THIAZOLOCYANINES

XIV.* AZOLOCYANINES FROM 3,5-DIARYLTHIAZOLIUM AND 3,5-DIARYLOXAZOLIUM SALTS

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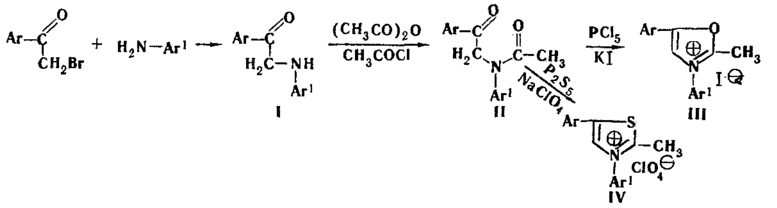
A method has been developed for the preparation of 3,5-diarylthiazolium and 3,5-diaryloxazolium salts, and cyanine dyes have been synthesized from these.

Thiazolocyanines with aryl radicals attached simultaneously to carbon and nitrogen atoms of the thiazole nucleus have not hitherto been obtained. Nevertheless, it is known that the introduction of aryl residues into the thiazole nuclei of thiazolocyanines and into the oxazole nuclei of oxazolocyanines imparts to them the property of component-stability, a property necessary for their use as photosensitizers in color films. Consequently, the development of methods for the synthesis of 3,5-diarylthiazolium and 3,5-diaryloxazolium salts and cyanine dyes from them is of some practical, as well as scientific, interest.

The synthesis of the azolium salts (III,IV) was effected by the reaction of bromomethyl aryl ketones with aromatic primary amines, the subsequent acetylation of the arylaminomethyl aryl ketones (I) formed, and the cyclization of their acetyl derivatives (II). Cyclization in the presence of phosphorus pentasulfide led to 3,5-diarylthiazolium salts (III) and cyclization in the presence of phosphorus pentachloride led to 3,5-diaryloxazolium salts (IV). Information on compounds I-IV is given in Table 1.



The azolium salts III and IV were then converted into cyanine dyes – monomethinecyanines and dimethinemerocyanines. As the figures given in Tables 2 and 3 show, a change in the nature of aryl radicals both on the nitrogen atom and in position 5 has almost no effect on the absorption maximum of the dyes of the types studied. Practically no differences in absorption are observed, either, in a comparison with the absorption maxima of the analogous dyes with ethyl groups on the nitrogen atoms.

EXPERIMENTAL

Arylaminomethyl Aryl Ketones (I). With gentle heating, 0.05 mole of a bromomethyl aryl ketone (ω-bromoacetophenone, p-methoxy-ω-bromoacetophenone) was dissolved in 40 ml of ethanol and 0.05 mole of an aromatic amine (aniline, β-naphthylamine, anisidine) was added. The mixture was stirred at room temperature for 1 hr. The precipitate was separated off, washed with ethanol and water, and crystallized from ethanol.

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*For Communication XIII, see [1].

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TABLE 1. Azolium Salts and Intermediates in Their Synthesis*

Compound	mp °C	Empirical formula	Element	Found, %	Calculated, %	Yield, %
ω-(β-Naphthylamino)acetophenone	148—149	$C_{18}H_{15}NO$	C H	82,21 5,67	82,75 5,76	Quant.
ω-Anilino-p-methoxyacetophenone	106—108	$C_{15}H_{15}NO_2$	C H	74,93 6,23	74,68 6,22	63
ω-(p-Methoxyphenylamino)acetophenone	178—180†					
ω-[Acetyl(phenyl)amino]acetophenone	131	$C_{16}H_{15}NO_2$	C H	75,20 6.05	75,89 5,92	85
ω-[Acetyl(p-methoxyphenyl)amino]acetophenone	82—84	$C_{17}H_{17}NO_3$	C H	71,68 6.20	72,08 6,01	82
ω-[Acetyl(phenyl)amino]-p-methoxyacetophenone	111—112	$C_{17}H_{17}NO_3$	C H	71,89 6,09	72,08 6,01	65
ω-[Acetyl(β-naphthyl)amino]acetophenone	86	$C_{20}H_{17}NO_2$	C H	79,27 5,86	79,21 5.61	85
2-Methyl-3,5-diphenyloxazolium iodide	232—235	$C_{16}H_{14}JNO$	I	35,31	34,99	85
2-Methyl-3-(β-naphthyl)-5-phenyloxazolium iodide	220—222	$C_{20}H_{16}JNO$	I	30,71	30,75	44
3-(p-Methoxyphenyl)-2-methyl-5-phenyloxazolium iodide	215—217	$C_{17}H_{16}JNO_2$	I	32,01	32,32	70
2-Methyl-3,5-diphenylthiazolium perchlorate	197—199	$C_{16}H_{14}ClNO_4S$	S	9,17	9,10	51
2-Methyl-3-(β-naphthyl)-5-phenylthiazolium perchlorate	223	$C_{20}H_{16}ClNO_4S$	S	7,90	7,97	38
5-(p-Methoxyphenyl)-2-methyl-3-phenylthiazolium perchlorate	183—184	$C_{17}H_{16}ClNO_4S$	S	8,87	8,36	54

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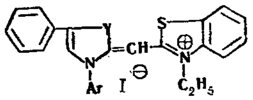
*Phenylaminoacetophenone has been described in the literature [2].

† The substance was identified in the form of the acetyl derivative.

TABLE 2. 2-[(3-Aryl-5-phenyl-4-thiazolin-2-ylidene)methyl]-3-ethylbenzothiazolium Iodides



Ar	Y	mp °C	λ_{max} nm*	Empirical formula	Element	Found, %	Calculated, %	Yield, %
Phenyl	O	281—282	412	$C_{25}H_{21}IN_2OS$	I	24,17 23,92	24,24	48
β-Naphthyl	O	271—273	412	$C_{29}H_{23}IN_2OS$	I	21,76 22,02	22,14	33
p-Methoxyphenyl	O	273—274	412	$C_{29}H_{23}IN_2O_2S$	I	22,56 22,49	22,74	50
Phenyl†	S	274—275	442	$C_{25}H_{21}ClN_2O_4S_2$	S	12,70 12,55	12,49	77

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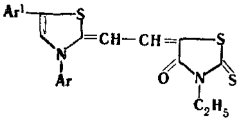
*The analogous dyes with Y = O and an ethyl group on the nitrogen atom have λ_{max} 412, and those with Y = S have λ_{max} 437 nm.

† In the form of the perchlorate.

Acetyl(arylaminomethyl) Aryl Ketones (II). A mixture of 0.05 mole of the hydrochloride of a compound I, 0.05 mole of acetyl chloride, and 60 ml of acetic anhydride was boiled for 3 hr. The acetic anhydride was driven off in vacuum, and the residue was triturated with ethanol, filtered off, and recrystallized from ethanol or ligroin (see Table 1).

3,5-Diaryloxazolium Salts (III). 0.03 mole of a compound II was triturated with 0.05 mole of phosphorus pentachloride. The mixture melted by spontaneous heating and then solidified, after which it was ground, treated with water, and extracted with benzene; the aqueous layer was then treated with 20% potassium iodide solution. The precipitate was washed with acetone.

TABLE 3. 5-[3,5-Diarylthiazolidin-2-ylideneethylidene]-3-ethyl-2-thioxothiazolidin-4-ones



Ar	Ar′	mp °C	λ_{max} nm	Empirical formula	S, %		Yield, %
					Found	Calc.	
Phenyl	Phenyl	212—214	555	$C_{22}H_{18}N_2OS_3$	22,58; 22,75	22,75	14
Phenyl	p-Methoxyphenyl	235	562	$C_{23}H_{20}N_2O_2S_3$	20,95; 20,81	21,24	18
β-Naphthyl	Phenyl	187	558	$C_{26}H_{20}N_2OS_3$	19,73; 19,89	20,34	30

3,5-Diarylthiazolium Salts (IV). 5 g of a compound II was triturated with 5 g of phosphorus pentasulfide and the mixture was heated at 140-150°C in a wide test-tube with stirring for 30 min. The melt was extracted several times with hot water, and the extracts were combined, evaporated to small volume, and treated with a solution of sodium perchlorate. The precipitate was dissolved in acetone and reprecipitated with ether (see Table 1).

Monomethinecyanines. Equimolecular amounts (0.002 mole each) of a 3,5-diaryl-2-methylazolium salt and the ethyl tosylate derivative of 2-methylthiobenzothiazole in 5 ml of anhydrous ethanol in the presence of 0.002 mole of triethylamine were heated to the boil for 45 min. The precipitate was recrystallized from ethanol (see Table 2).

Dimethinemerocyanines. Equimolecular amounts (0.001 mole each) of aryl perchlorate derivatives of 5-aryl-2-(ω-anilinovinyl)thiazoles, 3-ethylrhodanine, triethylamine (+10% excess) and acetic anhydride in 4 ml of absolute ethanol were heated to the boil for 45 min. The dyes were isolated by the addition of water and chromatographed in chloroform solution on alumina and were then crystallized from ethanol or a mixture of ethanol and nitromethane (see Table 3).

LITERATURE CITED

1. E. D. Sych and L. P. Umanskaya, Ukr. Khim. Zh., 34, 604 (1968).
2. A. Bischler, Ber., 25, 2865 (1892).