HETEROCYCLIC DIAZO COMPOUNDS

I. PROPERTIES OF BENZOTHIAZOLE-2-DIAZONIUM SALTS

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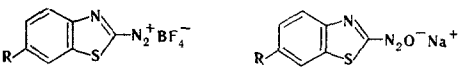
Benzothiazole-2-diazonium tetrafluoroborate and its 6-bromo, 6-methyl, and 6-methoxy derivatives are relatively stable and have high electrophilicities. They are rapidly converted in weakly alkaline media to the corresponding anti-diazotates, from which primary nitrosoamines can be obtained by acidification.

Heterocyclic diazo compounds that contain a pyridine nitrogen atom have high activity in diazo coupling, and a number of their properties approach those of diazo derivatives of the benzene ring with electron-acceptor substituents.

It seemed of interest to make a more detailed study of the properties of diazo compounds (I) based on 2-aminobenzothiazole with various substituents in the benzene ring.



I a-d II a-d

I, II a R = H; b R = Br; c R = CH_3; d R = CH_3O

The diazotization of the starting amines proceeded in accordance with the data in [1, 2]. The resulting diazo compounds were isolated from the solutions in the crystalline state as the tetrafluoroborates (Ia-d), which were relatively stable substances.

The bands of the diazo group in the IR spectra of the compounds are quite intense and lie at 2210-2260 cm^{-1}, the region characteristic for diazo compounds of the benzene ring with weak donor substituents. The electronic spectra of solutions of the diazo compounds in 50% sulfuric acid contain an intense band at ~400 nm, which is shifted markedly to the long-wave portion of the spectrum in the case of 6-methoxy derivative Id (Table 1).

Judging from qualitative experiments, the benzothiazolediazonium salts readily form azo dyes with various azo components in strongly acidic media. Thus salt Ib couples with an H acid and anisole in 40% sulfuric acid. Under similar conditions, the p-nitrobenzenediazonium salt does not form azo dyes. This constitutes evidence in favor of the high electrophilicity of diazo compounds based on benzothiazole [3].

The rate constant for thermal decomposition of 6-methoxy derivative Id in 0.5% sulfuric acid at 20°C, which was found by a spectrophotometric method, is $9.5 \cdot 10^{-5}$ sec^{-1}. The p-toluenediazonium salt undergoes decomposition at the same rate under the same conditions [4]. Thus the thermal stabilities of the diazo derivatives of 2-aminobenzo-thiazoles in solution approach the thermal stabilities of the diazo compounds of the benzene series.

The absorption maxima in the electronic spectra are shifted to the short-wave region when dilute solutions of salts Ia-d are made alkaline to pH 10 (Fig. 1); this is due to the formation of the sodium salts of the diazotates (IIa-d). The resulting solutions are incapable of entering into diazo coupling, and judging from the spectra, they regenerate the starting diazonium salt on acidification.

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TABLE 1. Benzothiazole-2-diazonium Tetrafluoroborates (Ia-d)

Compound	R	Empirical formula	N, % found	N, % calc.	λ_{max}, nm (lg ε)[a]	$\nu_{N_2^+}$,[b] cm^{-1}	Yield, %
Ia	H	$C_7H_4BF_4N_3S$	16,5	16,9	365 (4,12)	2260	78
Ib	Br	$C_7H_3BBrF_4N_3S$	12,2	12,8	386 (4,15)	2259	12
Ic	CH_3	$C_8H_6BF_4N_3S$	16,1	16	385 (4,15)	2248	31
Id	CH_3O	$C_8H_6BF_4N_3OS$	14,9	15,1	425 (4,10)	2217	62

Note: [a]In 50% H_2SO_4. [b]In nitromethane.

TABLE 2. Absorption Maxima of Benzothiazole-2-diazotates IIa-d (in 0.1 N NaOH) and 2-Benzothiazolylnitrosamines IIIa-d (in ethanol)

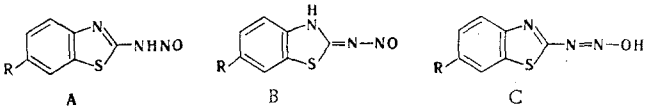
R	IIa-d empirical formula	IIa-d λ_{max}, nm	IIIa-d empirical formula	IIIa-d λ_{max}, nm
H	$C_7H_4N_3NaOS$	322	$C_7H_5N_3OS$	310[a]
Br	$C_7H_3BrN_3NaOS$	332	$C_7H_4BrN_3OS$	322
CH_3	$C_8H_6N_3NaOS$	328	$C_8H_7N_3OS$	320
CH_3O	$C_8H_6N_3NaO_2S$	338	$C_8H_7N_3O_2S$	342

Note: [a]In chloroform, λ_{max} 315 nm.

In preparative experiments the sodium salts of the diazotates (IIa-d) were formed readily even in the cold on treatment with alkali and were isolated in pure form. An intense band at 330 nm (Table 2) is observed in the electronic spectra of these compounds in 0.1 N NaOH. The diazotates are incapable of diazo coupling, and this property makes it possible to assign the anti-diazotate structure to them. One's attention is drawn to the unusual ease of formation of the anti-diazotates, which has previously been noted only in the case of p-nitrobenzenediazonium salts. Rapid conversion of diazo compounds to anti-diazotates in relatively weak media is apparently also characteristic for other diazo derivatives based on "pyridine" heterocycles. In this connection, the low yields of azo dyes obtained by several investigators [5, 6] become understandable.

Compounds that are only slightly soluble in water and have elementary compositions that correspond to primary nitrosamines were formed when an equivalent amount of acid was added to solutions of diazotates IIa-d. In the presence of excess mineral acid these compounds are capable of being converted to diazonium salts Ia-d; under the influence of alkali, they undergo reverse conversion to the diazotates. The electronic spectra of alcohol solutions of these compounds have one band that is extremely close in position to the band of the corresponding diazotates (Table 2).

At least three tautomeric forms – nitrosoamine A, nitrosoimine B, and diazo hydrate C – can be presented for the nitrosoamines obtained:



A B C

III a-d

To solve the problem as to which form is actually realized, we synthesized two models with fixed structures. 2-(N-Methyl-N-nitrosoamino)benzothiazole (IV, form A) was obtained by nitrosation of the corresponding 2-(methylamino)benzothiazole. 3-Methyl-2-nitrosoimino-benzothiazoline (V, form B) was synthesized by nitrosation of 2-imino-3-methylbenzothiazoline. The electronic spectra of the compound obtained by acidification of diazotates IIa and of IV in chloroform solution practically coincide, while the long-wave band of V is shifted bathochromically by 32 nm (Fig. 2).

The results provide evidence that the product of acidification of sodium benzothiazole-2-diazotate (IIa) exists in nitrosoamine form A. Inasmuch as the changes in the electronic spectra for other benzothiazole-2-diazotates and their corresponding acidification products are similar, we have also assigned the primary nitrosoamine structure (IIIa-d) to the latter.

Thus diazo compounds based on benzothiazole and its derivatives are extremely electrophilic and are very readily converted by alkalization to anti-diazotates, the conjugate acids of which are quite stable and exist in the nitrosoamine form.

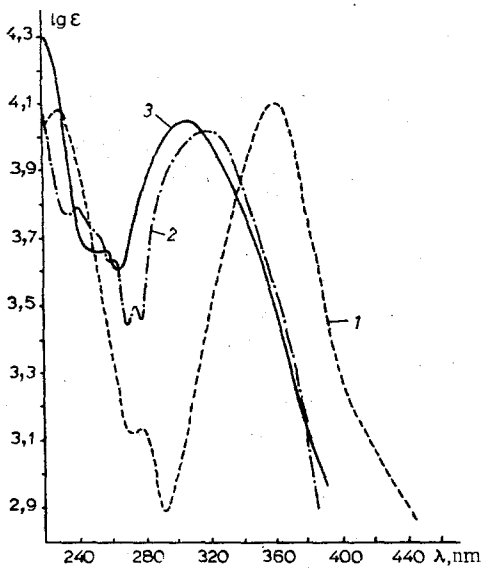


Fig. 1

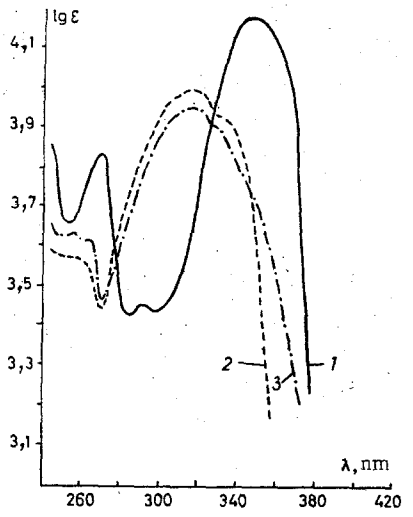


Fig. 2

Fig. 1. Electronic absorption spectra: 1) benzothiazole-2-diazonium tetrafluoroborate (Ia) in 50% H_2SO_4; 2) 2-benzothiazolyldiazotate IIa in 0.1 N NaOH; 3) 2-benzothiazolylnitrosoamine (IIIa) in alcohol.

Fig. 2. Electronic absorption spectra of chloroform solutions: 1) 3-methyl-2-nitrosoiminobenzothiazoline (V); 2) 2-benzothiazolylnitrosoamine (IIIa); 3) 2-(N-methyl-N-nitrosamino)benzothiazole (IV).

EXPERIMENTAL

Kinetic data on the thermal decomposition of diazonium salt Id and the UV spectra of the synthesized compounds were obtained with SF-4a and SF-8 spectrophotometers with quartz cuvettes and layer thicknesses of 1 cm. The solution concentration was $(0.6\text{-}1) \cdot 10^{-4}$ M. The IR spectra of solutions of the diazonium salts in nitromethane were recorded with a UR-20 spectrometer.

2-Aminobenzothiazole and its methyl derivative were obtained by the Gugerschoff method [7, 8], 2-amino-6-methoxybenzothiazole was obtained by the Kauffmann method [9], and 2-amino-6-bromobenzothiazole was synthesized by bromination of 2-aminobenzothiazole in glacial acetic acid [7].

Benzothiazole-2-diazonium Tetrafluoroborate (Ia). A 1 g (6.6 mmole) sample of 2-aminobenzothiazole was mixed at 0° with 13 ml of 42% tetrafluoroboric acid and 1 ml of concentrated H_2SO_4, and 0.48 g (6.8 mmole) of 30% sodium nitrite solution was added gradually to the mixture. The mixture was then held at 0° for 1.5 h. Tetrafluoroborate Ia was removed by filtration, washed successively with a small amount of tetrafluoroboric acid, ice water, alcohol, and ether, and vacuum dried over calcium chloride.

6-Methoxybenzothiazole-2-diazonium Tetrafluoroborate (Id). A 1 g (5.5 mmole) sample of 2-amino-6-methoxybenzothiazole was mixed with 11 ml of 56% sulfuric acid, after which the mixture was cooled to 0°, and 0.39 g (5.6 mmole) of sodium nitrite (in the form of a 30% solution) was added gradually at this temperature with stirring under the liquid layer. Stirring was continued at 0° for 1.5 h, after which the mixture was cold filtered to remove a small amount of solid, and 0.75 g (6.8 mmole) of sodium tetrafluoroborate was added to the filtrate. The precipitated Id was removed by filtration and washed as indicated above.

Compound Ic was similarly obtained. The diazotization of 2-amino-6-bromobenzothiazole was carried out in 70% sulfuric acid for 2 h.

Compounds Ia-d (Table 1) were purified by reprecipitation from nitromethane solution by the addition of ether.

Sodium Benzothiazole-2-diazotates (IIa-d). Ice and a diazonium salt solution, obtained by diazotization of 1 g (5.5 mmole) of 2-amino-6-methoxybenzothiazole under the conditions indicated above, were added gradually with external cooling to 40 ml of 20% sodium hydroxide solution. The resulting precipitate

was removed by filtration, and the filtrate was vacuum evaporated at 30-40°. The diazotate was removed by filtration and purified by reprecipitation from alcohol by the addition of ether. Analytically pure IId was obtained by repeated reprecipitation.

A similar procedure was used to obtain IIa-c. The yields were 5-18%. The composition of the diazotates was confirmed by elementary analysis for one to two elements.

2-Benzothiazolylnitrosoamines (IIIa-d). An equimolecular amount of 50% acetic acid was added to a cooled aqueous solution of purified sodium diazotate (1:50), and the resulting precipitate was removed by filtration, washed on the filter with ice water, and vacuum dried over calcium chloride. Pure primary nitrosoamines were obtained in quantitative yields. The composition of the nitrosoamines was confirmed by elementary analysis for one to two elements.

3-Methyl-2-iminobenzothiazole was obtained from N-methylaniline by the method in [10]; nitrosation was carried out by the method in [10].

2-(N-Methyl-N-nitrosoamino)benzothiazole (IV). Sodium nitrite [0.324 g (4.7 mmole)] in the form of a 20% solution was added with stirring at room temperature to a solution of 0.5 g (3.0 mmole) of 2-methylaminobenzothiazole in 3 ml of glacial acetic acid, after which the mixture was allowed to stand. The resulting light-yellow precipitate was removed by filtration, washed with water, and recrystallized from benzene (1:10). The yield was 85%. λ_{max} 315 nm (in alcohol), 320 nm (in chloroform). Found: C 50.2; H 4.0; N 21.7%. $C_8H_7N_3OS$. Calculated: C 50.0; H 3.7; N 21.8%.

LITERATURE CITED

1. A. Spilliadis and M. Hilsenrath, Rev. Chim., 17, 271 (1966).
2. Eastman Kodak Co., US Patent No. 2,868,775 (1959); Referativny Zh. Khim., 74,444 P (1960).
3. J. Goerdeler and H. Haubrich, Ber., 93, 397 (1960).
4. D. F. De Tar and A. R. Ballentine, J. Am. Chem. Soc., 78, 3916 (1956).
5. D. A. Drapkina, V. G. Brudz', and Z. S. Sidenko, Zh. Obshch. Khim., 32, 1535 (1962).
6. L. Pentimalli, Chim. Industria, 39, 11 (1957).
7. N. S. Drozdov, Zh. Obshch. Khim., 7, 1668 (1937).
8. C. Allen and J. Van Allan, in: Organic Syntheses, Vol. 3, Wiley.
9. C. G. Stuckwisch, J. Am. Chem. Soc., 71, 3417 (1949).
10. E. Besthorn, Ber., 43, 1519 (1910).