## LETTERS TO THE EDITOR

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

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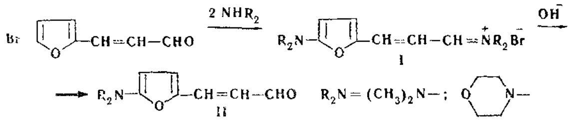
The reaction of 5-halofurylacroleins with secondary amines has been studied for the first time. It has been shown that, in contrast to furylacrolein, which takes part in such reactions with secondary amines at the C=C bond [1], 5-bromofurylacrolein forms quaternary salts of type I in addition to 5-halofurfurals [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: $\lambda_{max}$ 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: $\lambda_{max}$ 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: $\lambda_{max}$ 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: $\lambda_{max}$ 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 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.

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

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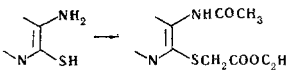
On studying the reaction of 6- and 5-chloro-substituted 3-amino-2-mercaptopyrimidines with α-chloroacetoacetic ester, we found that if it is carried out in ethanol in the presence of 2 moles of alkali, it is not the corresponding pyrido[2,3-b]-1,4-thiazines [1, 2] that are formed, but 6- and 5-chlorine-substituted 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%.



Ia-e IIa-e

**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:

1670 (CONH), 1740 ($CO-OC_2H_5$), 3270 $cm^{-1}$ (NH). Found, %: C 45.79; H 4.40; Cl 12.28; N 9.66; S 10.91. Calculated for $C_{11}H_{13}ClN_2O_3$, %: C 45.75; H 4.50; Cl 12.30; N 9.70; S 11.09.

**5-Acetylamino-2-amino-6-ethoxycarbonylmethylthio-4-methylpyrimidine (IIc).** Colorless crystals, mp 190°-191° C (from ethanol). IR spectrum: 1670 (CO—NH), 1720 ($CO-OC_2H_5$), 3210, 3290, 3420 $cm^{-1}$ ($NH_2$, NH). Found, %: C 46.46; H 5.65; N 20.12; S 11.36. Calculated for $C_{11}H_{16}N_4O_3S$, %: C 46.46; H 5.67; N 19.71; S 11.28.

**5-Acetylamino-6-ethoxycarbonylmethylthio-4-methoxypyrimidine (IId).** Colorless crystals, mp 157°-158° C (from ethanol). IR spectrum: 1670 (CO—NH), 1740 ($CO-OC_2H_5$), 3200, 3240 $cm^{-1}$ (NH). Found, %: C 46.48; H 5.30; N 14.98; S 11.77. Calculated for $C_{11}H_{15}N_3O_3S$, %: C 46.30; H 5.30; N 14.73; S 11.24.

**5-Acetylamino-4-chloro-6-ethoxycarbonylmethylthiopyrimidine (IIe).** Colorless crystals, mp 127°-128° C (from water), yield 78%. IR spectrum: 1680 (CO—NH), 1740 ($CO-OC_2H_5$); 3260 $cm^{-1}$ (NH). Found, %: C 41.70; H 4.39; Cl 12.11; N 14.49; S 11.51. Calculated for $C_{10}H_{12}ClN_3O_2S$, %: C 41.45; H 4.37; Cl 12.24; N 14.50; S 11.07.

**3-Acetylamino-2-ethoxycarbonylmethylthio-5, 6-dimethylpyrazine (IIf).** Colorless crystals, mp 142°-143° C (from a mixture of cyclohexane and benzene, 8 : 1), yield 61%. IR spectrum: 1670-1680 (CO—NH), 1738 ($CO-OC_2H_5$), 3235 $cm^{-1}$ (NH). Found, %: C 51.18; H 6.04; N 14.32. Calculated for $C_{12}H_{17}N_3O_3S$, %: C 50.86; H 6.05; N 14.83.

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# A NEW METHOD FOR THE SYNTHESIS OF 4-SUBSTITUTED sym-OCTAHYDROACRIDINES

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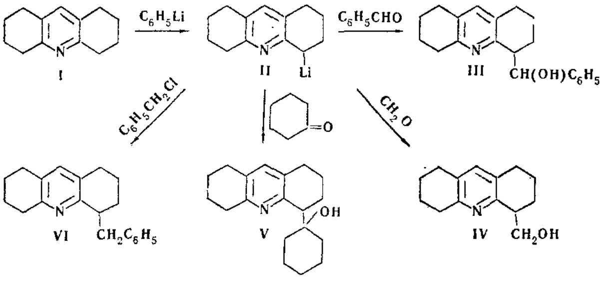
The direct introduction of substituents into position 4 of sym-octahydroacridine (I) was previously carried out by condensing it with aromatic aldehydes [1] and by the reaction of the N-oxide of this base with acetic anhydride [2]. The route proposed in the scheme has not been reported in the literature.



4-Lithio-sym-octahydroacridine (II) is formed by the slow mixing of dry ethereal solutions of I and phenyllithium at 20-25° C in an atmosphere of argon; on cooling to −10° C the compound deposits in the form of a pulverulent precipitate. The formation of III-VI takes place fairly smoothly in an atmosphere of nitrogen as the appropriate reactants are added to an ethereal solution of II. The structure of the carbinol III was confirmed by its dehydration to the known 4-benzylidene-sym-octahydroacridine [1]. The structure of IV was confirmed through its independent synthesis by the condensation of I with formaldehyde (with the participation of L. N. Donchak).

**4-Lithio-sym-octahydroacridine (II).** Red powder slowly carbonizing on heating. Found, %: Li 3.35, 3.36. Calculated for $C_{13}H_{16}LiN$, %: Li 3.59. On hydrolysis, the theoretical amount of I is formed.

**4-Hydroxybenzyl-sym-octahydroacridine (III).** Mp 147°-148° C (from petroleum ether). Found, %: C 81.41; H 7.92; N 5.08. Calculated for $C_{20}H_{23}NO$, %: C 81.80; H 7.92; N 4.77. IR spectrum (in $CCl_4$: band of O—H stretching vibrations at 3340 $cm^{-1}$ and on dilution at 3650 $cm^{-1}$. **Picrate,** mp 161°-162° C (from aqueous ethanol). Found, %: N 10.82. Calculated for $C_{20}H_{23}NO \cdot C_6H_3N_3O_7$, %: N 10.72.

**4-Hydroxymethyl-sym-octahydroacridine (IV).** Mp 92°-93° C (from heptane). Found, %: C 77.23; H 9.08; N 6.61. Calculated for $C_{14}H_{19}NO$, %: C 77.39; H 8.82; N 6.45. IR spectrum (in KBr) band of O—H stretching vibrations at 3350 $cm^{-1}$. **Picrate,** mp 132°-133° C (from xylene). Found, %: N 12.89. Calculated for $C_{14}H_{19}NO \cdot C_6H_3N_3O_7$, %: N 12.55.

**4-(1'-Hydroxycyclohexyl)-sym-octahydroacridine (V).** Mp 88°-89° C (from acetone). Found, %: C 79.86; H 9.51; N 5.15. Calculated for $C_{19}H_{27}NO$, %: C 79.94; H 9.24; N 4.90. IR spectrum (in $CCl_4$): band of O—H stretching vibrations at 3350 $cm^{-1}$. **Picrate,** mp 151°-152° C (from isobutanol). Found, %: N 10.84. Calculation for $C_{19}H_{27}NO \cdot C_6H_3N_3O_7$, %: N 10.89.

**4-Benzyl-sym-octahydroacridine (VI).** Bp 142°-146° C (0.03 mm), $n_D^{20}$ 1.5833. Found, %: C 86.78; H 9.04; N 5.01. Calculated for $C_{20}H_{23}N$, %: C 86.56; H 8.37; N 5.05. **Picrate,** mp 172°-173° C (from methanol). Found, %: N 11.21. Calculated for $C_{20}H_{23}N \cdot C_6H_3N_3O_7$, %: N 10.72.

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