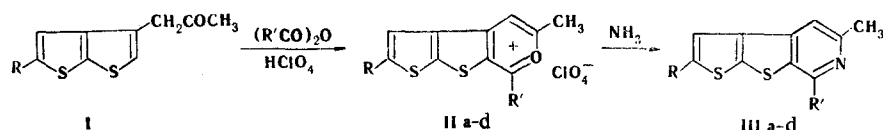


PYRYLIUM AND PYRIDINE DERIVATIVES OF THIENO[3,2-b]THIOPHENE —  
NEW HETEROAROMATIC SYSTEMS

N. N. Alekseev and S. V. Tolkunov

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We showed that when 3-acetylthieno[2,3-b]thiophenes are mixed at 0°C with an aliphatic acid anhydride and 70% perchloric acid, thieno[2',3':2,3]thieno[2,3-c]pyrylium perchlorate (II) are formed with the evolution of heat.



I R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>; II-III a R = R' = CH<sub>3</sub>; b R = CH<sub>3</sub>, R' = C<sub>2</sub>H<sub>5</sub>; c R = C<sub>2</sub>H<sub>5</sub>, R' = CH<sub>3</sub>; d R = R' = C<sub>2</sub>H<sub>5</sub>

The following compounds were thus obtained and recrystallized from acetic acid: 1,3,6-trimethylthieno[2',3':2,3]thieno[2,3-c]pyrylium perchlorate (IIa), yield 84%, mp 198-199°C; IIb, yield 86%, mp 166-167°C; IIc, yield 86%, mp 169-170°C; IId, yield 84%, mp 146-147°C. PMR spectrum of IIa (in CF<sub>3</sub>COOH): singlets of methyl groups (2.75; 2.94; 3.16), C-H of heterocyclic rings (7.46 and 7.99 ppm).

When boiled in a saturated ammoniacal alcoholic solution, compounds II form high yields of the corresponding thieno[2',3':2,3]thieno[2,3-c]pyridines (III), which can be recrystallized from ethanol: IIIa, yield 91%, mp 108-109°C; picrate, mp 241-242°C; IIIb; yield 90%, mp 66-67°C; picrate, mp 236-237°C; IIIc, yield 92%, mp 56-57°C; picrate, mp 215-216°C. Compound IIId was identified as a picrate, yield 93%, mp 207-208°C. PMR spectra of IIIa (in CCl<sub>4</sub>): singlets of methyl groups (2.56; 2.63; 2.65), C-H of heterocyclic rings (7.1 and 7.26 ppm). The IR spectra correspond to the accepted structures.

The data of elementary analysis of the compounds obtained for C, H, Cl, S correspond to the calculated values.