PYRIDYLETHYLATION OF SOME 4-AZOLIDONES

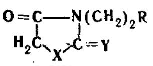
M. A. Lazovskaya, S. N. Baranov,
A. K. Sheinkman, and A. A. Rok

UDC 547.78:542.953.3

N-Pyridylethylated derivatives were obtained by the reaction of α- or γ-vinylpyridines with 4-azolidones and their 5-benzylidene-substituted derivatives. Their IR and UV spectra were studied.

The reaction of 4-azolidones with vinylpyridines could lead to compounds which contain a pyridylethyl group attached to the nitrogen, sulfur (oxygen), or carbon atoms in accordance with the possible tautomeric forms of 4-azolidones. We have investigated this reaction, since the introduction of a pyridine residue into the azolidone ring in a number of cases led to interesting, physiologically active, water-soluble compounds [1, 2].

It turned out that the vinylpyridine residue adds to the nitrogen atom of the azolidone ring to form I-VIII (see Table 1) in the reaction of vinylpyridines with 4-azolidones (without solvents or in the presence of acetic acid [3]).



I-VIII

I X = S, Y = O, R = Py-2; II X = S, Y = O, R = Py-4; III X = S, Y = O, R = 4-CH_3—Py-2; IV X = S, Y = O, R = 6-CH_3—Py-2; V X = S, Y = S, R = Py-2; VI X = S, Y = S, R = 6-CH_3—Py-2; VII X = O, Y = S, R = Py-2; VIII X = O, Y = S, R = 6-CH_3—Py-2

TABLE 1. N-Pyridylethylated Azolidones

Compound	mp	Found, %				Empirical formula	Calculated, %				Yield, %	mp of picrate
		C	H	N	S		C	H	N	S		
I	92—93[a]	54,1	4,9	12,7	14,7	$C_{10}H_{10}N_2O_2S$	54,0	4,5	12,6	14,4	76	162—163
II	139—149[a,b]	53,7	4,5	12,7	14,2	$C_{10}H_{10}N_2O_2S$	54,0	4,5	12,6	14,4	63	176—178
III	113—115[a]	56,1	5,3	11,9	14,0	$C_{11}H_{12}N_2O_2S$	55,9	5,1	11,9	13,6	98	171—173
IV	64—65[c]	55,6	5,0	12,3	13,8	$C_{11}H_{12}N_2O_2S$	55,9	5,1	11,9	13,6	85	118—120
V	111—112[a,b]	50,4	4,2	11,5	27,0	$C_{10}H_{10}N_2OS_2$	50,4	4,2	11,8	26,9	72	180—182
VI	164—165[c]	52,0	5,1	11,4	24,8	$C_{11}H_{12}N_2OS_2$	52,4	4,8	11,1	25,4	32	—
VII	61—62[c]	54,2	4,9	13,2	14,2	$C_{10}H_{10}N_2O_2S$	54,0	4,5	12,6	14,4	18	149—150
VIII	44—45[d]	55,9	5,2	12,0	13,0	$C_{11}H_{12}N_2O_2S$	55,9	5,1	11,9	13,6	16	103—104
IX	107—108[c]	62,2	5,0	8,6	19,5	$C_{17}H_{14}N_2OS_2$	62,6	4,3	8,6	19,6	61	208—209
X	110—112[e]	65,3	4,7	9,6	10,2	$C_{17}H_{14}N_2O_2S$	65,8	4,5	9,0	10,3	40	197—198
XI	153—154[c,f]	65,2	5,0	10,2	10,3	$C_{17}H_{14}N_2O_2S$	65,8	4,5	9,0	10,3	87	223—225
XII	161[a,b]	62,9	4,5	8,8	19,6	$C_{17}H_{14}N_2OS_2$	62,6	4,3	8,6	19,6	74	209—210

---

[a] From carbon tetrachloride.
[b] From isopropyl alcohol.
[c] From petroleum ether.
[d] By precipitation with hexane from ether.
[e] From aqueous dioxane.
[f] From ethyl acetate.

Donets Physical-Organic-Chemistry Branch, L. V. Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of the UkrainianSSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 599-600, May, 1971. Original article submitted September 13, 1969.

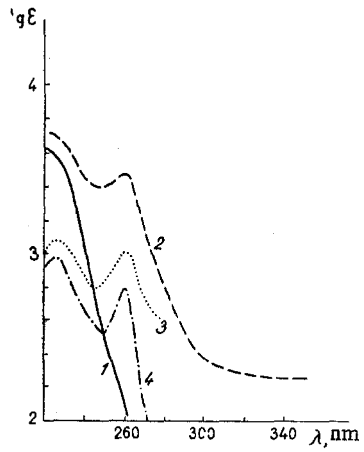
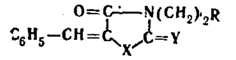


Fig. 1. UV spectra of 10^{-3} M ethanol solutions of: 1) thiazolidine-2,4-dione; 2) N-[β-(4-pyridyl)ethyl]thiazolidine-2,4-dione (II); 3) N-[β-(2-pyridyl)ethyl]thiazolidine-2,4-dione (I); 4) N-[β-(4-methyl-2-pyridyl)-ethyl]thiazolidine-2,4-dione (III).

The azolidones could not be pyridylethylated at the methylene group by changing the reaction conditions and by adding alkaline catalysts. Moreover, the O- or S-pyridylethylation products were not obtained.

Compounds of the I, II, and V type reacted with benzaldehyde to form the corresponding 5-benzylidene derivatives (X, XI, and IX), which were also obtained by the pyridylethylation of 5-benzylidene-4-azolidones (XII).



IX-XII

IX X = S, Y = S, R = Py-2; X X = S, Y = O, R = Py-2;
XI X = S, Y = O, R = Py-4; XII X = S, Y = S, R = Py-4

The UV spectra of I-III (see Fig. 1) contain absorption maxima at 225 and 260 nm, the first of which is associated with the presence of a thiazolidine ring in the molecule, the second of which (VII and VIII) is associated with the presence of a pyridine ring. The IR spectra of the compounds are characterized by an absorption band at 1135 cm^{-1}, which corresponds to a thio group and proves that pyridylethylation of 2-thio-4-oxazolidone proceeds at the nitrogen atom rather than at the sulfur atom, just as in benzazolethiones [4].

EXPERIMENTAL

All of the compounds were chromatographed in a loose, thin layer of aluminum oxide. The IR spectra of KBr pellets were obtained with a UR-20 spectrometer, while the UV spectra were obtained with an SF-4 spectrometer.

N-[β-(2-Pyridyl)ethyl]thiazolidine-2,4-dione (I). A mixture of 3.14 g (0.027 mole) of thiazolidine-2,4-dione and 2.87 g (0.027 mole) of freshly distilled 2-vinylpyridine was shaken for 24 h, and the precipitate was filtered, washed with ether, and chromatographed to give a product with R_f 0.11 [benzene–hexane–chloroform (6 : 1 : 30)]. UV spectrum (in ethanol), λ_{max}, nm (log ε): 225 (2.96), 260 (2.86).

Compounds II-VIII and XII were similarly obtained.

N-[β-(2-Pyridyl)ethyl]-5-benzylidenerhodanine (IX). Benzaldehyde [0.95 g (0.009 mole)] and 0.74 g of fused sodium acetate were added to 2.22 g (0.009 mole) of N-[β-(2-pyridyl)ethyl]rhodanine (V) in 15 ml of glacial acetic acid, and the mixture was heated on a water bath for 0.5 h and refluxed for 10 min. The mixture was cooled and diluted with water, and the precipitate was filtered and washed with water and carbon tetrachloride. This product did not depress the melting point of the product obtained by the reaction of 2-vinylpyridine with 5-benzylidenenerhodanine.

Compounds X and XI were similarly obtained.

LITERATURE CITED

1. S. L. Shapiro, J. M. Rose, and L. Freedman, J. Am. Chem. Soc., 79, 2811 (1957).
2. S. L. Shapiro, J. M. Rose, E. Roskin, and L. Freedman, J. Am. Chem. Soc., 80, 1648 (1958).
3. S. N. Baranov, A. K. Sheinkman, and M. A. Lazovskaya, USSR Author's Certificate No. 233,672 (1968); Byull. Izobret., No. 3 (1969).
4. I. Ya. Postovskii and I. N. Vereshchagina, Khim. Geterotsikl. Soedin., 621 (1965).