LETTERS TO THE EDITOR

SELECTIVE WILLGERODT-KINDLER REACTION WITH THE PARTICIPATION OF 2-METHYL-5-VINYLPYRIDINE

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The information available in the literature does not permit definite conclusions on the relative reactivity of alkyl and vinyl groups in Willgerodt-Kindler oxidation-reduction reactions [1]. We have established that in the case of 2-methyl-5-vinylpyridine (I) treatment with mixtures of an amine and sulfur leads smoothly to thioamides of 2-methylpyridine-5-acetic acid, i.e., only the double bond is affected. Thus, if a mixture of compound **I** (1 mole), 1.33 mole of sulfur, and a small excess of morpholine is heated at 140–145° C for 1–1.5 hr, after cooling 2-methylpyridine-5-acetthiomorpholide (**II**) gradually precipitates, yield 50–52%, mp 91–92° C, λ_{max} 279 nm (log ε 4.15) R_f on Al_2O_3 0.58 (acetone – hexane 1:1). Found, %: C 60.78, 60.90; H 6.94, 7.03; S 13.22, 13.35. Calculated for $C_{12}H_{16}N_2OS$, %: C 61.01; H 6.70; S 13.55. An additional amount of the substance can be obtained by distilling the filtrates in vacuum (bp 215–225° C, 8 mm). The yield rises considerably when the amount of sulfur is increased.

The IR spectrum of compound II had absorption bands at 2975, 2925, and 2860 cm^{-1} (CH_3 and CH_2 groups) and at 1500, 1445, 1365, 1300, and 1120 cm^{-1}, which are characteristic for N—C=S, C—N, and C=S bonds, together with a system of aromatic bands for a 2,5-disubstituted pyridine. The mass spectrum of II lacks the molecular ion but has strong peaks with m/e 129 and 86–88 (fragments of the thiocarbonylmorpholine moiety) and peaks at 105–107 and 77–79 which have been observed earlier in the spectra of 2-methyl-5-R-pyridines [2].

Hydrolysis of the thiomorpholide with boiling hydrochloric acid and subsequent esterification with ethanol gave ethyl 2-methylpyridine-5-acetic acid, bp 125–127° C (7 mm); d_4^{20} 1.066; n_D^{20} 1.4985 (picrate, mp 121.5–122° C), and from it were obtained the amide, mp 168–169° C (from ethanol), λ_{max} 267.5, 274 nm (log ε 3.54, 3.41) and the hydrazide, mp 123–123.5° C (from ethanol containing ether), λ_{max} 268.5, 274 nm (log ε 3.63, 3.52). The results of the analysis and the IR and mass spectra of these substances agree with the structure ascribed to them.

Among the by-products of the Willgerodt-Kindler reaction was identified (2-methyl-5-pyridyl)ethyl mercaptan, yield 6–8%, bp 121–124° C (15 mm), n_D^{20} 1.5541, λ_{max} 269.5 nm (log ε 3.54). Found, %: C 63.00, 63.05; H 7.20, 7.40. Calculated for $C_8H_{11}NS$, %: C 62.69; H 7.24. **Picrate**, 146–147° C (from ethanol decomp.) and thioacetmorpholide, bp 160–175° C (10 mm), mp 88.5–89° C (from benzene containing hexane) [3], mol. wt. 145 (by mass spectroscopy), λ_{max} 278.5 nm (log ε 3.89).

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THE NITRATION OF 2-ETHOXYCARBONYLAMINOCHROMONE

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In 2-acylaminochromones, position 3 should be fairly nucleophilic, but by the action of nitric acid on 2-ethoxycarbonylaminochromone (I) in sulfuric acid solution we obtained 2-ethoxycarbonylamino-6-nitrochromone (**II**) and not the corresponding 3-nitro derivative (**III**). This is evidently due to the conversion of the pyrone ring into a benzopyrilium cation in the strongly acid medium, which leads to a decrease in the electron density in position 3. In fact, when **I** was nitrated in the absence of mineral acids by copper nitrate in a mixture of acetic anhydride and acetic acid, we succeeded in changing the orientation of the nitro group and we obtained 2-ethoxycarbonylamino-3-nitrochromone (III).

A solution of 6.99 g (0.03 mole) of **I** in 75 ml of concentrated H_2SO_4 was treated with 1.5 ml of HNO_3 (d 1.52) and the resulting solution was left for 48 hr and poured onto ice. The precipitate that deposited was filtered off to give 6.86 g (82%) of **II**, mp 259° C (decomp. from CH_3COOH). The substance is soluble in sodium carbonate solution but insoluble in sodium hydrogen carbonate solution. Found, %: C 51.94, 51.96; H 3.70, 3.49; N 10.17, 10.17. Cal-