LETTERS TO THE EDITOR

N-SUBSTITUTED β-(5-AMINO-2-FURYL)ACROLEINS

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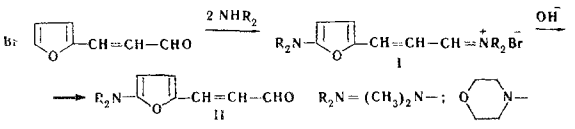
The reaction of 5-halofurylacroleins with secondary amines has been studied for the first time. It has been shown that, in contrast to furylacrolein, which takes part in such reactions with secondary amines at the C=C bond [1], 5-bromofurylacrolein forms quaternary salts of type I in addition to 5-halofurfurals [2]. When compounds (I) were treated with aqueous alkali, N-substituted β-(5-amino-2-furyl)acroleins (II) were obtained for the first time.



Dimethyl [β-(5-dimethylamino-2-furyl)allylidene] ammonium bromide. Yield 54%; dark violet crystals, mp 212°-214° C (from ethanol). Found, %: N 10.18. Calculated for $C_{11}H_{17}BrN_2O$, %: N 10.28. UV spectrum: λ_{max} 306 and 490 nm, log ε 3.48 and 5.00. IR spectrum: 1610 (C=C), 1556 (C=$\overset{+}{N}$<), 1380, 1003, 880, (furan) cm^{-1}

[β-(5-Morpholino-2-furyl)allylidene]morpholinium bromide. Yield 49%; violet crystals with mp 236°-238° C (from ethanol). Found, %: N 7.92. Calculated for $C_{15}H_{21}BrN_2O_3$, %: N 7.82. UV spectrum: λ_{max} 304 and 498 nm, log ε 3.26 and 5.02. IR spectrum: 1608 (C=C), 1556 (C=$\overset{+}{N}$<), 1380, 1010, 896, (furan), cm^{-1}.

β-(5-Dimethylamino-2-furyl)acrolein. Yield 90%; violet crystals, mp 32°-33° C (from benzene). Found, %: N 8.76. Calculated for $C_9H_{11}NO_2$, %: N 8.49. UV spectrum: λ_{max} 422 and 446 nm, log ε 4.40 and 4.40. IR spectrum: 1656 (C=O), 1624 (C=C) cm^{-1}.

β-(5-Morpholino-2-furyl)acrolein. Yield 84%; orange-red crystals, mp 89°-90° C. Found, %: N 6.93. Calculated for $C_{11}H_{13}NO_3$, %: N 6.76. UV spectrum: λ_{max} 420 and 440 nm, log ε 4.40 and 4.40. IR spectrum: 1658 (C=O), 1620 (C=C) cm^{-1}.

The UV spectra of compounds I and II exhibited a strong bathochromic shift (~100 nm) with a considerable increase in intensity in comparison with the corresponding compounds obtained from the halofurfurals [3]. The IR spectrum of I had a displacement of the frequencies of the stretching vibrations of the C=$\overset{+}{N}$< bond into the 1550-1540 cm^{-1} region which shows the considerable increase in the degree of conjugation within the system on the introduction of a double bond.

REFERENCES

1. M. Yu. Lidak and S. A. Hiller, Izv. AN Latv. SSR, ser. khim., 81, 1961.

2. Z. N. Nazarova and V. S. Pustovarov, Authors' certificate no. 185931, 1966; Byull. izobr. no. 18, 1966.

3. Z. N. Nazarova, V. N. Novikov, and V. S. Pustovarov, ZhOrKh, 2, 161, 1966.

15 May 1967 Rostov on Don State University

THE REACTION OF AMINOMERCAPTO DERIVATIVES OF PYRIDINE, PYRIMIDINE, AND PYRAZINE WITH α-CHLOROACETOACETIC ESTER

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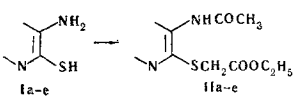
On studying the reaction of 6- and 5-chloro-substituted 3-amino-2-mercaptopyrimidines with α-chloroacetoacetic ester, we found that if it is carried out in ethanol in the presence of 2 moles of alkali, it is not the corresponding pyrido[2,3-b]-1,4-thiazines [1, 2] that are formed, but 6- and 5-chlorine-substituted 3-acetyl-2-ethoxycarbonylmethylthiopyridines (IIa-b). The structure of IIa and IIb has been confirmed by their IR and PMR spectra and also by independent synthesis from 6- and 5-substituted 3-acetylamino-2-mercaptopyridines with ethyl chloroacetate. The reactions of 5-amino-6-mercaptopyrimidines and 3-amino-2-mercapto-5,6-dimethylpyrazine with α-chloroacetoacetic ester take place similarly under the conditions described, giving compounds IIc-f with yields of 60-80%.



3-Acetylamino-6-chloro-2-ethoxycarbonylethylthiopyridine (IIa). Colorless crystals, mp 131°-132° C (from C_2H_5OH). IR spectrum: 1670 (CO-NH), 1740 (CO-OC_2H_5), 3280 cm^{-1} (NH). PMR spectrum (in $CHCl_3$): 3.92 ppm ($2H-CH_2$). Found, %: C 46.04; H 4.78; Cl 12.40; N 9.66; S 11.00. Calculated for $C_{11}H_{13}ClN_2O_3S$, %: C 45.75; H 4.50; Cl 12.30; N 9.70; S 11.09.

3-Acetylamino-5-chloro-2-ethoxycarbonylmethylthiopyridine (IIb). Colorless crystals, mp 124°-126° C (from C_2H_5OH). IR spectrum: