and the chloroform extract was dried with calcium chloride. The chloroform was evaporated, and the solid precipitate was crystallized from chloroform.

2-Imino-3-methyl-5-benzylidenethiazolidin-4-one (V). A mixture of 2.20 g (0.017 mole) of 2-imino-3-methylthiazolidin-4-one, 2.21 g (0.02 mole] of benzaldehyde, three to four drops of pyridine, and 30 ml of absolute ethanol was refluxed for 45 min, after which the undissolved starting compound was removed by filtration, and the filtrate was evaporated to precipitate the product, which was crystallized from ethanol.

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SYNTHESIS AND STUDY OF THE PROPERTIES OF TETRAZOLES, AZIDES, TRIAZENES, AND AZO COMPOUNDS OF THE THIADIAZOLE SERIES

L. I. Skripnik, I. A. Ol'shevskaya, L. N. Fedorova, N. I. Rybalka, and N. F. Plaksienko

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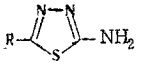
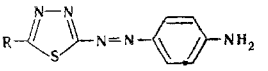
Azo compounds and bistriazenes were obtained by diazo coupling of diazotized 5-amino-2-R-1,3,4-thiadiazoles; tetrazolo[4,5-b]-1,3,4-thiadiazoles, to which azido–tetrazole tautomerism is peculiar, were obtained by replacement of the diazo group by an azido group. The structures of the products were confirmed by their IR and UV spectra.

Research on the synthesis of azides, tetrazoles, triazenes, and azo compounds on the basis of 5-amino-2-R-1,3,4-thiadiazoles with the general formula

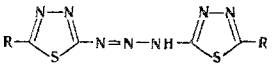


was carried out in order to search for efficient stabilizers of silver halide photographic emulsions, as well as new light-sensitive and photosemiconductor materials.

5-Amino-2-R-1,3,4-thiadiazoles have the properties of aromatic amines. Their diazotization can be realized in hydrochloric acid with an aqueous solution of sodium nitrite or in a mixture of concentrated propionic and acetic acids or in orthophosphoric acid with nitrosylsulfuric acid. The corresponding azo compounds Ia-e (Table 1) are formed by coupling the resulting diazonium salts with aniline hydrochloride in an aqueous medium (pH 4-5); diazotization in the presence of excess starting amine leads to the formation of triazenes IIa-e (Table 1):



I a-e



II a-e

T. G. Shevchenko Kiev State University, Kiev 252017. Vinnitsa Polytechnic Institute, Vinnitsa 286021. Vinnitsa Medical Institute, Vinnitsa 286018.

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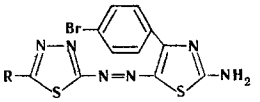
TABLE 1. Azo Compounds and Triazenes of the 1,3,4-Thiadiazole Series

Compound	R	mp, °C	λ_{max}, nm (in ethanol)	N found, %	Empirical formula	N calc., %	Yield, %
Ia	H	81	505	33,8	$C_8H_7N_5S$	34,1	31
Ib	CH_3	84	480	31,6	$C_9H_9N_5S$	31,9	32
Ic	C_2H_5	90	486	30,2	$C_{10}H_{11}N_5S$	30,0	33
Id	p-C_3H_7	103	490	28,6	$C_{11}H_{13}N_5S$	28,3	32
Ie	C_6H_5	108	510	24,5	$C_{14}H_{11}N_5S$	24,9	51
IIa	H	89—90[a]	320	46,1	$C_4H_8N_7S_2$	45,9	43
IIb	CH_3	111—112[a]	333	40,9	$C_6H_7N_7S_2$	40,6	37
IIc	C_2H_5	93—94[a]	342	36,8	$C_8H_{11}N_7S_2$	36,4	31
IId	p-C_3H_7	95—96[a]	346	33,0	$C_{10}H_{15}N_7S_2$	32,9	38
IIe	C_6H_5	137—138[a]	400	27,2	$C_{16}H_{11}N_7S_2$	26,8	45
IIIa	H	93—94[b]	525	23,2	$C_{11}H_7BrN_6S_2$	23,3	32
IIIb	CH_3	155—156[c]	495	22,5	$C_{12}H_9BrN_6S_2$	22,6	42
IIIc	C_2H_5	111—112[c]	502	21,8	$C_{13}H_{11}BrN_6S_2$	21,9	44
IIId	p-C_3H_7	124—125[c]	510	20,4	$C_{14}H_{13}BrN_6S_2$	20,5	35
IIIe	C_6H_5	168—169[c]	520	19,2	$C_{17}H_{11}BrN_6S_2$	19,4	38

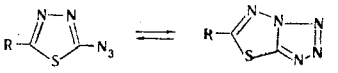
[a] With decomposition. [b] From acetone. [c] From ethanol.

Azo compounds IIIa-e (Table 1) are also formed by coupling a diazonium salt with a 2-aminothiazole that has a free 5 position:



III a-e

When the 1,3,4-thiadiazole diazonium salts are treated with sodium azide in an acidic medium by the method in [1], the diazo group is replaced by an azido group to give IVa-e, to which azido-tetrazole tautomerism [2] is peculiar (Table 2):



IV a-e

a R=H, b R=CH_3, c R=C_2H_5, d R=n-C_3H_7, e R=C_6H_5

We obtained IVa for the first time in this research; according to the data in [3], IVb-e are tetrazoles, and the substances that we obtained have the same melting points.

We undertook special studies in order to ascertain the true structures of these compounds (Table 2). According to [4], azides can be identified from the intense band in the IR spectrum that corresponds to the asymmetrical stretching vibrations of the azido group at 2100-2200 cm^{-1}, while tetrazoles can be identified from the band at 950-1250 cm^{-1}, which corresponds to the skeletal vibrations of the tetrazole ring [5]. It is apparent from Table 2 that IVa-c exist in the crystalline state in the form of tetrazolo[4,5-b]-1,3,4-thiadiazoles, while both tautomers of IVb, c are present in solution in chloroform, and only the azide form of the compounds is present in carbon tetrachloride. Compound IVd has the azide structure in both the individual state and in solutions, while IVe always exists in the azide $\rightleftarrows$ tetrazole tautomeric equilibrium. The phenomenon of azide $\rightleftarrows$ tetrazole equilibrium is consequently peculiar to tetrazolo[4,5-b]-1,3,4-thiadiazoles, just as it is to other condensed tetrazoles [6].

In addition to their theoretical value, the synthesized azides, triazenes, and azo compounds are also of practical interest. They can be used as light-sensitive materials in unusual silverless photography [7] and as sensitizers of silver halide photoemulsions.

TABLE 2. Azido-1,3,4-thiadiazoles

Compound	Decomposition temp. (from ethanol)	N found, %	Empirical formula	N calc., %	UV spectrum, λ_{max}, nm (log ε)	IR spectrum, cm^{-1} In KBr		In $CHCl_3$		In CCl_4		Yield, %
						N_3	tetrazole ring	N_3	tetrazole ring	N_3	tetrazole ring	
IVa	93—94	54,7	C_2HN_5S	55,1	242 (3,6721)	—	960 1450	-	940 1350	—	940 1450	43
IVb	92—93	48,9	$C_3H_3N_5S$	49,0	247 (3,7220)	—	960 1340 1450	2135 s	940 1340	2135 s	—	52
IVc	45—46	44,6	$C_4H_5N_5S$	45,1	247 (3,7931)	-	960 1380 1440	2133 s	960 1380	2135 s	—	53
IVd	bp 77 (1 mm)	39,1	$C_5H_8N_5S$	39,3	245 (3,7093)	2135s	—	2135 s	—	2135 s	—	65
IVe	103—104	33,8	$C_8H_5N_5S$	34,5	287 (4,1903)	2135 w	960 1330 1440	2136 m	980 1390	2134 m	960 1380 1440	60

EXPERIMENTAL

The electronic absorption spectra of the compounds were recorded with an SF-10 spectrophotometer. The IR spectra were recorded with a UR-10 spectrometer.

The starting 2-amino-1,3,4-thiadiazole and 5-amino-2-alkyl-1,3,4-thiadiazole were obtained by the method in [8], and 5-amino-2-phenyl-1,3,4-thiadiazole was obtained by the method in [9].

5-(p-Aminophenylazo)-1,3,4-thiadiazoles (Ia-e). A 5-mmole sample of 5-amino-1,3,4-thiadiazole was dissolved in 120 ml of concentrated HCl by heating on a water bath, and the solution was cooled to −5°C and treated with a solution of 5 mmole of sodium nitrite in 6.5 ml of water. The diazotization was monitored from the presence of free nitrous acid in the diazonium solution. The resulting diazonium yellow-diazonium solution was used in the diazo coupling reaction. For this, 5 mmole of a solution of aniline hydrochloride and 1.7 ml of concentrated HCl in 4 ml of water and a solution of 46 g of sodium acetate in 100 g of water were added to the diazonium solution while maintaining the pH of the solution at no higher than five. The reaction mixture was allowed to stand for 10 min in ice and for 20 min in air, after which the red precipitate was removed by filtration, washed successively with cold and hot water, and purified by crystallization from alcohol (Table 1).

Bis(2-thiadiazolyl)triazenes (IIa-e). A 5-mmole sample of 5-amino-1,3,4-thiadiazole was dissolved by heating in 50 ml of concentrated HCl on a water bath, after which the solution was cooled to −5°C, and a solution of 2.5 mmole of sodium nitrite in 3.5 ml of water was added dropwise with stirring. The resulting bright-yellow diazonium solution was allowed to stand in ice for 15 min, after which 100 ml of a saturated solution of sodium acetate (pH 5) was added. The precipitate was removed by filtration, washed with benzene, and purified by crystallization from toluene (Table 1).

2-[2-Amino-4-(p-bromophenyl)-5-thiadiazolyazo][-1,3,4-thiadiazoles (IIIa-c). A 10-mmole sample of finely ground sodium nitrite was added with cooling to 5 ml of 98% sulfuric acid, after which a mixture of propionic and acetic acids (3:17) was added in small portions, during which the temperature was raised to 60°C. The temperature was lowered to 24°C, and 10 mmole of 5-amino-1,3,4-thiadiazole was added at 24°C in the course of 25 min. A 2.4-mmole sample of 2-amino-4-(p-bromophenyl)thiazole was dissolved in the minimum amount of alcohol, crystalline sodium acetate was added, and the diazonium solution was added slowly at pH 5-6. The resulting precipitate was removed by filtration, washed on the filter with water, alcohol, and ether, and crystallized from acetone. Red-brown crystals of the azo compounds (Table 1) were isolated by slow crystallization.

Azido-1,3,4-thiadiazoles (IVa-e). A 10-mmole sample of 5-amino-1,3,4-thiadiazole in a mixture of 1.5 ml of propionic acid and 8.5 ml of acetic acid or in 10 ml of orthophosphoric acid was added slowly to nitrosylsulfuric acid prepared from 30 mmole of ground sodium nitrite and 15 ml of concentrated H_2SO_4, and the mixture was maintained at from 24 to 42°C in the course of 0.5 h. It was then cooled, 20-30 mmole (a certain excess) of sodium azide in the minimum amount of water was added with stirring, and the mixture was made alkaline with respect to litmus with a 30% solution of alkali. The precipitated salts were removed by filtration, and the resulting azide or tetrazole was extracted from the filtrate with organic solvents (benzene and chloroform). The product was purified after the solvent was removed (Table 2).

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SYNTHESIS AND STEREOCHEMISTRY OF 1-ALKYL-2-METHOXYCARBONYL-3-PHENYLAZIRIDINES

A. V. Eremeev and V. G. Semenikhina

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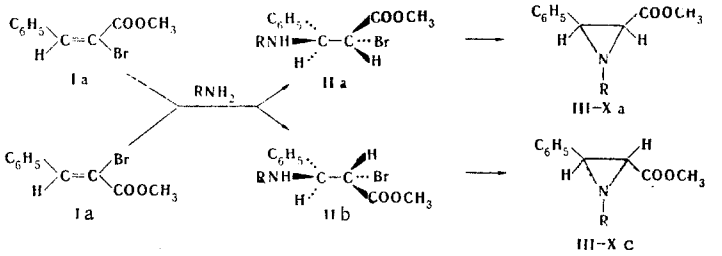
Mixtures of cis- and trans-1-alkyl-2-methoxycarbonyl-3-phenylaziridines are formed in the reaction of methyl α-bromocinnmate with excess amine, amino alcohol, and amino acid methyl ester hydrochloride. The ratios of the isomers depend on the solvent used.

The reactions of α,β-dibromo ketones, as well as α,β-dibromo carboxylates, with excess amine lead to aroylaziridines and aziridine-carboxylates [1-7]. In addition, it is known that the only product in the reaction of methyl erythro-α,β-dibromohydrocinnamate or methyl esters of cis- and trans-α-bromocinnamic acids with benzylamine is cis-1-benzyl-2-methoxycarbonyl-3-phenylaziridine [8].

The present paper is devoted to the synthesis and study of the stereochemistry of a number of 1-alkyl-2-methoxycarbonyl-3-phenylaziridines.

1-Alkyl-2-methoxycarbonyl-3-phenylaziridines (IIIa,b-Xa,b, Table 1) were obtained by the action of excess amine, amino alcohol, or amino acid methyl ester hydrochloride on a methanol or benzene solution of methyl α-bromocinnamate, which is produced in the form of a mixture of approximately equal amounts of stereoisomers (Ia, b) as a result of dehydrobromination of the α,β-dibromohydrocinnamic acid ester [8].



It was established on the basis of the PMR spectroscopic data that the trans isomers are formed along with cis-1-alkyl-2-methoxycarbonyl-3-phenylaziridines and that their ratios depend on the solvent used. Thus, the main product in methanol is the cis isomer (Table 1). In an aprotic solvent (benzene) the amount of the trans isomer increases to 42-45%, as demonstrated in the case of VI-VIII. The presence of cis and trans isomers in the reaction mixture can be explained by the formation of intermediate methyl dl-erythro-

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.

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