RESEARCHES ON BENZ-AND NAPHTHAZOLES

XIX. Reaction of Benzazole Series Formazans with Bromosuccinimide*

N. P. Bednyagina, N. V. Serebryakova, and Yu. A. Rybakova

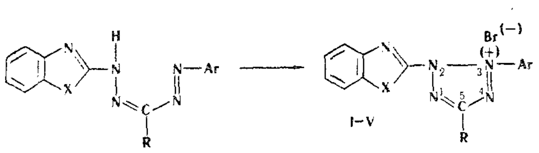
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 4, pp. 750–752, 1967

UDC 547.785.5'796.1:542.944.1:541.651.2

Bromosuccinimide converts unsymmetrical 1-(1'-alkylbenzimidazolyl)-5-aryl-3-methylformazans and 1-benzthiazolyl-5-aryl-3-methyl (or aryl)formazans to the corresponding tetrazolium salts. Symmetrical 1, 5-di(1'-benzylbenzimidazolyl-2')-3-methylformazan gives a bromoamine, which is not transformed to a tetrazolium salt, and is separated as a dihydrobromide.

One of the methods of preparing tetrazolium salts is reaction of bromosuccinimide with 1, 5-diarylformazans [1], and the same method is used to obtain tetrazolium salts from 1-thiazolyl- and 1-selenazolyl-formazans [2, 3]. A study has now been made of this reaction for a number of previously prepared unsymmetrical formazans of banzazoles [4, 5] and symmetrical 1, 5-dibenzimidazolylformazans [6].

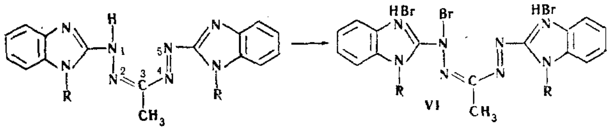
Unsymmetrical benzazolylformazans readily react with bromosuccinimide in cold chloroform. The solution changes in color from red to pale yellow, and the crystalline tetrazolium salt separates on standing (IV). The salts formed are readily soluble in water and can easily be reduced back to formazans (e.g., by hydrosulfite). These salts are stable when boiled in organic solvents able to undergo free radical bromination (toluene, acetone). Many of them decompose when kept, in the crystalline state, in air and light. Salts II-IV crystallize as hydrobromides similar to the tetrazolium salts obtained from 1-thiazolyl-5-arylformazans [2].



X = NR, S R = CH$_3$, C$_6$H$_5$ Ar = p-C$_6$H$_4$CH$_3$ and C$_6$H$_4$NO$_2$

Symmetrical 1, 5-dibenzimidazolylformazans behave differently. Thus in dimethylformamide, 1, 5-di(benzylideneimidazolyl-2')-3-methylformazan and bromosuccinimide give a yellowish-brown crystalline substance, which analysis shows to contain three bromine atoms per formazan molecule, and when boiled with toluene it (VI) can brominate it up to the benzyl bromide stage. It can be a bromoamine perbromide or dihydrobromide. Tetrazolium perbromides, described for 1-selenazolyl-3-arylformazans [3], can also brominate acetone, being themselves thereby converted to a tetrazolim bromide. Unlike them, compound VI is converted by boiling with toluene into the hydrobromide of the starting formazan. When substance VI is reprecipitated from dimethylformamide with ether, it loses hydrogen bromide and gives an unstable substance with one atom of bromine per molecule, which can also brominate toluene.

These facts make it possible to assign, with a high degree of probability, a structure of a bromoamine dihydrobromide to compound VI.



R = CH$_2$C$_6$H$_5$

Possibly in the treatment with bromosuccinimide, the dye azomethine chain assumed a configuration excluding approach of nitrogen atoms 1 and 5 to one another by a distance equal to a single bond length (an example of steric hindrance of that type is described [7] in the preparation of indazolium salts). Because of their amide character, either of the nitrogen atoms at positions 1 and 5 have a rather depressed basicity, and cannot acquire a cationic charge. In both cases the dye's conjugated chain is interrupted by bromine at position 1. Due to this the imidazole ring becomes independent, and the compound forms a dibromide (while formazan forms a monohydrobromide with a cyanine structure [8]). In agreement with this is the observed enhancement of the color by 130 mm on pas-

2-Benzazolyl-3-aryl-5-methyl(phenyl)tetrazolium Bromides

No.	X	R	Ar	Mp, °C	Formula	Found, %		Calculated, %		Yield %
						Br	N	Br	N	
I	N—CH$_3$	CH$_3$	C$_6$H$_4$CH$_3$	133—134	C$_{17}$H$_{17}$BrN$_6$	20,72	22.33	20.74	21.81	90
II	N—CH$_2$C$_6$H$_5$	CH$_3$	C$_6$H$_4$CH$_3$	88—100	C$_{23}$H$_{21}$BrN$_6$ · HBr	29,81	15.02	29.47	15.49	70—80
III	N—CH$_2$C$_6$H$_5$	CH$_3$	C$_6$H$_4$NO$_2$	148—149	C$_{22}$H$_{18}$BrN$_7$O$_2$ · · HBr	27.62	16.62	27.89	17.11	42
IV	S	CH$_3$	C$_6$H$_4$CH$_3$	128—129	C$_{16}$H$_{14}$BrN$_5$S · · 2HBr	23.62	12.80	23.24	12.73	40
V	S	C$_6$H$_5$	C$_6$H$_4$CH$_3$	196—197	C$_{21}$H$_{16}$N$_5$BrS	17.95	14.61	17.75	15.55	36—40

---

*For Part XVIII see [9].

sing from formazan to bromoamine (λ_{max} 536 and 405 mm).

EXPERIMENTAL

2-(1'Benzylbenzimidazolyl-2')-3-p-tolyl-5-methyltetrazolium bromide (II). A $CHCl_3$ solution of bromosuccinimide (3 mM) was added to a warm solution of 1 mM formazan in chloroform, until a permanent pale yellow color appeared. On dilution with ether a light yellow crystalline precipitate of tetrazolium salt II came down. Salts I, III, IV, and V were prepared in the same way.

1,5-Di(1'-benzylbenzimidazolyl-2')-3-methylformazyl bromide (VI). 1 mM 1,5-Di(1'-benzylbenzimidazolyl)-3-methylformazan was dissolved in 7 ml dimethylformamide. A solution of 4 mM bromosuccinimide in 5 ml glacial AcOH was added to it at room temperature, and the color of the solution changed from violet to reddish brown. The products were diluted with 50 ml dry ether. After some hours clusters of brownish orange crystals had grown on the bottom and walls of the flask, yield 60%, mp 155°-158° C (with explosion). The compound was insoluble in water, but soluble in $CHCl_3$ and benzene. Acetone, ethanol and toluene solutions rapidly turned violet on boiling or adding alkali. Found: C 48.72; H 3.63; Br 32.27; N 14.97%, calculated for $C_{30}H_{25}BrN_8 \cdot 2HBr$: C 48.81; H 3.67; Br 32.83; N 15.13%.

1 mM Compound VI was refluxed for 1 hr with 10 ml toluene. The solution turned from pale brown to dark violet, and acquired an odor of benzyl bromide. On cooling a precipitate of the starting formazan came down, yield 90%. Three consecutive precipitations of compound VI from dimethylformamide with dry ether gave dark brown crystals mp 145-146 (decomp). Found: Br 14.96; N 19.03%, calculated for $C_{30}H_{25}BrN_8$: Br 13.86; N 19.41%.

REFERENCES

1. R. Kuhn and W. Münzig, Chem. Ber., **86**, 858, 1953.
2. H. Beyer and Th. Pyl, Chem. Ber., **87**, 1505, 1954.
3. E. Bulka, G. Rodekirsh, and H. Beyer, Chem. Ber., **95**, 658, 1962.
4. Yu. A. Rybakova and N. P. Bednyagina, KhGS [Chemistry of Heterocyclic Compounds], 421, 1965.
5. N. P. Bednyagina, N. V. Serebryakova, and G. N. Lipunova, KhGS [Chemistry of Heterocyclic Compounds], 342, 1967.
6. N. P. Bednyagina, G. N. Tyurenkova, and Yu. A. Rybakova, ZhOKh, **34**, 1288, 1964.
7. R. Kuhn and W. Münzig, Chem. Ber., **85**, 29, 1952.
8. N. P. Bednyagina, and Yu. A. Rybakova, KhGS [Chemistry of Heterocyclic Compounds], collection: 1, 1967.

8 December 1965

Kirov Urals Polytechnic Institute,
Sverdlovsk