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

Josef Přikryl [a,*], Michal Černý [a], Hana Bělohlavová [a], Vladimír Macháček [b], Antonín Lyčka [c]

[a] *Institute of Polymeric Materials, University of Pardubice, Nám. Cs. Legií 565, 53210 Pardubice, Czech Republic*
[b] *Department of Organic Chemistry, University of Pardubice, Nám. Cs. Legií 565, 53210 Pardubice, Czech Republic*
[c] *Research Institute for Organic Syntheses, Rybitví 296, 53218 Pardubice 20, Czech Republic*

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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} H_2SO_4 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.

Keywords: Azo coupling; 5-Nitrobenzo[*c*]-2,1-thiazol-3-diazonium; Triazenes; Disperse dyes

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)aminopropanoate 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).

* Corresponding author. Fax: +420 466826037022.
E-mail address: josef.prikryl@upce.cz (J. Přikryl).

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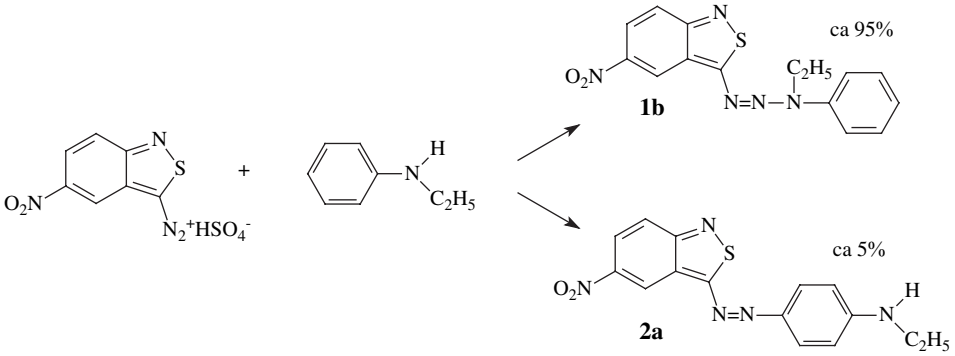


Scheme 1.

The way of preparation and the properties of triazenes **1a–f** ($R^1 = CH_3$, $R^2 = H$; $R^1 = C_2H_5$, $R^2 = H$; $R^1 = C_6H_5$, $R^2 = H$; $R^1 = n\text{-}C_4H_9$, $R^2 = H$; $R^1 = n\text{-}C_4H_9$, $R^2 = CH_3$; $R^1 = CH_2CH_2CN$, $R^2 = CH_3$; $R^1 = CH_2CH_2OH$, $R^2 = Cl$) 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 $R^1 = C_6H_5$, $R^2 = H$ and $R^1 = CH_2CH_2OH$, $R^2 = Cl$ [1] and with $R^1 = n\text{-}C_4H_9$, $R^2 = H$ [2]. The triazenes are brilliant orange substances with $\lambda_{max} \sim 460$ nm and $\varepsilon_{max} \sim 2.5 \times 10^4\ l\,mol^{-1}\,cm^{-1}$. 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 mol l^{-1} H_2SO_4 in aqueous acetic acid (1:1 v/v) at 25 °C to give 5-nitro-2,1-benzisothiazole-3-diazonium with a half-life $\tau_{1/2} = 417$ 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].

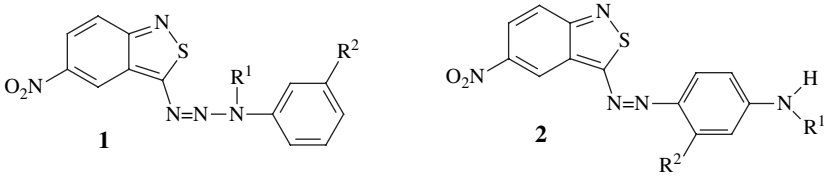
2. Results and discussion

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 ($R^2 = CH_3$; 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.

Table 1
Survey of triazenes prepared

Compound	Elemental analysis data (calc./found)					M.p. (°C)	Electron spectra		Triazene **1** versus dye **2** ratio in azo coupling	
	%C	%H	%N	%S	%Cl		λ_{max} (nm)	$\varepsilon_{max} \times 10^{-4}$ (l/mol cm)	Spectrophotometric	HPLC
1a ($R^1 = CH_3$, $R^2 = H$)	53.32/53.37	4.15/3.94	22.21/22.35	10.17/10.23	–	217–218	461	2.36	92:8	–
	$C_{14}H_{11}N_5O_2S$ (313.33 g/mol)									
1b ($R^1 = C_2H_5$, $R^2 = H$)	55.04/55.09	4.00/3.94	21.39/21.43	9.79/9.92	–	170–171	463	2.48	95:5	96:4 (**1b**:**2a**)
	$C_{15}H_{13}N_5O_2S$ (327.36 g/mol)									
1c ($R^1 = Ph$, $R^2 = H$)	60.79/60.99	3.49/3.53	18.66/18.83	8.54/8.42	–	181–182	467	2.50	59:41	53:47 (**1c**:**2b**)
	$C_{19}H_{13}N_5O_2S$ (375.40 g/mol)									
1d ($R^1 = n$Bu, $R^2 = CH_3$)	58.52/58.59	5.18/5.11	18.96/18.96	8.68/8.64	–	120–121	468	2.35	84:16	–
	$C_{18}H_{19}N_5O_2S$ (369.44 g/mol)									
1e ($R^1 = C_2H_4CN$, $R^2 = CH_3$)	55.73/56.18	3.85/3.85	22.94/23.16	8.75/8.33	–	185–187	457	2.55	51:49	54:46 (**1e**:**2c**)
	$C_{17}H_{14}N_6O_2S$ (366.40 g/mol)									
1f ($R^1 = C_2H_4OH$, $R^2 = Cl$)	47.69/47.95	3.20/3.18	18.54/18.68	8.49/8.40	9.38/9.54	191–192	458	2.30	92:8	–
	$C_{15}H_{12}N_5O_3SCl$ (377.81 g/mol)									
1g ($R^1 = n$Bu, $R^2 = H$)	57.45/57.53	4.82/4.77	19.70/19.95	9.02/9.10	–	125–127	465	2.71	96:4	–
	$C_{17}H_{17}N_5O_2S$ (355.41 g/mol)									
1h ($R^1 = C_2H_4OH$, $R^2 = H$)	52.47/52.06	3.82/3.79	20.40/20.17	9.34/9.39	–	184–186	462	2.33	89:11	–
	$C_{15}H_{13}N_5O_3S$ (343.36 g/mol)									
1i ($R^1 = C_2H_4CN$, $R^2 = H$)	54.54/54.59	3.43/3.34	23.85/23.92	9.10/9.10	–	214–216	453	2.37	88:12	–
	$C_{16}H_{12}N_6O_2S$ (352.37 g/mol)									
1j ($R^1 = benzyl$, $R^2 = H$)	61.68/61.91	3.88/3.90	17.98/18.11	8.23/8.19	–	178–179	462	2.49	85:15	–
	$C_{20}H_{15}N_5O_2S$ (389.43 g/mol)									
1k ($R^1 = n$Bu, $R^2 = Cl$)	52.37/52.55	4.14/4.09	17.96/17.66	8.22/8.35	9.09/9.37	148–149	460	2.23	93:7	–
	$C_{17}H_{16}N_5O_2SCl$ (389.86 g/mol)									
1l ($R^1 = H$, $R^2 = H$)	52.17/52.21	3.03/3.01	23.40/23.22	10.71/10.64	–	198–201	414, 540	2.37, 3.39 (Fig. 1)	86:14	89:11 (**1l**:**2d**)
	$C_{13}H_9N_5O_2S$ (299.31 g/mol)									
1m ($R^1 = H$, $R^2 = Cl$)	46.78/46.61	2.42/2.52	20.98/21.07	9.61/9.49	10.62/10.71	188–190	441, 543	2.44, 3.14 (Fig. 2)	85:15	–
	$C_{13}H_8N_5O_2SCl$ (333.75 g/mol)									
1n ($R^1 = H$, $R^2 = CH_3$)	53.66/53.71	3.54/3.62	22.35/22.24	10.23/10.39	–	183–185	419, 535	2.48, 3.11	52:48	56:44 (**1n**:**2e**)
	$C_{14}H_{11}N_5O_2S$ (313.33 g/mol)									

Table 2
Survey of azo dyestuffs type **2** prepared by azo coupling reaction in aromatic ring

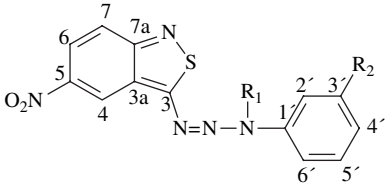
Compound	Formula (M.W.)	M.p. (°C)	λ_{max} (nm)	$\varepsilon_{max} \times 10^{-4}$ (l/mol cm)	Corresponding isomeric triazene	Method of preparation
2a ($R^1 = C_2H_5$, $R^2 = H$)	$C_{15}H_{13}N_5O_2S$ (327.36)	228–230	588	3.96	**1b**	See Scheme 2
2b ($R^1 = Ph$, $R^2 = H$)	$C_{19}H_{13}N_5O_2S$ (375.40)	269–271	579	3.88	**1c**	Preparation from reaction mixture
2c ($R^1 = C_2H_4CN$, $R^2 = CH_3$)	$C_{17}H_{14}N_6O_2S$ (366.40)	239–241	578	3.99	**1e**	Preparation from reaction mixture
2d ($R^1 = H$, $R^2 = H$)	$C_{13}H_9N_5O_2S$ (299.31)	180–182	565	3.87	**1l**	Preparation from reaction mixture
2e ($R^1 = H$, $R^2 = CH_3$)	$C_{14}H_{11}N_5O_2S$ (313.33)	240–242	573	3.89	**1n**	Preparation from reaction mixture
3 Struct. see Scheme 2	$C_{16}H_{14}N_5O_5S_2Na$ (443.43)	>340	585	3.66	–	See Scheme 2

from ca 13 up to ca 50% (compare **1e**, **1n** with **1i**, **1l** in Table 1). Likewise, phenyl group at nitrogen atom of the coupling component ($R^1 = Ph$; Scheme 2) increases the amount of isomeric azo dyestuff as compared with that of R^1 = alkyl (**1c** versus **1a**, **1b**, **1d**).

Triazenes are also formed in the azo coupling reactions with anilines containing primary amino group ($R^1 = H$), see compounds **1l**, **1m** and **1n**, which were obtained by azo coupling of 5-nitro-2,1-benzisothiazole-3-diazonium hydrogensulphate with aniline, 3-chloroaniline and 3-toluidine (Table 1). Spectra of these triazenes in visible region are markedly affected by the pH of their methanolic solutions. In acid medium (0.05 M acetic acid in methanol) their solutions are yellow (for **1l** $\lambda_{max} = 414$ nm, **1m** $\lambda_{max} = 441$ nm, **1n** $\lambda_{max} = 419$ nm), whereas in alkaline medium (0.05 M NaOH in methanol) they are violet (for **1l** $\lambda_{max} = 540$ nm, **1m** $\lambda_{max} = 543$ nm, **1n** $\lambda_{max} = 535$ nm); see the absorption spectra in Figs. 1 and 2. The above-described acid–base behaviour is obviously due to the presence of considerably acidic proton in NH of triazene grouping. The conjugated base formed by its removal is stabilised by resonance, the structure with free electron pair and negative charge at heterocyclic nitrogen and classical benzenoid system being a significant contributor to the resonance hybrid (Scheme 3).

Azo compounds **2** cannot be obtained by direct azo coupling reaction of 5-nitro-2,1-benzisothiazole-3-diazonium hydrogensulphate with *N*-monosubstituted anilines in acceptable yield and purity: the obtained mixtures always contain

Table 3
^{1}H and ^{13}C shifts of compounds **1a–f** in DMSO-d_6 (triazenes **1a–1f**, see Ref. [1])



1a-1n

Pos. no.	**1a**		**1b**		**1c**		**1d**		**1e**		**1f**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
3	–	178.62	–	178.68	–	177.53	–	178.56	–	177.49	–	177.64
3a	–	124.84	–	124.82	–	125.15	–	124.71	–	125.19	–	124.99
4	8.97	119.48	8.91	119.39	8.36	119.10	8.86	119.51	9.01	119.71	8.86	119.10
5	–	143.20	–	143.16	–	143.48	–	143.17	–	143.53	–	143.34
6	8.21	122.79	8.19	122.77	8.16	122.90	8.17	122.72	8.18	122.90	8.17	122.67
7	7.84	122.92	7.82	122.90	7.82	122.90	7.79	122.85	7.81	122.75	7.80	122.75
7a	–	161.55	–	161.54	–	161.44	–	161.49	–	161.50	–	161.35
1′	–	143.20	–	142.05	–	[a]	–	142.28	–	142.08	–	144.46
2′	7.72	119.20	7.71	118.99	[a]	[a]	7.51	119.29	7.55	119.63	7.79	119.10
3′	7.61	129.75	7.60	129.91	[a]	[a]	–	139.51	–	139.47	–	133.87
4′	7.43	126.86	7.42	126.82	[a]	[a]	7.23	127.56	7.24	127.60	7.41	126.02
5′	7.61	129.75	7.60	129.91	[a]	[a]	7.44	129.66	7.47	129.62	7.58	131.00
6′	7.72	119.20	7.71	118.99	[a]	[a]	7.49	116.33	7.52	116.41	7.70	117.94
R^2	–	–	–	–	–	–	2.45	21.24	2.46	21.22	–	–
R^{1b}	4.01	35.61	4.65	42.56	[a]	[a]	4.60	46.76	4.87	42.81	4.66	50.51
			1.42	11.12	[a]	[a]	1.80	27.65	3.22	14.60	3.91	56.44
					[a]	[a]	1.47	19.84	–	118.77	5.20 (OH)	–
					[a]	[a]	1.02	13.65				

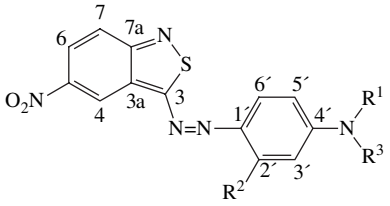
[a] Phenyl groups are not equivalent and provide a complicated pattern both in ^{1}H and ^{13}C NMR spectra.
[b] Arranged according to the increasing distance from nitrogen atom.

Table 4
^{1}H and ^{13}C shifts of triazenes **1g–1k** in DMSO-d_6

Pos. no.	**1g**		**1h**		**1i**		**1j**		**1k**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
3	–	178.47	–	178.49	–	178.49	–	177.82	–	177.66
3a	–	124.81	–	124.75	–	124.75	–	125.14	–	125.11
4	8.84	119.18	8.84	119.36	9.04	119.36	8.80	119.23	8.87	119.05
5	–	143.16	–	143.20	–	143.61	–	143.41	–	143.42
6	8.16	122.71	8.13	122.67	8.21	122.67	8.17	122.78	8.19	122.76
7	7.79	122.82	7.76	122.79	7.84	122.79	7.81	122.89	7.83	122.83
7a	–	161.45	–	161.46	–	161.46	–	161.44	–	161.38
1′	–	142.26	–	143.20	–	142.16	–	142.40	–	143.42
2′	7.70	119.04	7.73	119.62	7.74	119.62	7.74	119.04	7.77	118.45
3′	7.59	129.85	7.57	129.58	7.61	129.58	7.57	129.87	–	134.24
4′	7.42	126.79	7.40	126.70	7.44	126.70	7.40	126.75	7.45	126.18
5′	7.59	129.85	7.57	129.58	7.61	129.58	7.57	129.87	7.60	131.36
6′	7.70	119.04	7.73	119.62	7.74	119.62	7.74	119.04	7.67	117.41
R^2	–	–	–	–	–	–	–	–	–	–
R^{1a}	4.60	46.69	4.69	50.80	4.90	42.90	5.94	50.10	4.61	46.33
	1.81	27.60	3.92	56.49	3.24	13.97	–	134.93	1.78	27.45
	1.48	19.82	5.21 (OH)	–		118.80	7.39	127.29	1.48	19.67
	1.02	13.62					7.39	128.85	1.02	13.54
							7.31	127.56		

[a] Arranged according to the increasing distance from nitrogen atom.

Table 5
^{1}H and ^{13}C shifts of triazenes **1l–1n** and azo dyes **2a–2f** and **3** in DMSO-d_6



2a-2e and **3**

Pos. no.	**1l**	**1m**	**1n**	**2a**		**2b**	**2c**	**2d**	**2e**	**3**	
	δ_H	δ_H	δ_H	δ_H	δ_C	δ_H	δ_H	δ_H	δ_H	δ_H	δ_C
3	–	–	–	–	181.1	–	–	–	–	–	180.9
3a	–	–	–	–	126.4	–	–	–	–	–	126.6
4	9.48	9.47	9.48	9.01	119.4	9.13	9.09	9.08	9.01	9.00	119.4
5	–	–	–	–	143.7	–	–	–	–	–	143.8
6	8.25	8.25	8.25	8.20	122.9	8.27	8.23	8.23	8.19	8.18	122.9
7	7.76	7.83	7.76	7.83	122.9	7.95	7.87	7.87	7.80	7.81	123.0
7a	–	–	–	–	162.0	–	–	–	–	–	162.0
1′	–	–	–	–	143.4	–	–	–	–	–	143.5
2′	7.85	7.85	7.68	7.92	128[b]	8.08	–	7.95	–	7.92	128.0[b]
3′	7.61	–	–	6.82	113[c]	7.24	6.78	6.82	6.60	7.12	114.0[c]
4′	7.49	7.78	7.65	–	155.4	–	–	–	–	–	153.5
5′	7.61	7.61	7.47	6.82	113[c]	7.24	6.81	6.82	6.67	7.12	114.0[c]
6′	7.85	7.53	7.30	7.92	128[b]	8.08	8.09	7.95	8.03	7.92	128.0[b]
NH	~15	~15	14.8	8.79	–	9.76	8.09	7.45	7.48	–	–
R^2	–	–	2.46	–	–	–	2.62	–	2.52	–	–
R^{1a}	–	–	–	3.34	37.5	7.37	3.65	–	–	4.39[d]	65.6[d]
	–	–	–	1.28	14.1	7.49	2.89	–	–	3.80[e]	45.7[e]
	–	–	–	–	–	7.21	–	–	–	1.26[e]	11.7[e]

[a] Arranged according to the increasing distance from nitrogen atom.
[b] Very broad signal.
[c] Broad signal.
[d] NCH_2SO_3Na.
[e] NCH_2CH_3.

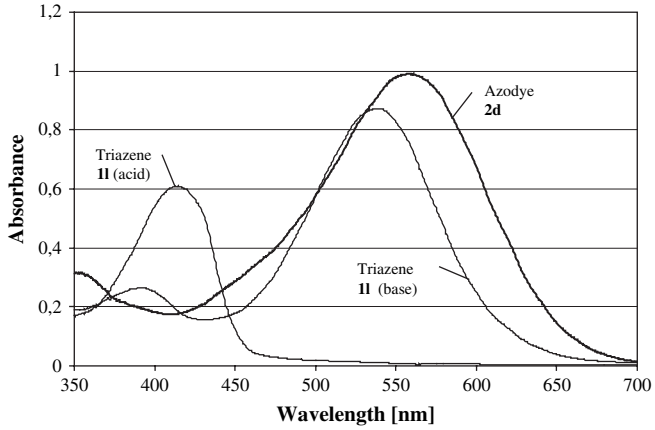


Fig. 1. Absorption spectra of products of azo coupling reaction of 5-nitro-2,1-benzisothiazole-3-diazoniun with aniline. Triazene **1l** in methanol in the presence of 0.05 M acetic acid (acid) and 0.05 M NaOH (base). Isomeric azo dyestuff **2d** in methanol. Concentration always 2.58×10^{-5} mol l^{-1}.

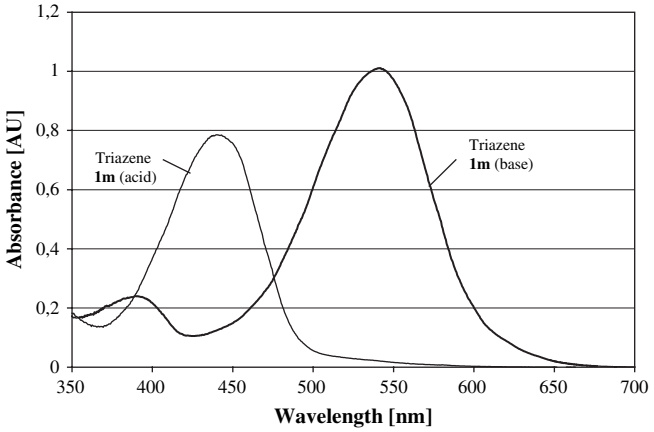


Fig. 2. Absorption spectra of triazene **1m** in methanol in the presence of 0.05 M acetic acid (acid) and 0.05 M NaOH (base) at concentration 3.21×10^{-5} mol l^{-1}.

a predominant amount of isomeric triazene **1** (Table 1), and the presence of the orange triazene **1** completely depreciates the blue hue of azo dyestuff **2**.

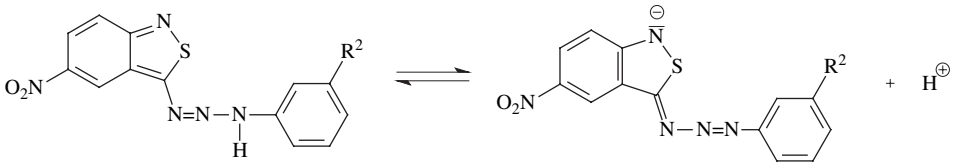
The above-mentioned facts contradict claims of several patents [6–10] describing the preparation of dyestuffs of this structural type **2** by standard direct azo coupling reaction. Kraska and Sokolowska-Gajda [11] studied the structure of reaction products from 5-nitro-2,1-benzisothiazole-3-diazonium and six *N*,*N*-dialkylanilines and three *N*-alkylanilines. The uniformity of the azo coupling reaction products obtained was checked by thin-layer chromatography (DC-Alufolien Kieselgel 60, 95% ethanol), and the products were identified on the basis of IR spectra. The authors ascribed the azo structure to all their products [11]. The reaction of 5-nitro-2,1-benzisothiazole-3-diazonium with tertiary anilines really produces blue azo compounds, which is proved by the presence of absorption band with $\lambda_{max} = 578–600$ nm in their spectra, in accordance with our findings [1]. The authors [11] describe their azo coupling reaction products with *N*-alkylanilines ($R^1 = -CH_2CH_2COOCH_3$, $-CH_2CH_2COOC_2H_5$, $-CH_2CH_2CN$) as grey or violet compounds with two bands in visible spectrum ($\lambda_1 \sim 482$ nm, $\lambda_2 \sim 605$ nm) or one very broad band ($\lambda \sim 588$ nm). They explain [11] the properties of the azo coupling reaction products from *N*-alkyl- and *N*,*N*-dialkylanilines by partial aggregation of the former substances in solution.

We have reproduced the reaction of 5-nitro-2,1-benzisothiazole-3-diazonium with 3-(3-methylphenylamino)propanenitrile and found out that triazene **1e** and azo dyestuff **2c** are formed in approximately equimolecular ratio (Table 1). The absorption spectrum of this two-component mixture is given in Fig. 4 (for the individual absorption spectra, see Fig. 3).

Azo compounds as chief products of azo coupling reactions with 5-nitro-2,1-benzisothiazole-3-diazonium hydrogensulphate can only be obtained by the application of tertiary amines (*N*,*N*-disubstituted anilines) or by temporary conversion of a secondary amine into tertiary amine through the replacement of the NH proton by a group that is easily split off. In this way, the formation of triazenes **1** is excluded. This method was used in preparation of azo dyestuff **2b** by azo coupling reaction with sodium *N*-ethyl-*N*-phenylaminomethanesulphonate (Scheme 4).

We isolated and characterised both the sodium *N*-ethyl-*N*-[4-(5-nitro-2,1-benzisothiazol-3-yl)diazenylphenyl]aminomethanesulphonate **3** and the product of its hydrolysis, 3-(4-ethylaminophenyldiazenyl)-5-nitro-2,1-benzisothiazole **2b** (see Table 1). The said procedure gives azo compounds **2** in high yields.

The stability of triazenes **1** in acid media is unusual. 1-(5-Nitro-2,1-benzisothiazol-3-yl)-3-ethyl-3-phenyltriazene dissolved in 0.5 mol l^{-1} H_2SO_4 in aqueous acetic acid (1:1 v/v) is decomposed only slowly at 25 °C to give 5-nitro-2,1-benzisothiazole-3-diazonium with a half-life $\tau_{1/2} = 6.95$ h (417 min) [1]. Similar is also the stability of other triazenes, e.g. **1e** (decomposition half-life $\tau_{1/2} = 13.4$ h), or **1g** (decomposition half-life $\tau_{1/2} = 10.15$ h) in the same medium; see Figs. 5 and 6. A somewhat lower stability in acids was observed with triazene **1l** (decomposition half-life $\tau_{1/2} = 1.83$ h; again in the same medium; see Figs. 7 and 8). The formation of 5-nitro-2,1-benzisothiazole-3-diazonium by decomposition of



1 (acid) **1** (base)

Scheme 3.

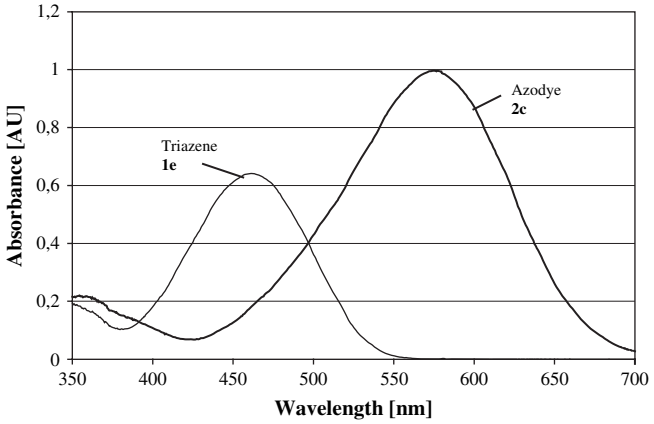


Fig. 3. Absorption spectra of products of azo coupling reaction of 5-nitro-2,1-benzisothiazole-3-diazonium with 3-(3-methylphenylamino)propanenitrile. Triazene **1e** and isomeric azo dyestuff **2c** in methanol; concentration always 2.50×10^{-5} mol l^{-1}.

triazenes **1a–k** is documented by the formation of violet dyestuff with the present 4,5-dihydroxynaphthalene-2,7-disulphonic acid (it plays the role of a scavenger of diazonium salt; the azo compound produced has $\lambda_{max} = 590$ nm). The diazonium salt set free by the decomposition of triazene does not undergo azo coupling reaction with the original amine, obviously due to the high acidity of medium in which the decomposition of triazene takes place and due to the low concentration of free amine. Therefore, once formed, triazene **1** cannot be transformed into dyestuff **2** any more.

Triazenes **1l**, **1m**, **1n** formed by azo coupling reactions with primary anilines and containing NH group in their triazene groupings ($R^1 = H$) are decomposed to give 3-amino-5-nitro-2,1-benzisothiazole and not 5-nitro-2,1-benzisothiazole-3-diazonium. The gradually increasing amount of 3-amino-5-nitro-2,1-benzisothiazole was proved for the first time by repeated measurements of ^{1}H NMR spectra of these triazenes in DMSO-d_6 solution (carried out within several days at r.t.), and later on by goal-directed experiments, when the triazene was dissolved

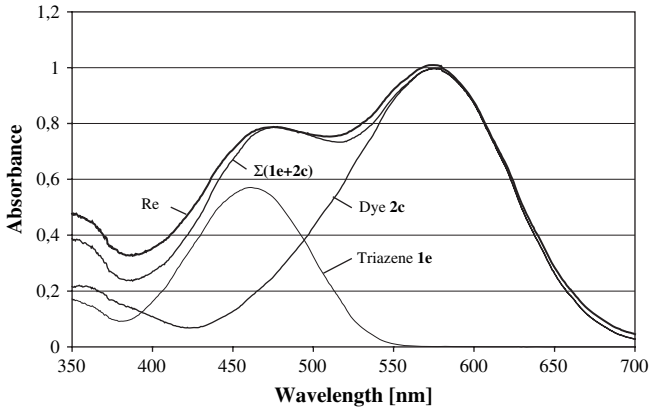


Fig. 4. Absorption spectra in methanol. Crude reaction mixture (curve Re) after azo coupling reaction of 5-nitro-2,1-benzisothiazole-3-diazonium with 3-(3-methylphenylamino)propanenitrile (22 mg/l) in comparison with the absorption spectra of the respective triazene **1e** (2.25×10^{-5} mol l^{-1}), azo dyestuff **2c** (2.50×10^{-5} mol l^{-1}) and their sum in the mixture $\sum$(**1e** + **2c**).

in concentrated acetic acid with addition of hydrochloric acid, and the solution was subsequently stirred at the temperature of 60 °C. TLC chromatography allowed monitoring of gradual conversion of the triazene into 3-amino-5-nitro-2,1-benzisothiazole. After diluting the reaction mixture with water, the precipitated 3-amino-5-nitro-2,1-benzisothiazole was isolated with a yield of ca 80%. In the cases of triazenes **1a–k**, which are produced by azo coupling reactions with *N*-monosubstituted anilines, no splitting is possible except for that giving the starting 5-nitro-2,1-benzisothiazole-3-diazonium. In the cases of the triazenes formed by azo coupling reactions with anilines containing primary amino group (**1l**, **1m**, **1n**) tautomeric equilibriums are possible (Scheme 5), which may be the reason for the fact that the decomposition of these triazenes does not give 5-nitro-2,1-benzisothiazole-3-diazonium, and instead gives diazonium salts derived from the original coupling (passive) components (aniline, 3-chloroaniline, 3-toluidine), see Scheme 5. Of course, according to the Hammet–Curtin principle, the position of tautomeric equilibrium in triazene grouping does not affect the way of splitting into diazonium ion.

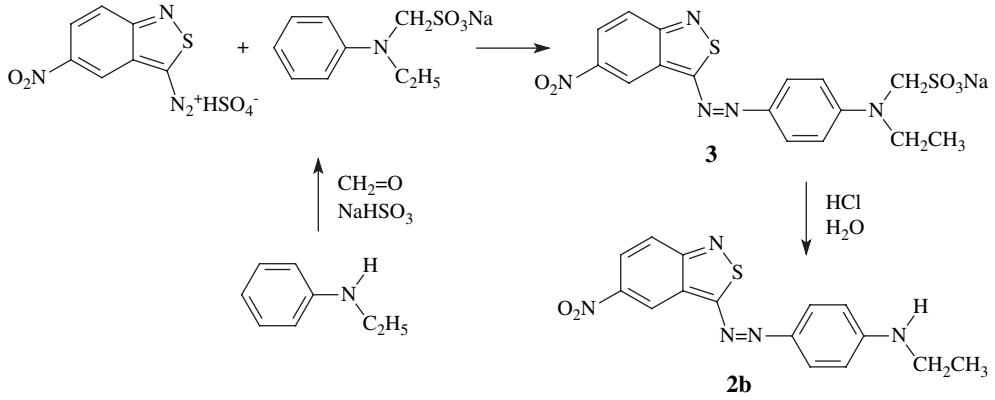
The benzenediazonium salt set free does not undergo any azo coupling reaction with the present 4,5-dihydroxynaphthalene-2,7-disulphonic acid at the given conditions in strongly acidic medium; see the kinetics of decomposition of triazene **1l**; Figs. 7 and 8.

3. Conclusions

It was proved that the azo coupling reactions of *N*-monosubstituted anilines with 5-nitro-2,1-benzisothiazole-3-diazonium produce unusually stable triazenes, formed as major products predominating over product of normal azo coupling in aromatic ring. This fact complicates the preparation of azo dyestuffs from *N*,*N*-disubstituted anilines used as coupling (passive) components in which *N*-monosubstituted anilines are present as main impurities. Even their small amounts result in formation of orange, very resistant triazenes that deteriorate the blue hue of azo dyestuffs – the desired chief products. A typical example is C.I. Disperse Blue 148. If the triazenes are formed in this way, they are difficult to remove, because they exhibit high stability both at high temperatures and in acidic media.

Triazene **1b** was successfully applied as a brilliant orange disperse dye for PES fibres. For this purpose, it was submitted to usual fine wet grinding with dispersants and glass pearls. The dispersion was dried in a spray drier. In the process of HT-dyeing at 130 °C the dyestuff exhibited no signs of decomposition. The dyed fibre, however, exhibited low light fastness (Xenotest 1–2).

For syntheses of usual blue dyestuffs based on *N*,*N*-disubstituted anilines it is necessary to prevent the formation of triazenes by the best possible removal of traces of *N*-monosubstituted anilines. An efficient solution to this problem is, e.g., acetylation with acetic anhydride giving the respective *N*-acetyl derivatives, which do not undergo any azo coupling reaction. This procedure was made use in patent [12].



Scheme 4.

Azo dyestuffs of general structure **2**, containing one (or two) hydrogen atom(s) at amino nitrogen of the coupling (passive) component cannot be obtained by direct azo coupling reaction in good quality and yield. The azo coupling always produces a mixture of triazene **1** and isomeric dyestuff **2** in various molar ratios. The preparation of dyestuffs of general formula **2** is possible with temporary conversion of secondary amine into tertiary amine by replacing the proton in NH group by an alkyl group that is easy to split off (see Scheme 4).

4. Experimental

4.1. 3-Amino-5-nitro-2,1-benzisothiazole

3-Amino-5-nitro-2,1-benzisothiazole technical product (fa Synthesia, Pardubice, Czech Rep.), was rid of traces of 2-amino-5-nitrobenzonitrile and 2-aminocarbonyl-4-nitrobenzonitrile by heating in 85% sulphuric acid at 110 °C for 30 min. Then the solution was diluted with water and alkalised with aqueous ammonia to pH 10. The suspension formed was heated to boiling, hot filtered, washed on filter with hot 3% ammonia solution, then with hot water until neutral, and dried at 105 °C. No by-products were detected by means of HPLC. The substance does not melt up to 300 °C, being decomposed above 300 °C in accordance with Ref. [13]. The ^{1}H chemical shifts (DMSO-d_6): 9.11 (1H, d, $^{4}J(4,6) = 2.2$ Hz, H-4), 7.96 (1H, dd, $^{3}J(6,7) = 9.7$ and $^{4}J(4,6) = 2.2$ Hz, H-6), 7.32 (1H, d, $^{3}J(6,7) = 9.7$ Hz, H-7), 8.79 (2H, br s, NH_2); the ^{13}C chemical shifts (DMSO-d_6): 178.85 (C-3), 117.61 (C-3a), 121.90 (C-4), 138.27 (C-5), 122.56 (C-6), 120.68 (C-7), 160.50 (C-7a).

N-Substituted anilines used as the coupling (passive) components were commercial products purchased from Lachema, Fluka, or Sigma–Aldrich.

4.1.1. Diazotisation of 3-amino-5-nitro-2,1-benzisothiazole in nitrosylsulphuric acid

Solid $NaNO_2$ (3.48 g; 0.05 mol) was added in small portions to 25 ml 96% sulphuric acid (0.45 mol) with stirring and cooling at such a rate as to prevent the formation of

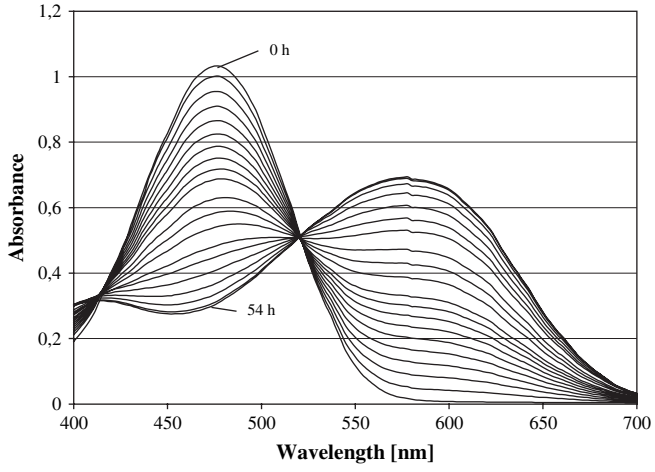


Fig. 5. Spectral record of decomposition of triazene **1g** in 0.5 mol l^{-1} H_2SO_4 in aqueous acetic acid 1:1 (v/v) in the presence of 4,5-dihydroxynaphthalene-2,7-disulphonic acid (2.5×10^{-3} mol l^{-1}) at 25 °C. The spectral records were obtained at time intervals of 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 13, 15, 18, 21, 25, 30, 35, 43 and 54 h from the moment of mixing of the solutions.

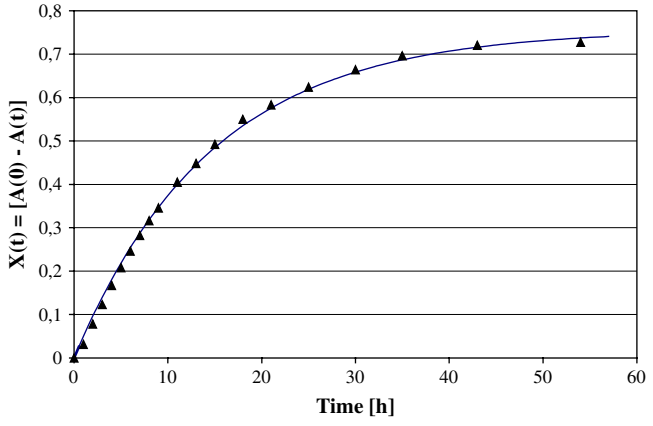


Fig. 6. Absorbance–time dependence $X(t) = A(0) - A(t) = [A(0) - A(\infty)][1 - \exp(-kt)]$ at 475 nm for the decomposition of triazene **1g** in 0.5 mol l^{-1} H_2SO_4 in aqueous acetic acid 1:1 (v/v) in the presence of 4,5-dihydroxynaphthalene-2,7-disulphonic acid (2.5×10^{-3} mol l^{-1}) at 25 °C. The parameters found for the initial absorbance $A(0) = 1.0331$ by non-linear regression are as follows: $A(\infty) = 0.27712$, rate constant $k = 0.06831$ h^{-1} (decomposition half-life $t_{(1/2)} = \ln 2k^{-1} = 10.15$ h).

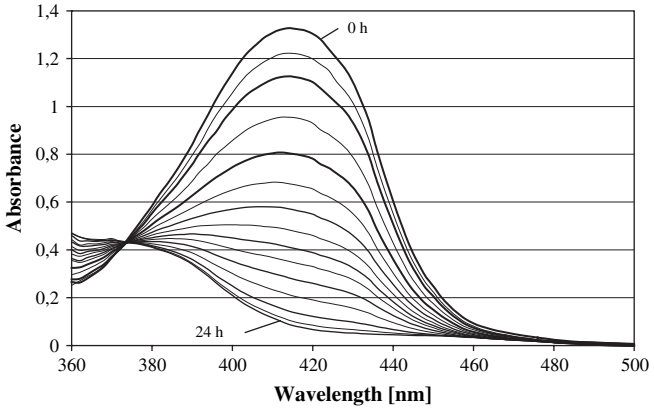


Fig. 7. Spectral record of decomposition of triazene **1l** in 0.5 mol l^{-1} H_2SO_4 in aqueous acetic acid 1:1 (v/v) in the presence of 4,5-dihydroxynaphthalene-2, 7-disulphonic acid (2.5×10^{-3} mol l^{-1}) at 25 °C. The spectral records were obtained at time intervals of 0, 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 7, 9, 12 and 24 h from the moment of mixing of the solutions. In this case, the decomposition products of triazene do not undergo the azo coupling reaction with 4,5-dihydroxynaphthalene-2,7-disulphonic acid.

nitrous gases. The solution was stirred and slowly heated to 70 °C until complete dissolution of the present salts. Then it was cooled with stirring to 25–30 °C, and 9.77 g (0.05 mol) 3-amino-5-nitro-2,1-benzisothiazole was gradually added, whereupon the reaction mixture was stirred at 25–30 °C for another 3 h.

*4.2. 3-Ethyl-3-phenyl-1-(5-nitro-2,1-benzisothiazol-3-yl)triazene **1b***

N-Ethylaniline (6.36 g; 0.0525 mol) was dissolved in 60 ml 1 mol l^{-1} aqueous HCl (0.06 mol). After the addition of 0.25 g charcoal and 0.25 g kieselguhr, the mixture was stirred for 10 min and filtered. The obtained solution of *N*-ethylanilinium chloride was treated with 2 g dispersant (C_{12}–C_{13} sodium alkyltriethoxysulphate) and, with stirring, 68 g (0.5 mol) $CH_3COONa \cdot 3H_2O$. The formed emulsion of *N*-ethylaniline was mixed with 450 g finely crushed ice, whereupon the diazonium salt solution (0.05 mol) was added drop by drop with stirring. The reaction mixture was stirred for 3 h, and then the orange-brown precipitate of triazene **1b** was collected by suction, the filter cake was washed with 500 ml distilled water and dried at 80 °C. The yield of crude product was 13.7 g (84%). It was purified by three recrystallisations from acetone. M.p. 125–127 °C.

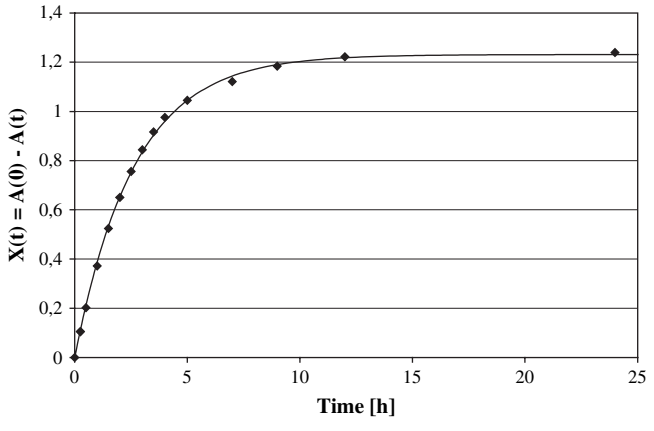


Fig. 8. Absorbance–time dependence $X(t) = A(0) - A(t) = [A(0) - A(\infty)][1 - \exp(-kt)]$ at 414 nm for the decomposition of triazene **1l** in 0.5 mol l^{-1} H_2SO_4 in aqueous acetic acid 1:1 (v/v) in the presence of 4,5-dihydroxynaphthalene-2,7-disulphonic acid (2.5×10^{-3} mol l^{-1}) at 25 °C. The parameters found for the initial absorbance $A(0) = 1.3281$ by non-linear regression are as follows: $A(\infty) = 0.0973$, rate constant $k = 0.37809\ h^{-1}$ (decomposition half-life $t_{(1/2)} = \ln 2k^{-1} = 1.83$ h).

*4.3. 3-(But-1-yl)-3-phenyl-1-(5-nitro-2,1-benzisothiazol-3-yl)triazene **1d***

N-Phenylbutan-1-amine (7.83 g; 0.0525 mol) was dissolved in 90 ml 1 mol l^{-1} aqueous HCl (0.09 mol). After the addition of 0.25 g charcoal and 0.25 g kieselguhr, the mixture was stirred for 10 min and filtered. The obtained solution of *N*-butylanilinium chloride was treated with 2 g dispersant (C_{12}–C_{13} sodium alkyltriethoxysulphate) and, with stirring, 95 g (0.7 mol) $CH_3COONa \cdot 3H_2O$. The formed emulsion of *N*-phenylbutan-1-amine was mixed with 500 g finely crushed ice, whereupon the diazonium salt solution (0.05 mol) was added drop by drop. The reaction mixture was stirred for 3 h, and then the orange-brown precipitate of triazene **1b** was collected by suction. The filter cake was washed with 500 ml distilled water and dried at 80 °C. The yield of crude product was 12.6 g (71%). It was purified by three recrystallisations from acetone. M.p. 170–171 °C.

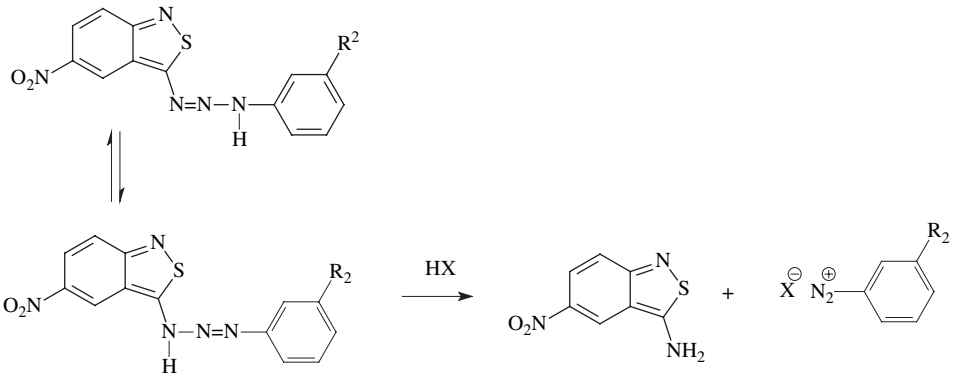
The other triazenes were prepared in the same way (Table 1).

*4.4. Sodium N-ethyl-N-[4-(5-nitro-2,1-benzisothiazol-3-yl)diazenylphenyl]aminomethanesulphonate **3***

Compound **3** was prepared by azo coupling reaction of 5-nitro-2,1-benzthiazole-3-diazonium hydrogensulphate with sodium *N*-ethyl-*N*-phenylaminomethanesulphonate. The latter compound was prepared by the reaction of *N*-ethylaniline with formaldehyde and sodium hydrogensulphite by a procedure analogous to that used for other alkali aminoalkanesulphonates [14,15].

Hydroxymethanesulphonic acid, Na-salt: 252 g $Na_2S_2O_5$ (content 95%) was dissolved in 400 ml distilled water at 50 °C with stirring, and aqueous solution of formaldehyde was added gradually. The reaction is exothermic; a controlled addition of formaldehyde and mild cooling of the reaction mixture in a water bath kept the temperature of reaction mixture below 70 °C.

Throughout the addition of formaldehyde, the pH of reaction mixture was monitored: at first it is constant (pH ca 5–6), but after exceeding the stoichiometric amount and reaching a mild surplus of formaldehyde, the pH value begins to increase. The addition of formaldehyde was stopped after reaching pH ca 9. Altogether 212 g, 35.5%, solution of formaldehyde (ca 2.51 mol) was added. A small surplus of formaldehyde was removed by adding 3 g $Na_2S_2O_5$, which resulted



Scheme 5.

in a pH decrease to ca 7–7.5. The total consumption was 255 g $Na_2S_2O_5$ (1.25 mol). The reaction mixture was stirred at 70 °C for 30 min and then cooled to r.t. Yield was 845 g aqueous solution of sodium hydroxymethanesulphonate with the concentration of 2.97 mol/kg.

Sodium N-ethyl-N-phenylaminomethanesulphonate: 60.6 g *N*-ethylaniline (0.5 mol) was mixed with 177 g solution of sodium hydroxymethanesulphonate (0.525 mol) prepared in the above-mentioned way. The reaction mixture was stirred at 75 °C for 6 h. The originally immiscible system of two liquids gradually changed into one homogeneous phase. After the addition of 1 g charcoal and 1 g kieselguhr, the solution was filtered to give 237 g of yellowish filtrate with the total content of 0.5 mol sodium *N*-ethyl-*N*-phenylaminomethanesulphonate, which corresponds to the concentration of 2.11 mol/kg.

Azo coupling reaction proper: 50.24 g (0.106 mol) of aqueous solution of the sodium *N*-ethyl-*N*-phenylaminomethanesulphonate prepared in the above-given way was dissolved in 140 ml water, and 250 g $CH_3COONa \cdot 3H_2O$ (1.84 mol) and 600 g ice were added to it with stirring. Then, the solution of diazonium salt (0.1 mol) was added drop by drop. The reaction mixture was stirred 10 h, and the separated solid dyestuff was filtered off. The yield was 130.4 g aqueous paste with the dry matter content of 34%, which represents 44.3 g dry crude dyestuff **3** (yield 93%). According to thin-layer chromatographical analysis (Silufol, ethyl acetate/toluene/formic acid 85% 3:2.5:2.7 v/v/v), the obtained dyestuff contained, beside the main component **3**, a small amount of triazene **1b**, and traces of blue dyestuff **2a** formed by hydrolysis of dyestuff **3**. In order to obtain the pure substance **3**, we finely ground 10 g dry crude compound **3**, and triazene **1b** and azo compound **2a** were removed by repeated extraction with dichloromethane in a Soxhlet extractor. The undissolved residue of compound **3** after the extraction was recrystallised six times from methanol. The yield of pure compound **3** was 5.2 g.

*4.5. 3-(4-Ethylaminophenyldiazenyl)-5-nitro-2,1-benzisothiazole **2a***

Compound **2a** was prepared from azo dyestuff **3** by splitting off of $CH_2SO_3^-$ group by hydrolysis: 100 g aqueous paste (34 g dry matter) of crude dyestuff **3**, prepared in the above-described way was mixed with 500 ml 10% HCl, the suspension was stirred and heated to 75 °C, and then stirred at this temperature for 60 min. The course of hydrolysis of compound **3** giving azo dyestuff **2a** was monitored by TLC (Silufol, *n*-hexane/acetone 5:3). After the finished hydrolysis, the reaction mixture was diluted with 500 ml water and cooled to r.t. The separated azo dyestuff **2a** was collected by suction; the filter cake was washed with ca 700 ml water until neutral, and dried. The yield was 28.7 g crude azo dyestuff **2a** (90% referred to compound **3**; 84% referred to the starting diazonium salt). After three crystallisations from ethanol, M.p. 228–230 °C.

*4.6. Preparation of triazene **1e** beside the isomeric azo dyestuff **2c** by separation of reaction mixture after the azo coupling reaction*

The filter cake after the azo coupling reaction of 5-nitro-2,1-benzthiazole-3-diazonium with 3-(3-methylphenylamino)-propanenitrile was repeatedly mixed at 60 °C in a mixture of *N*,*N*-dimethylformamide/methanol/acetic acid (10:10:1 v/v/v), and the reaction suspension was filtered. The filtrate after cooling to r.t. mainly separated triazene **1e**, whereas the azo dyestuff **2c** predominantly remained dissolved. The triazene was filtered off, and the dyestuff in the filtrate was precipitated by dilution with water and isolated by filtration. The said procedure was repeated several times. The separated crude components were then purified by repeated recrystallisations from acetone. An analogous procedure was adopted for separation of the reaction mixtures of triazene **1c** and azo dyestuff **2b**.

*4.7. Preparation of triazene **1n** beside the isomeric azo dyestuff **2e** by separation of reaction mixture after azo coupling reaction*

The filter cake after the azo coupling reaction of 5-nitro-2,1-benzthiazole-3-diazonium with 3-methylaniline was repeatedly mixed with a mixture of acetone/ammonia (1:1 v/v), heated to boiling and hot filtered. The filtrate predominantly contained the violet ammonium salt of triazene **1n** (which is very soluble in alkalis), whereas predominantly undissolved was the less soluble azo dyestuff **2c**. The filtrate was diluted

with water and neutralised with acetic acid to separate the crude triazene. The separated crude components were then purified by repeated recrystallisations from acetone. Similar method was used to isolate triazene **1l** and isomeric azo dyestuff **2d** from the reaction mixture.

*4.8. Decomposition of triazene **1n** in acids giving 3-amino-5-nitro-2,1-benzisothiazole*

Triazene **1n** (2 g) was dissolved in concentrated acetic acid (50 ml) with addition of concentrated hydrochloric acid (10 ml). The solution was stirred at 60 °C. TLC (Silufol, toluene/ethyl acetate 5:1 v/v) was used for monitoring the gradual transformation of triazene into 3-amino-5-nitro-2, 1-benzisothiazole. The triazene disappeared after 3 h. The reaction mixture was diluted with water to total 1 l volume, stirred, and the separated solid was collected by suction to give 0.98 g 3-amino-5-nitro-2,1-benzisothiazole (ca 80% of theoretical yield). An analogous way was also adopted to test the decomposition of triazenes **1l** and **1m**.

The ^{1}H and ^{13}C NMR spectra were measured with a Bruker AVANCE 500 spectrometer at the frequencies of 500.13 and 125.77 MHz, respectively. The measurements were carried out with the substances dissolved in DMSO-d_6 at 25 °C. The chemical shifts are referenced to the central signals of the multiplet of the solvent: $\delta(^{1}H)$ 2.55, $\delta(^{13}C)$ 39.6.

The electronic spectra of the substances dissolved in methanol and the kinetics of decomposition of triazenes in 0.5 mol l^{-1} H_2SO_4 in aqueous acetic acid (1:1 v/v) were measured at 25 °C by means of a diode array spectrophotometer Hewlett Packard 8453.

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