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. Calculated for $C_{12}H_{10}N_2O_6$, %: C 51.81; H 3.62; N 10.08. The acid hydrolysis of II formed the known 2-hydroxy-5-nitroacetophenone, mixed melting point 101–102° C.

With water cooling, a solution of 1.17 g (0.05 mole) of I in 20 ml of acetic acid and 12 ml of acetic anhydride was added slowly to a mixture of 1.33 g (0.055 mole) of $Cu(NO_3)_2 \cdot 3H_2O$, 3 ml of glacial acetic acid, and 2 ml of acetic anhydride (the temperature rose to 25° C). Then the mixture was stirred for 30 min and poured onto ice. This gave 0.5 g (36%) of substance III, mp 136.5–137° C (from ethanol). III is soluble in aqueous bicarbonate solution. Found, %: C 51.65, 51.90; H 3.78, 3.59; N 10.06, 10.09. Calculated for $C_{12}H_{10}N_2O_6$, %: C 51.81; H 3.62; N 10.08. On alkaline hydrolysis, the substance formed salicylic acid.

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SYNTHESIS AND DEFOLIATING ACTIVITY OF 2-BENZOTHIAZOLYL 5-CHLORO-2-PYRIDYL SULFIDE

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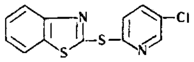
In order to obtain new defoliants from 2-mercaptobenzothiazole [1], we have synthesized 2-benzothiazolyl 5-chloro-2-pyridyl sulfide from 2-bromo-5-chloropyridine and 2-mercaptobenzothiazole in dioxane solution.



The 2-bromo-5-chloropyridine was obtained from 2-amino-5-chloropyridine [2].

The fall of the leaves of the cotton plant on the 12-th day when 3 kg/ha was used was 85–90%.

EXPERIMENTAL

A solution of 9.6 g (0.05 mole) of 2-bromo-5-chloropyridine and 8.4 g (0.05 mole) of 2-mercaptobenzothiazole in 40 ml of dioxane was kept at the boiling point for 3 hr and was then cooled and washed with 10% sodium hydroxide solution to eliminate the unchanged 2-mercaptobenzothiazole. The oil was separated off and the alkaline residue was extracted with ether. The ethereal extracts and the oil were dried over magnesium sulfate. The ether was evaporated off and the residue was distilled in vacuum to give 11.8 g (85%) of 2-benzothiazolyl 5-chloro-2-pyridyl sulfide with bp 240–242° C (3 mm); mp 100–101° C (from methanol). Found, %: S 23.10; N 9.84; Cl 12.65. Calculated for $C_{12}H_7S_2N_2Cl$, %: S 22.96; N 10.05; Cl 12.74.

The sulfone, obtained by Case's method [3] had mp 209–210° C (from benzene). Found, %: S 20.29. Calculated for $C_{12}H_7O_2N_2S_2Cl$, %: S 20.59.

The presence of an SO_2 group was confirmed by absorption bands in the IR spectra in the 1110–1130 and 1325–1340 cm^{-1} regions.

Hydrochloride, mp 93° C (from absolute ethanol). Found, %: S 20.19. Calculated for $C_{12}H_7S_2N_2Cl \cdot HCl$, %: S 20.31.

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