate with aromatic amines

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Abstract

The reaction of 5-nitro-2,1-benzisothiazole-3-diazonium hydrogensulphate with anilines, *N*-alkylanilines and diphenylamine gives *N*-substituted 3-(4-aminophenyldiazenyl)-5-nitro-2,1-benzisothiazoles **2** and isomeric 1-(5-nitro-2,1-benzisothiazol-3-yl)-3-substituted-3-phenyltriazenes **1**. The predominant reaction products are triazenes **1**, being present up to 95% in reaction products. A larger amount of azo compounds **2** are formed in the reaction of 5-nitro-2,1-benzisothiazole-3-diazonium with diphenylamine (about 45%), with *N*-alkyl-3-methylanilines and 3-methylaniline (as much as 50%). The triazenes formed are extraordinarily stable in acid medium (the decomposition half-lives in 0.5 mol l⁻¹ H₂SO₄ in aqueous acetic acid (1:1 v/v) are in the order of hours), which is explained by a different site of their protonation: while 1,3-diaryltriazenes are protonated at the –NH–N=N– group, triazenes **1** are protonated at the heterocyclic nitrogen. The triazenes **1** formed by azo coupling reaction with anilines containing primary amino group undergo an acid–base reaction in methanolic solutions, connected with distinct change in colour, which indicates a considerable acidity of the proton in –NH–N=N– grouping.

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1. Introduction

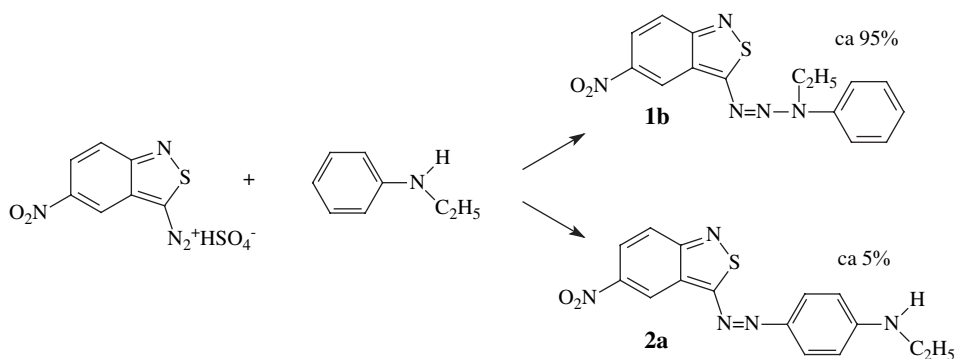
In the production of the azo dyestuff C.I. Disperse Blue 148 by azo coupling of 5-nitro-2,1-benzisothiazole-3-diazonium hydrogensulphate with methyl-3-(*N*-ethyl-*N*-phenyl)amino-propanoate it was found that the resulting blue dyestuff contains small amounts of an unknown orange dyestuff; in spite of its low content, this substance strongly worsens the hue of the main blue dye (makes it duller). The presence of this orange substance was also found in commercial brands of C.I. Disperse Blue 148, where it usually represents a dominant impurity. We have found out that the unknown substance is 1-(5-nitro-2,1-benzisothiazol-3-yl)-3-ethyl-3-phenyltriazene **1b**, which is formed by azo coupling reaction of 5-nitro-2,

1-benzisothiazole-3-diazonium hydrogensulphate with *N*-ethylaniline. *N*-Ethylaniline represents a usual impurity in the coupling component, methyl-3-(*N*-ethyl-*N*-phenyl)aminopropanoate (due to incomplete conversion in the addition reaction of *N*-ethylaniline to methyl propenoate). Triazene **1b** is a product of the azo coupling reaction taking place at the secondary amino group of *N*-ethylaniline, whereas the azo coupling reaction at the aromatic ring of *N*-ethylaniline proceeds to a slight extent only, and the expected azo dye **2a** is formed in small amount (Scheme 1).

We have found that also other *N*-substituted anilines like *N*-ethylaniline react with 5-nitro-2,1-benzisothiazole-3-diazonium hydrogensulphate. The main (prevailing) product of the azo coupling reaction is always 1-(5-nitro-2,1-benzisothiazol-3-yl)-3-substituted-3-phenyltriazene of general formula **1**, while the azo compounds (*N*-substituted 3-(4-aminophenyldiazenyl)-5-nitro-2,1-benzisothiazoles) of general formula **2** are formed as side products only (Scheme 2).

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Scheme 1.

The way of preparation and the properties of triazenes **1a–f** ($R^1 = \text{CH}_3$, $R^2 = \text{H}$; $R^1 = \text{C}_2\text{H}_5$, $R^2 = \text{H}$; $R^1 = \text{C}_6\text{H}_5$, $R^2 = \text{H}$; $R^1 = n\text{-C}_4\text{H}_9$, $R^2 = \text{H}$; $R^1 = n\text{-C}_4\text{H}_9$, $R^2 = \text{CH}_3$; $R^1 = \text{CH}_2\text{CH}_2\text{CN}$, $R^2 = \text{CH}_3$; $R^1 = \text{CH}_2\text{CH}_2\text{OH}$, $R^2 = \text{Cl}$) were published in our earlier paper [1]. The above-given triazenes were characterised by elemental analysis, ^1H and ^{13}C NMR spectra and APCI mass spectra. In three cases, X-ray structural analyses were also carried out with $R^1 = \text{C}_6\text{H}_5$, $R^2 = \text{H}$ and $R^1 = \text{CH}_2\text{CH}_2\text{OH}$, $R^2 = \text{Cl}$ [1] and with $R^1 = n\text{-C}_4\text{H}_9$, $R^2 = \text{H}$ [2]. The triazenes are brilliant orange substances with $\lambda_{\text{max}} \sim 460 \text{ nm}$ and $\varepsilon_{\text{max}} \sim 2.5 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. They are surprisingly stable in acid media in contrast to the 1,3-diaryltriazenes so far known, which are rapidly split in acid medium to give the diazonium ion and amine [3–5]. We have found out that 1-(5-nitro-2,1-benzisothiazol-3-yl)-3-ethyl-3-phenyltriazene is decomposed in $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ in aqueous acetic acid (1:1 v/v) at $25 \text{ }^\circ\text{C}$ to give 5-nitro-2,1-benzisothiazole-3-diazonium with a half-life $\tau_{1/2} = 417 \text{ min}$ [1]. We ascribe the high stability of triazenes **1** to the different sites of protonation of these substances, as compared with 1,3-diaryltriazenes. While 1,3-diaryltriazenes are protonated at the NH group of triazene grouping, triazenes **1** are presumably protonated at the heterocyclic nitrogen [1].

2. Results and discussion

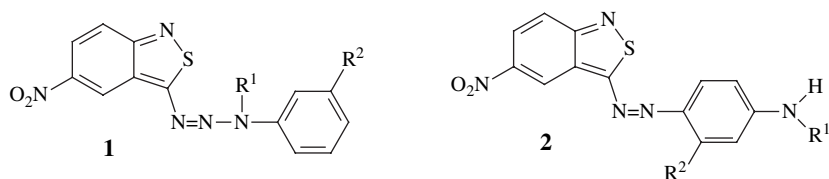
Further triazenes have been prepared by the reaction of 5-nitro-2,1-benzisothiazole-3-diazonium hydrogensulphate with *N*-substituted anilines, whereby their number published in Ref. [1] was extended by compounds **1g–n**. The substituents were chosen with regard to potential practical exploitation of these substances (Table 1). In several cases, from the azo coupling reaction mixtures we have also isolated the isomeric azo

compounds **2a–e**, in which the azo coupling reaction had taken place at the aromatic ring (Table 2).

Triazenes **1a–k** were fully characterised by both ^1H and ^{13}C NMR spectra (Tables 3 and 4). In triazenes **1l–m**, due to tautomeric exchange of the proton between nitrogen atoms N(1) and N(3) of triazene grouping, the signals of carbon atoms in ^{13}C NMR spectrum are so broadened that a part of them cannot be identified at all. In the case of azo compounds **2**, the signals of carbon atoms of phenylazo group are considerably broadened due to the partial double bond character of the C–N bond adjacent to azo group and the therewith connected hindered rotation [1]. Therefore, triazenes **1l–m** and azo compounds **2b–e** were only characterised by their ^1H NMR spectra (Table 5).

Approximate molar ratios of triazenes **1** and corresponding isomeric azo compounds **2** (formed by azo coupling reaction in benzene ring) obtained from various substrates are given in Table 1. These ratios were determined spectrophotometrically using the two-component azo coupling reaction mixtures containing always the orange triazene **1** (λ_{max} below 470 nm) and the blue azo dyestuff **2** (λ_{max} above 560 nm). In the cases of the triazenes whose corresponding isomeric azo dyestuffs were isolated in pure state the isomer ratios (i.e. **1b/2a**, **1c/2b**, **1e/2c**, **1l/2d**, **1n/2e**) were also determined by means of HPLC. The procedures of separation and determination are described in more detail in Section 4. The results obtained by the two methods were in good agreement (Table 1).

In the azo coupling reactions, triazenes **1** usually distinctly predominate over azo dyestuffs **2**, the ratios **1/2** being affected by the structure of the coupling (passive) component to a certain extent, too. The methyl group at 3-position ($R^2 = \text{CH}_3$; Scheme 2) increases the reactivity of *o*-position of aromatic ring towards C-coupling reaction, which results in an increase in the azo dyestuff content (to the detriment of the triazene)



Scheme 2.

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