CONDENSATION OF 2-PYRIDINEALDEHYDE METHIODIDE WITH ALKYL IODIDE DERIVATIVES OF HETEROCYCLIC BASES

II. Synthesis of 1-(N-Methyl-2-pyridyl)-2-(N-alkylheteryl)ethylene Diiodides*

B. P. Lugovkin

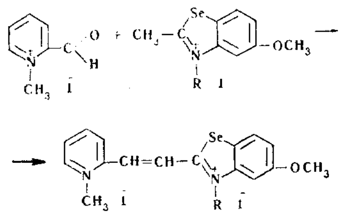
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 6, pp. 1071–1074, 1968

UDC 547.821.3'789.6.8.07:542.953

The crotonic condensation of 2-pyridinealdehyde methiodide with alkyl iodide derivatives of heterocycles with active methyl groups has been studied. 1-(N-Methyl-2-pyridyl)-2-(N-alkylheteryl)ethylene diiodides have been synthesized.

In the preceding article [1], it was found that 1-(2-pyridyl)-2-heteryl-ethylenes add methyl iodide with difficulty, while in heterocyclic systems with benzothiazole and benzoselenazole radicals, methyl iodide quaternizes the nitrogen atom of only the pyridine ring. In development of these investigations, the condensation of 2-pyridinealdehyde methiodide with alkyl iodide derivatives of heterocyclic compounds containing active methyl groups has been studied. The reaction has been carried out with the methiodides and ethiodides of: quinaldine, 2, 6-dimethylquinoline, which contains an active α-methyl group [2], lepidine, 2-methylbenzothiazole, 2-methylbenzoselenazole, 5-methoxy-2-methylbenzothiazole, and 5-methoxy-2-methylbenzoselenazole.

The products of the crotonic condensation which takes place when the components are heated in glacial acetic acid are 1-(N-methyl-2-pyridyl)-2-(N-alkylheteryl)ethylene diiodides (I–XIV).



XIII, XIV

XIII R = CH_3, XIV R = C_2H_5

The quaternary compounds obtained are colored crystalline substances stable on storage. They dissolve on heating in water, methanol, and ethanol, and with difficulty in glacial acetic acid; the methyl ethyl iodides are somewhat more soluble.

The characteristics and conditions for the synthesis of the diiodides are given in the table.

The UV spectra of ethanolic solutions of compounds **I, III**, V, VII, **IX, XI**, and **XIII** show the absorption band of a —CH=CH— group in the 300–400 nm region with a maximum at 310–350 nm.

In the reaction of 2-pyridinealdehyde ethiodide (mp 155° C) with the ethiodides of heterocycles with an active methyl group (benzothiazoles and 5-methoxybenzoselenazoles) it was impossible to isolate 1-(N-ethyl-2-pyridyl)-2-(N-ethyl-2-heteryl)ethylene diiodides.

EXPERIMENTAL

Synthesis of the 1-(N-methyl-2-pyridyl)-2-(N-alkylheteryl)ethylene diiodides (I–XIV). The alkyl iodide derivative of a heterocycle with an active methyl group was added to an equimolecular amount of 2-pyridinealdehyde methiodide (mp 183–184° C) dissolved with heating in glacial acetic acid*; in the experiments on the synthesis of III and VII–XIV the aldehyde methiodide was added to a hot solution of the heterocycle alkyl iodide derivative. After the solution had been boiled, the crystalline precipitate that deposited was filtered off on the following day (IV, V, and VI after several days) and washed with dry ether.

The compounds synthesized were recrystallized from dilute (3 : 1) acetic acid (I, 1.5 ml; XIII and XIV, from 5–6 ml).

The UV spectra** were taken in ethanol at a concentration of $5 \cdot 10^{-5}$ mole/l on an SF-4 spectrophotometer with a layer thickness of 1 cm.

REFERENCES

1. B. P. Lugovkin, KhGS [Chemistry of Heterocyclic Compounds], 2, 571, 1966.

2. B. P. Lugovkin, KhGS [Chemistry of Heterocyclic Compounds], 1, 382, 1965.

7 June 1966

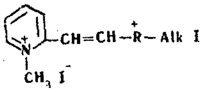
All-Union Scientific-Research Institute of Labor Protection, Kazan

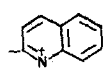
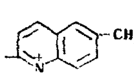
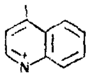
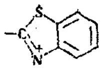
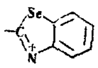
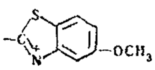
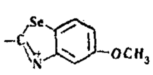
---

*For part I, see [1].

*The amount of solvent was selected according to the solubility of the starting materials and its suitability for the crystallization of the diiodide obtained.

**N. F. Rakova measured the UV spectra in the Kazan Branch of NIKFI [All-Union Scientific-Research Ciné-Photo Institute].



Compound	$\overset{+}{R}$	Alk	Starting materials, g: aldehyde methiodide	Starting materials, g: heterocycle alkyl iodide derivative	Solvent, ml	Time of heating, min	Mp, °C	Color of the crystals	λ_{max}, nm	Empirical formula	I, %: found	I, %: calc.	Yield, %
I*		CH_3	0.25	0.28	5	30	230—231	Claret-brown with a luster	350	$C_{18}H_{18}I_2N_2$	49.53	49.19	75.4
II	The same	C_2H_5	1.0	1.2	5	30	225—226	Light cherry-red with a luster		$C_{19}H_{20}I_2N_2$	48.23	47.89	83.2
III		CH_3	1.0	1.2	40	30	228—229	Dark orange	345	$C_{19}H_{20}I_2N_2$	48.49	47.89	76.3
IV	The same	C_2H_5	0.95	1.2	5	30	213—214	Cherry-red		$C_{20}H_{22}I_2N_2$	46.31	46.65	71.1
V*		CH_3	0.87	1.0	5	30	237—238	Claret-brown with a luster	328	$C_{18}H_{18}I_2N_2$	49.50	49.19	34.3
VI	The same	C_2H_5	1.0	1.2	5	30	230—231	Dark cherry-red		$C_{19}H_{20}I_2N_2$	48.60	47.89	30.0
VII		CH_3	0.42	0.49	25	10	214—215	Dark brown with a luster	330	$C_{16}H_{16}I_2N_2S$	48.98	48.62	75.8
VIII	The same	C_2H_5	0.25	0.31	10	15	223—224	Dark brown		$C_{17}H_{18}I_2N_2S$	47.71	47.35	57.7
IX		CH_3	0.37	0.5	25	10	227—228	Dark brown with a luster	310	$C_{16}H_{16}I_2N_2Se$	44.84	44.59	66.7
X	The same	C_2H_5	0.18	0.26	5	15	226—227	Dark brown		$C_{17}H_{18}I_2N_2Se$	43.68	43.52	62.0
XI		CH_3	0.5	0.65	25	10	231—232	Dark cherry-red with a luster	325	$C_{17}H_{18}I_2N_2OS$	45.72	45.98	78.3
XII	The same	C_2H_5	0.26	0.35	25	15	224—225	Red-brown		$C_{18}H_{20}I_2N_2OS$	45.18	44.84	73.4
XIII		CH_3	0.58	0.83	200	10	236—237	Brown with a luster	315	$C_{17}H_{18}I_2N_2OSe$	42.68	42.36	81.6
XIV	The same	C_2H_5	0.17	0.26	25	15	228—229	Dark cherry-red		$C_{18}H_{20}I_2N_2OSe$	41.74	41.39	88.3

---

*We obtained compounds I and V previously by the reaction of the free bases with methyl iodide; yield of I 60% and of V 14.5%; mixed samples gave no depression of the melting point.