SYNTHESIS AND REACTIONS OF HETEROCYCLIC COMPOUNDS

I. Azides of Benzthiazole and Benzimidazole

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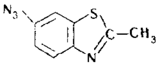
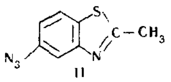
5-Azido-2-methylbenzthiazole, 6-azido-1, 2-dimethyl-, and 5-azido-2-methyl-1-phenylbenzimidazoles were prepared. By the reactions of these azides with alkyl halides the quaternary slats based on the cyanine dyes were obtained.

Since methods of preparation and reactions of aliphatic and aromatic azides have been comprehensively described in the literature, whereas the heterocyclic azides have not been well studied, the preparation of azides of heterocyclic compounds and a study of their properties would be of considerable practical and theoretical interest.

The object of this work was to obtain isomeric azidobenzthiazoles and azidobenzimidazoles and to study their properties.

5-Azido-2-methylbenzthiazole (II), 6-azido-1, 2-dimethyl- and 5-azido-2-methyl-1-phenylbenzimidazoles (III, IV) were obtained in manner similiar to the preparation of 6-azido-2-methylbenzthiazole (I) [1], involving the reaction between the diazo compounds of the corresponding amines and sodium azide.


I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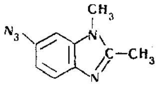
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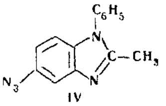
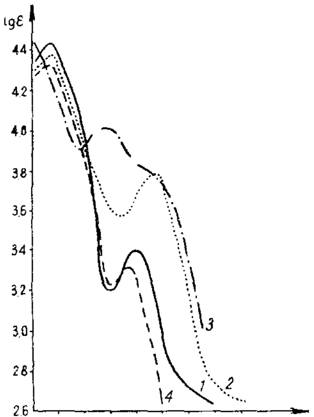

IV

The azides obtained are yellowish compounds which crystallize readily from alcohol, and decompose with the evolution of nitrogen on heating and in the presence of concentrated sulfuric acid. Crystals darken on exposure to light.

At present there is very little data concerning the quaternary salts of the azides. The iodomethylate of 4-azidoquinoline was only obtained as recently as 1962 [2].

When azides I–III were heated with methyl iodide and azides III and IV were heated with ethyl iodide in a sealed ampul at a temperature of 60–100°, the quaternary salts V–IX were obtained (Table 1).



UV spectra: 1) 6-azido-2-methylbenzthiazole; 2) 5-azido-2-methylbenzthiazole; 3) iodomethylate of 6-azido-2-methylbenzthiazole; 4) iodomethylate of 5-azido-2-methylbenzthiazole.

The quaternary salts V-IX are colorless crystalline substances that crystallize readily from alcohol in the form of fine needles. They are readily soluble in water. Like the azides, in sunlight they darken and decompose on heating and under the action of concentrated sulfuric acid with the liberation of nitrogen.

UV and IR spectra were used to determine the structures of the azides and their quaternary salts. The figure shows the UV spectra obtained by us of the azide II, the quaternary salts V and VI, and the well-known 6-azido-2-methylbenzthiazole (I). From the UV and IR spectra it is possible to conclude that the azido group is preserved in the quaternary salts,

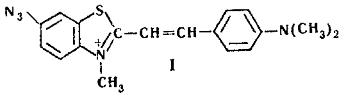
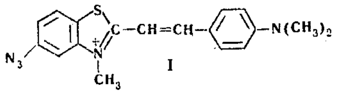
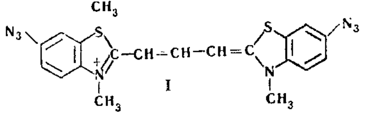
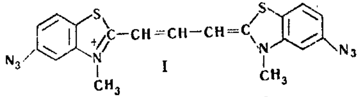
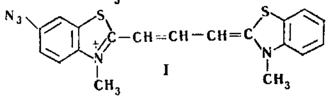
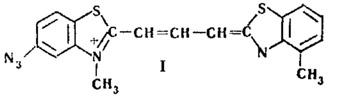
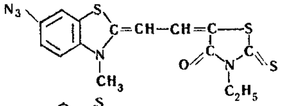
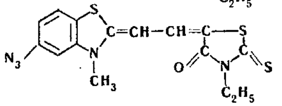
Table 1

Quaternary Salts of the Azides

No. of the compound	Compound	T. decomp., °C	γ_{as} N_3, cm^{-1}	Empirical formula	N, %		Yield, %
					found	calculated	
V	Iodomethylate of 6-azido-2-methylbenzthiazole	173—174	2160	$C_9H_9IN_4S$	16.73; 16.79	16.85	63
VI	Iodomethylate of 5-azido-2-methylbenzthiazole	152	2120	$C_9H_9IN_4S$	16.38; 16.34	16.85	46
VII	Iodomethylate of 6-azido-1,2-dimethylbenzimidazole	172—173	—	$C_{10}H_{12}IN_5$	20.82; 20.96	21.27	74
VIII	Iodoethylate of 6-azido-1,2-dimethylbenzimidazole	167—168	2120	$C_{11}H_{14}IN_5$	20.67; 20.39	20.40	60
IX	Iodoethylate of 5-azido-2-methyl-1-phenylbenzimidazole	180—181	2100	$C_{16}H_{16}IN_5$	16.96; 17.17	17.28	53

Tabel 2

Characteristics of the Prepared Cyanine Dyes

Compound	Formula of dye	T. decomp., °C	λ_{max}, nm	$\varepsilon_{max} \cdot 10^{-4}$	Bathochromic shift, nm	γ_{as} N_3, cm^{-1}	Empirical formula	Found, %		Calculated, %		Yield, %
								N	S	N	S	
X		170—172	535	5.5	7	2116	$C_{18}H_{18}IN_6S$	14.24; 14.32	7.18; 7.03	15.11	6.92	66.6
XI		199—202	540	5.04	12	2123	$C_{18}H_{18}IN_6S$	14.92; 15.00	6.85; 7.02	15.11	6.92	71.4
XII		—	578	14.24	20	2110	$C_{19}H_{15}IN_8S_2$	20.60; 20.76	—	20.51	—	51
XIII		—	576	14.00	18	2114	$C_{19}H_{15}IN_8S_2$	20.05; 20.17	—	20.51	—	46.6
XIV		213—215	570	12.50	12	2114	$C_{19}H_{16}IN_5S_2$	13.74; 13.82	12.15; 12.64	13.80	12.64	79
XV		208—210	566	11.80	8	2120	$C_{19}H_{16}IN_5S_2$	13.11; 13.22	12.24; 12.30	13.80	12.64	68
XVI		270—272	536	6.2	15	2120	$C_{15}H_{13}N_5OS_3$	18.62; 18.91	25.48; 25.54	18.65	25.60	51
XVII		284	530	6.04	9	2114	$C_{15}H_{13}N_5OS_3$	18.31; 18.40	25.51; 25.78	18.65	25.60	68

V–IX. In the IR spectra there are strong bands in the 2100–2200 cm^{-1} region which are characteristic for asymmetric valency oscillations by the azo group.

The quaternary salts of the azides were converted into cyanine dyes by well-known methods. Products included styryls, symmetrical and asymmetrical carbocyanines, and merocyanines, X–XVII (Table 2).

The IR spectra of the cyanine dyes shows strong bands in the 2100–2200 cm^{-1} region of asymmetrical valency oscillations from the azido group (see Table 2). This confirms the fact that the azo group is preserved in cyanine dyes also.

The absorption maxima and molecular extinctions obtained by us of the dyes, and the displacement of the absorption maximum in relation to the thiacyanines without benzene substituents are presented in Table 2 [3].

It is apparent from Table 2 that introduction of the azido group onto the benzene ring of the benzthiazole group in the cyanine dye leads to a considerable displacement of the absorption maximum into the long-wave region of the spectrum. A bathochromic shift is observed for all presented thiacyanines. In addition, the insignificant deviation of dyes XIV (2 nm) and XV (1 nm) indicates that introduction of the azido group onto the benzene ring of benzthiazole has little influence on its basicity.

EXPERIMENTAL

6-Azido-2-methylbenzthiazole (I) was obtained as described in the literature [1] by the action of sodium azide on diazotized 6-amino-2-methylbenzthiazole. γ_{as} N_3 2123 cm^{-1}.

5-Azido-2-methylbenzthiazole (II) was obtained in method similar to compound I from 8.2 g (0.05 mole) of 5-amino-2-methylbenzthiazole and 3.4 g (0.05 mole) of sodium azide. Yield, 8.5 g (90%), mp 56°. Found, %: N 29.19, 29.09. Calculated for $C_8H_6N_4$, %: N 29.47. γ_{as} N_3 2120 cm^{-1}.

6-Azido-1,2-dimethylbenzimidazole (III) was obtained by the action of 3.7 g (0.07 mole) of sodium azide on 8 g (0.05 mole) of diazotized 6-amino-1,2-dimethylbenzimidazole. Yield, 7.6 g (82%), mp 66°. Found, %: N 37.60, 37.10. Calculated for $C_9H_9N_5$, %: N 37.40. γ_{as} N_3 2125 cm^{-1}.

5-Azido-2-methyl-1-phenylbenzimidazole (IV) was obtained in a similar manner from 8.8 g (0.04 mole) of 5-amino-2-methyl-1-phenylbenzimidazole and 3.7 g (0.07 mole) of sodium azide. Yield, 8.6 g (88%), mp 108–110°. Found, %: N 27.88, 27.09. Calculated for $C_{14}H_{11}N_5$, %: N 28.09. γ_{as} N_3 2100 cm^{-1}.

Quaternary salts V–VII (Table 1) were obtained by heating 0.01 mole of the corresponding azide with a fourfold quantity of methyl iodide in a sealed ampul at 60–70° for 7 hours. The salt obtained were washed free from the original azide with ether and then crystallized from ethanol or methanol by means of activated carbon.

Quaternary salts VIII and IX (Table 1) were obtained by heating 0.01 mole of azide with a tenfold quantity of ethyl iodide in a sealed ampoule at 100° for 2 hours. The original azide was first dissolved in an excess of ethyl iodide; on heating the quaternary salt of the azide was precipitated. The salt was removed by filtration from excess ethyl iodide and then crystallized from alcohol using activated carbon.

Styryls X, XI (Table 2) were obtained by heating equimolar quantities of the iodomethylates V and VI and p-dimethylamino benzaldehyde in acetic anhydride in a water bath. After cooling the precipitate was removed by filtration, and washed on a filter with hot and cold water, and then with alcohol and ether. It was crystallized from alcohol.

Symmetrical carbocyanines XII, XIII (Table 2) were obtained by heating a mixture of a quaternary salt and orthoformic ether in acetic anhydride. On the following day the residue was removed by filtration, washed well with water, and alcohol and ether. The compounds were crystallized from alcohol.

Asymmetrical carbocyanines XIV, XV (Table 2) were obtained by heating equimolar quantities of the quaternary salt of the azide with 2-(3-methyl-2-benzthiazolinyl)acetaldehyde in acetic anhydride. The residue was washed with water, alcohol, and ether. It was crystallized from alcohol.

Merocyanines XVI, XVII (Table 2) were obtained by heating equimolar quantities of the iodomethylates of the corresponding azides and acetanilidomethylene-N-ethyl rhodanine in ethyl or n-butyl alcohol in the presence of triethylamine for 30 minutes. The compounds were purified by chromatography with solutions of chloroform on aluminium oxide.

REFERENCES

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