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CONDENSATION OF 2-PYRIDINE ALDEHYDE WITH HETEROCYCLIC BASES

Synthesis of 1-α-Pyridyl-2-quinolyl-, Benzothiazolyl- and Benzoselenazolylethylenes and their Methiodides

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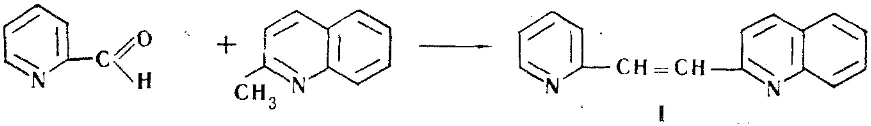
Crotonaldehyde-type condensation of 2-pyridine aldehyde with heterocyclic compounds containing an active methyl group is investigated. The pyridyl(2)-heteryllidene bases synthesized are characterized as their methiodides.

As a development of research on reaction of 2-pyridine aldehyde with rhodanines [1], a study has been made of its condensation with quinoline, benzothiazoline, and selenazoline heterocyclic rings, containing active methyl groups.

Reaction was effected in the presence of an acid catalyst, zinc chloride, which brings about reaction between the reactants at a lower temperature, without use of increased pressure [2, 3]. Lower yields of pyridyl-2-heteryllidene compounds were obtained from the reactions with quinaldine and 2-methylbenzothiazole when no catalyst was used.

Condensation of the aldehyde with quinaldine by heating at 155–160° C gave 1-(pyrid-2-yl)-2-(quinol-2-yl) ethylene as almost colorless needles.



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Heating this compound with methyl iodide in acetic anhydride solution gives the dimethiodide II.

Heating the aldehyde with lepidine gives a syrupy liquid. The expected 1-(pyrid-2-yl)-2-quinol-4-yl) ethylene is identified as its crystalline dimethiodide IX.

By condensing the aldehyde with 2-methylbenzothiazole, 2-methyl-5-methoxybenzothiazole, and 2-methyl-5-methoxybenzoselenazole the following are synthesized: 1-(pyrid-2-yl)-2-(benzothiazol-2-yl) ethylene (III), 1-(pyrid-2-yl)-2-(5-methoxybenzothiazol-2-yl) ethylene (V), and 1-(pyrid-2-y-)-2-(5-methoxybenzoselenazol-2-yl) ethylene (VII).

With methyl iodide these compounds give only monomethiodides IV, VI, VIII, derived from the pyridine ring, analogous to the reactions of 6-quinolidine bases [4, 5].

The condensation of 2-pyridine aldehyde with the selected heterocyclic bases was accompanied by formation of resin. The bases synthesized (Table 1) react with difficulty with methyl iodide. They are crystalline compounds which are quite stable on standing in air. They are soluble in organic solvents, with difficulty in ether, and with very great difficulty in petrol ether, and are insoluble in water.

The methiodides (Table 2) of the bases synthesized are colored crystalline compounds, stable on standing. They are soluble in water, sparingly soluble in alcohols and glacial acetic acid.

Experimental

Pyridyl(2)-heteryllidene bases (I, III, V, VIII). A mixture of 2-pyridine aldehyde (bp 180–181° C), methyl heterocyclic compound (equimolecular amounts) and fused $ZnCl_2$ (20% on the weight of the aldehyde) was heated in a metal-bath* till water ceased to be evolved. The reaction product was dissolved by heating with 25 ml dilute HCl (1: 1).

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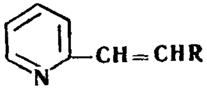
* Bath temperature measured.

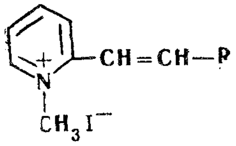
Table 1

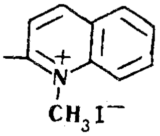
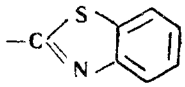
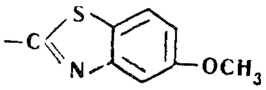
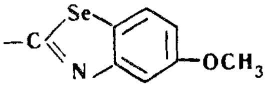
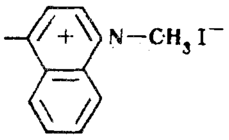


Compound No.	R	Quantities of reactants		Reaction conditions		Mp °C	Formula	Found, %				Calculated, %				Yield, %
		Alde-hyde	Base	Temperature	Heating time, min			C	H	N	S (Se)	C	H	N	S (Se)	
I	2-Quinolyl-	3.5	4.68	155—160	15	98	$C_{16}H_{12}N_2$	82.62	5.37	12.24		82.71	5.21	12.07	—	22.4
III	2-Benzothiazolyl-	2.0	2.79	140—145	5	126	$C_{14}H_{10}N_2S$	70.86	4.55	11.42	13.93	70.53	4.23	11.76	13.46	26.3
V	5-Methoxybenzothiazol-2-yl	2.0	3.34	165—170	5	92	$C_{15}H_{12}N_2OS$	67.42	4.29	10.68	12.36	67.11	4.51	10.44	11.95	21.7
VII	5-Methoxybenzoselenazol-2-yl	1.0	2.11	150—155	5	121	$C_{15}H_{12}N_2OSe$	56.79	3.64	8.71	Se 24.84	57.08	3.83	8.88	Se 25.11	37.7

75 ml water was then added, and the whole then neutralized with solid Na_2CO_3. A viscous liquid separated, the solution was poured off, and the liquid left behind washed with water, after which it was extracted with 60–80 ml (in 20 ml portions) of benzene, with boiling. After separating off the solvent, the crystalline residue was pressed, washed with ether, and recrystallized from a small amount of benzene, petrol ether being added. A further quantity of lidene base was obtained after evaporating the solvent off from the mother liquors.

Table 2



Compound number	R	Mp	Color of crystals	Formula	I, % Found	Calculated	Yield, %
II		234—235	Claret -colored	$C_{18}H_{18}I_2N_2$	48.82	49.19	60.0
IV		223	Yellow	$C_{15}H_{13}IN_2S$	33.01	33.39	27.3
VI		233—234	Golden yellow	$C_{16}H_{15}IN_2OS$	30.97	30.94	37.0
VIII		243—244	Claret -colored	$C_{16}H_{15}IN_2OSe$	27.29	27.75	36.7
IX		237	Pale-brown	$C_{18}H_{18}I_2N_2$	48.75	49.19	*

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* Yield after recrystallizing corresponds to 14.5% of the free base.

Preparation of methiodides. A mixture of 0.5–0.6 g base and 1–1.5 ml methyl iodide in 3 ml Ac_2O was refluxed for 30–60 min.* Next day the methiodide was filtered off, and washed with MeOH. It was recrystallized from 2–3 ml dilute AcOH '2:1).

1-(Pyrid-2-yl)-2-(quinol-4-yl) ethylene dimethiodide (IX). A mixture of 2 g aldehyde, 2.67 g lepidine, and 0.4 g fused $ZnCl_2$ was heated for 10 min at 140–145° C, and the products worked up as described above. The resultant viscous liquid was dissolved in 5 ml Ac_2O, 2 ml MeI added, and the mixture refluxed for 1 hr. Next day the solution was poured off, and the resinous residue recrystallized from 5 ml dilute AcOH (2:1), yield 1.4 g.

REFERENCES

1. B. P. Lugovkin, KhGS [Chemistry of Heterocyclic Compounds], p. 869, 1965.

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* It was not possible to obtain the quaternary salt by heating for 4 hr in glacial AcOH.

2. C. Friedlander, Ber., 38, 159, 1905.
3. B. P. Lugovkin, ZhOKh, 33, 71, 1963.
4. B. P. Lugovkin, ZhOKh, 31, 1687, 1961.
5. B. P. Lugovkin, ZhOKh, 32, 2545, 1962.

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