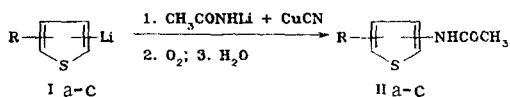


# ELECTROPHILIC ACETAMINATION OF THIOPHENE CARBANIONS

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Recently the alkyl- and arylamination of carbanions was conducted using copper derivatives of alkyl- and arylamines [1, 2]; however, this reaction was not conducted with respect to thiophene carbanions. Aminothiophenes were produced from thiophene carbanions by two-step synthesis through intermediate explosive azides [3]. The efforts of Trost et al. [4] to use arylthiomethyl azides for this purpose, as well as our attempts to synthesize aminothiophenes from thiophene carbanions and derivatives of hydroxylamine (see the literature in [2]) gave no results, which may be associated with the well-known instability of the end products of the reactions. It seemed that methods in which the end products of amination were not aminothiophenes but their stable acyl derivatives might prove promising. We were unable to find any data on the reactions of carbanions with copper derivatives of amides.

We found that in the interaction of lithium thiophenes I with N-lithiumacetamide and CuCN, followed by oxidation by molecular oxygen, in addition to bithienyls, acetylaminothiophenes II are formed with yields up to 25%:



I, IIa, b R = H; c R = 5-EtS; 2-Li (Ia, c), 3-Li (Ib), 2-AcNH (IIa, c); 3-AcNH (IIb)

To 2.12 g (36 mmoles) of dry acetamide in 50 ml absolute THF at 20°C we slowly added 4.6 g (65 mmoles) of a 1.5 N ether solution of n-butyllithium, mixed for 30 min at -20°C, then gradually added 1.61 g (18 mmoles) of anhydrous CuCN. After 30 min a solution of thienyllithium Ia, produced from 1.01 g (12 mmoles) thiophene in 5 ml of ether and 0.77 g (12 mmoles) of 1.5 N ether solution of n-butyllithium, was slowly added to the mixture, mixed for 2 h at temperatures from -20 to -30°C, then a stream of oxygen passed through for 30 min, after which the mixture was poured out into water, the THF evaporated under vacuum, ether added to the residue, filtered off, and the sludge on the filter and the filtrate were extracted with ether; the ether extracts were washed with water and dried. The residue after removal of the ether was treated with hexane. The precipitate formed was filtered off. We obtained 0.2 g (12%) of compound IIa, mp 159.5-160.5°C (from benzene) [5].

3-Acetylaminothiophene (IIb), mp 145°C [5], was obtained from 3-thienyllithium at -70°C. 5-Ethylthio-2-acetylaminothiophene (IIc) was obtained analogously in a 25% yield, mp 108-110°C (from benzene with hexane). PMR spectrum ( $\text{CD}_3\text{OD}$ ): 1.16 (t), 2.65 (q,  $J = 7.8$  Hz,  $\text{C}_2\text{H}_5$ ), 2.08 (s,  $\text{CH}_3\text{CO}$ ), 6.48 (d), 6.85 ppm (d,  $J_{3,4} = 3.5$  Hz, 3- and 4-H).

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