

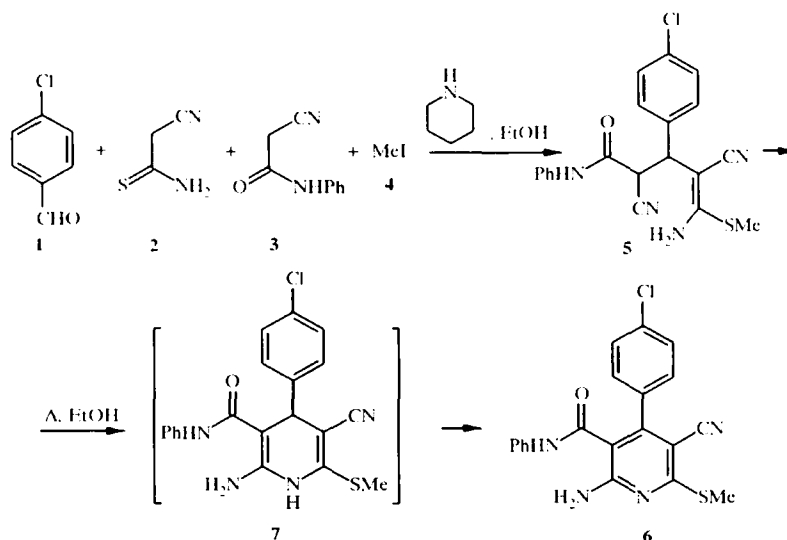
# ISOLATION OF A STABLE MICHAEL ADDUCT – AN INTERMEDIATE IN THE SYNTHESIS OF SULFUR- CONTAINING AMINOPYRIDINES

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Michael adducts formed with the participation of cyanothioacetamide have hardly been studied at all [1]. They remain a sparse and little investigated group of organic compounds, and the need to solve the problem of their production, determination of their structure, and their further transformations is quite apparent.

During the reaction of 4-chlorobenzaldehyde (**1**), cyanothioacetamide (**2**), cyanoacetanilide (**3**), and methyl iodide (**4**) in ethanol in the presence of piperidine (~20°C) we first obtained the stable sulfide **5** and realized its transformation into pyridine **6**, which probably takes place through dihydropyridine **7** unstable toward oxidation processes.



**1-Amino-3-(4-chlorophenyl)-2,4-dicyano-1-methylthio-4-phenylcarbamoyl-1-butene (5).** Yield 81%; mp 204-205°C. IR spectrum (vaseline oil),  $\text{cm}^{-1}$ : 3180-3270, 3480 (NH,  $\text{NH}_2$ ), 2241, 2185 (CN), 1650, 1680 sh (CO).  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm: 2.24 (3H, s, SMe); 4.33 (1H, d,  $J = 11.9$  Hz, 3-H); 4.68 (1H, d,

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$^1J = 11.9$  Hz, 4-H); 6.96 (2H, s,  $\text{NH}_2$ ); 7.18-7.57 (9H, m,  $\text{H}_{\text{arom}}$ ); 10.54 (1H, s, NH). Mass spectrum (EI, 70 eV),  $m/z$  ( $I_{\text{rel}}$ , %): 39 (73), 45 (44), 65 (72), 77 (51), 93 (95), 126 (64), 160 (49), 190 (100), 237 (41), 282 (30), 396 (4) [ $\text{M}^+$ ]. Found, %: C 60.42; H 4.46; N 14.25.  $\text{C}_{20}\text{H}_{15}\text{ClN}_4\text{OS}$ . Calculated, %: C 60.52; H 4.32; N 14.12.

**6-Amino-4-(4-chlorophenyl)-3-cyano-2-methylthio-5-phenylcarbamoylpyridine (7)**. Yield 78%; mp 279-281°C. IR spectrum (vaseline oil),  $\text{cm}^{-1}$ : 3265-3468 (NH,  $\text{NH}_2$ ), 2221 (CN), 1695 (CO).  $^1\text{H}$  NMR spectrum ( $\text{DMSO-d}_6$ ),  $\delta$ , ppm: 2.77 (3H, s, SMe); 7.18-7.67 (11H, m,  $\text{H}_{\text{arom}}$  and  $\text{NH}_2$ ); 11.12 (1H, s, NH). Found, %: C 60.99; H 3.97; N 14.08.  $\text{C}_{20}\text{H}_{15}\text{ClN}_4\text{OS}$ . Calculated, %: C 60.83; H 3.83; N 14.19.

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## REFERENCES

1. Yu. A. Sharanin, M. P. Goncharenko, and V. P. Litvinov, *Usp. Khim.*, **67**, 442 (1998).