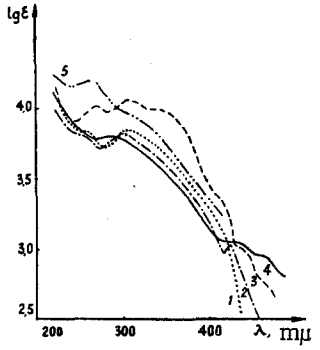

UV spectra: 1) p-chlorobenzylidenethiazane-thione; 2) 5-benzylidenethiazanedithione; 3) 5-p-nitrobenzylidenethiazanedithione; 4) 5-veratrylidenethiazanedithione; 5) 5-p-dimethylaminobenzylidene-3-p-ethoxyphenylthiazanedithione.

Experimental

Condensing thiazane-2,4-dithiones with aldehydes. A mixture of 10-20 mmole thiazane-2,4-dithione, 15-20 mmole aromatic aldehyde, 10-20 mmole fused NaOAc, and 10-15 ml glacial acetic acid was refluxed for 2.5-4 hr in a flask. Precipitation from the initially clear solution was observed only in the condensation with p-nitrobenzaldehyde. Next the reaction mixture was diluted with water, or else that was done after distilling off part of the solvent, the precipitate filtered off, and purified by recrystallization from EtOH and AcOH, as well as by washing with ether and dioxane.

To prepare 5-p-dimethylaminobenzylidene-3-p-ethoxyphenylthiazane-2,4-dithione, a mixture of 3.28 mmole 3-p-ethoxyphenylthiazane-2,4-dione, 3.49 mmole p-dimethylaminobenzaldehyde, and 10 ml glacial acetic acid was refluxed for 1 hr, and then evaporated in air almost to dryness. The residue was washed with ether, water, and boiling EtOH.

The UV spectra of the compounds investigated were determined in EtOH solution, using an SF-4 spectrophotometer. The IR spectra were determined with the compounds tabletted with KBr, using a UR-10 spectrophotometer.

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DIRECT N-ARYLATION OF 5-MEMBERED HETEROCYCLIC NITROGEN RINGS

III. Synthesis of N-Arylimidazoles*

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 1, pp. 143-145, 1966

Ring-substituted bromoaryl derivatives are used to arylate imidazole at the NH group.

Continuing our researches on the direct N-arylation of nitrogen ring compounds [1, 2], we have synthesized 1-arylimidazoles with various substituents (halogen atom, formyl, acetyl, methoxy, and dimenthylamino group) in the aryl group. The reaction was carried out by reacting the bromoaryls with imidazole under the previously described conditions [2].

The presence of an acetyl or formyl group para to the bromine enables the reaction time to be sharply cut. Thus only 13 hours heating gives a 65% yield of p-(N-imidazolyl) acetophenone. Because of possible side reactions [see 3] during formylation, cutting reaction time favorably affects the arylation product yield. Cutting the times from 30 to 18 hr raises the yield of p-(N-imidazolyl) benzaldehyde from 8 to 30%.

The N-arylimidazoles obtained contain reactive groups, and they can be changed further at the aryl group. Thus heating the methoxy derivatives with hydrobromic acid is a route to N-hydroxyphenylimidazoles.

* For Part II see [2].

Synthesis of 1-Arylimidazoles

Aryl group in the arylimidazole	Mp, °C (solvent for crystallization)	Formula	Found, %		Calculated, %		Yield, %	Derivatives						
			C	H	C	H		nature	Mp, °C (solvent for crystallization)	Formula	Found, %		Calculated, %	
											C	H	C	H
o-Methoxyphenyl	bp . 98° (2 mm	$C_{10}H_{10}N_2O$	68.84	5.89	68.95	5.79	50	Picrate	164—165 EtOH		47.58	3.22	47.65	3.25
m-Methoxyphenyl	bp . 165° (5 mm						58	Picrate	148—149 H_2O	$C_{16}H_{13}N_5O_8$	47.50	3.31	47.65	3.25
p-Methoxyphenyl	67—68 H_2O		68.87	5.80	68.95	5.79	60	Picrate	163 EtOH		47.89	3.36	47.65	3.25
p-Bromophenyl	121—122 H_2O-EtOH	$C_9H_7BrN_2$	48.38	3.21	48.46	3.16	45	Hydrochloride	205—206 EtOH + Et_2O	$C_{10}H_{10}N_2O$. . HCl. H_2O[a]	52.53	5.71	52.52	5.73
p-Dimethylaminophenyl[b]							47	Picrate	201—202 EtOH	$C_{17}H_{16}N_6O_7$	49.12	3.95	49.04	3.87
p-Formylphenyl	149—150 H_2O	$C_{10}H_8N_2O$	69.74	4.71	69.75	4.68	30	2,4-dinitrophenylhydrazone	276—277 pyridine	$C_{16}H_{12}N_6O_4$	54.45	3.55	54.55	3.43
p-Acetophenyl	118—119 H_2O-EtOH	$C_{11}H_{10}N_2O$	71.04	5.38	70.95	5.41	65	Picrate	181—182 EtOH	$C_{17}H_{13}N_5O_8$	50.29	3.15	50.37	3.16
								Semicarbazone	232 H_2O-EtOH	$C_{12}H_{13}N_5O$	59.10	5.30	59.25	5.39
o-Hydroxyphenyl[c]	227—228 EtOH		67.26	5.12	67.47	5.03	70	m-Nitrophenyldiazonium coupling product	239—240 pyridine-H_2O	$C_{15}H_{11}N_5O_3$	58.61	3.63	58.57	3.58
m-Hydroxyphenyl[c]	173 H_2O	$C_9H_8N_2O$	67.33	5.30	67.47	5.03	98							
p-Hydroxyphenyl[c]	199—200 H_2O		67.20	5.30	67.47	5.03	92							

a) Found, %: H_2O 8.20. Calculated, %: 7.88.

b) Compound rapidly oxidizes in air, isolated as its picrate.

c) Obtained by dealkylating methoxyphenylimidazole.

Experimental

A mixture of 0.1 mole imidazole, 0.15 mole aryl bromide, 13 g powdered K_2CO_3, and 0.6 g cuprous bromide was refluxed for 30 hr, cooled, filtered, the filtrate made acid, the nitrobenzene steam-distilled off, and the solution left neutralized. The N-arylimidazole base was extracted with $CHCl_3$, and purified by distilling under reduced pressure, or by recrystallization (table).

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PYRIMIDINES

VI. Synthesis and Some Reactions of 2-Diazoacetyl-4, 6-diphenylpyrimidine*

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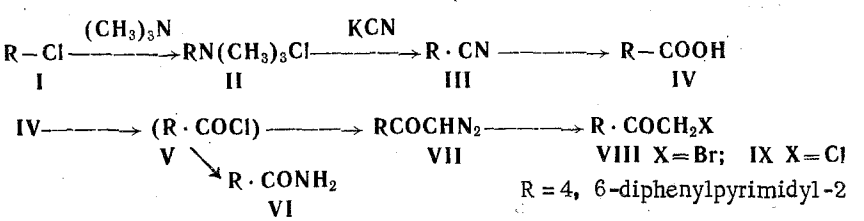
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 1, pp. 145-148, 1966

2-Diazoacetyl-4, 6-diphenylpyrimidine is prepared from 2-chloro-4, 6-diphenylpyrimidine via the nitrile and the corresponding acid, and it is readily converted to 2-bromoacetyl and 2-chloroacetyl-4, 6-diphenylpyrimidine. It was not possible to bring about the Wolff reaction.

Diazoketones are quite reactive compounds, and are often used as starting materials for synthesizing various compounds. However, only a few diazoketones of the pyrimidine series are known, and they all have the grouping $COCHN_2$ at position 4 or 5 [2, 3]. The literature does not contain any discussion of the problem of preparing 2-diazoacetylpyrimidines, or of their reactions.

It was of interest to investigate the possibility of obtaining 2-diazoacetylpyrimidines from the readily accessible 2-hydroxy derivatives, convertible in high yield to 2-chloropyrimidines [4]. Usually diazoketones are prepared by reacting acid chlorides with diazomethane. We have synthesized 4, 6-diphenylpyrimidine-2-carboxylic acid (IV) from 2-chloro-4, 6-diphenylpyrimidine (I) in the way described in [5].



The acid chloride can be prepared by treating acid IV with thionyl chloride or phosphorus pentachloride. It is unnecessary to isolate the acid chloride V for the further reactions. Its formation can be proved, and its quality assessed, by treating the impure acid chloride V with aqueous ammonia, to give 4, 6-diphenylpyrimidine-2-carboxamide (VI) in over 90% yield, so here V is pure enough for preparative purposes. Such a product was reacted with diazomethane to give 2-diazoacetylpyrimidine (VII). However, it did not prove possible to obtain VII analytically pure, but it was quite pure enough for synthetic work, judging by its reactions with hydrochloric and hydrobromic acids. In that way the hitherto unknown 2-bromoacetyl (VIII) and 2-chloroacetyl-4, 6-diphenylpyrimidine (IX) were synthesized.

One of the most interesting reactions of diazoketones, the Wolff rearrangement, gives unsatisfactory yields or does

* For Part V see [12].