amount of the condensing agent. The reaction mixture was treated with a saturated aqueous solution of NH_4Cl. Compounds **1c** and **2b** were crystallized after evaporation of the solvent, and products **1a,d,e** and **2a** were isolated *via* Cu chelates and their subsequent decomposition with H_2S in ether.

5,7-Dimethyl-2-trifluoro(trichloro)methylchromones (3a,b) were obtained by passing dry HCl through ether solutions of compounds **2a,b** for 0.5 h. The precipitate of NH_4Cl was filtered off, the ether was evaporated, and the residue was recrystallized from ethanol.

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2-Cyanopenta-(2*E*,4)-dienoic acid and its amide

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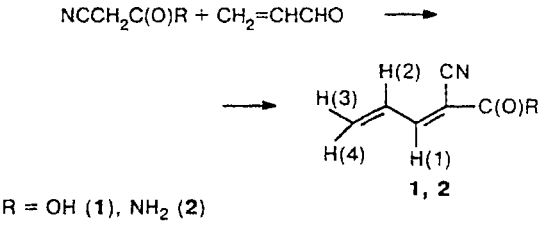
Knoevenagel condensation of acrolein with $NCCH_2COOK$ or $NCCH_2CONH_2$ in 1 *M* aqueous solutions of K and Na phosphates gave 2-cyanopenta-(2*E*,4)-dienoic acid and its amide, respectively.

Key words: 2-cyanopenta-(2*E*,4)-dienoic acid; 2-cyanopenta-(2*E*,4)-dienamide; acrolein; Knoevenagel condensation.

Due to their ability to undergo anionic polymerization and copolymerization under mild conditions, alkyl 2-cyanopenta-(2*E*,4)-dienoates serve as efficient modifiers of 2-cyanoacrylate glues and photoresist compositions.[1–3] However, while the above esters have been known for over 30 years, the free 2-cyanopenta-(2*E*,4)-dienoic acid (**1**) and its amides have not been described in the literature, though attempts at these syntheses have been undertaken.[4] At the same time, these compounds may be of interest as possible objects for solid-phase topochemical transformations, as components or starting compounds for obtaining materials with nonlinear optical properties and biological activity, and in the syntheses of new monomers and polymers.

In order to synthesize the acid **1** and its amide (**2**), we used Knoevenagel condensation of potassium cyanoacetate or cyanoacetamide, respectively, with acrolein in aqueous solutions of potassium or sodium phosphates (by analogy with Ref. 5).



R = OH (**1**), NH_2 (**2**)

1, 2

The structure of acid **1** and amide **2** was confirmed by the data of elemental analyses and ^1H NMR and IR spectroscopy. *E*-Configuration of the Δ^2-bond for the acid **1** was established by an X-ray study (which will be reported elsewhere), while that for amide **2** is assumed by analogy with sorbamide.[6]

Experimental

IR spectra were recorded on a Magna-IR-750 spectrometer (in pellets with KBr). NMR spectra were obtained on a Bruker AMX-400 instrument in acetone-d_6.

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2-Cyano-(2*E*,4)-pentadienoic acid (1). Freshly distilled acrolein (6.3 g, 0.11 mol) was added over 20 min at 10°C to a solution of $NCCH_2CO_2K$ (12.3 g, 0.1 mol) in 1 *M* aqueous NaH_2PO_4 (pH 5.4). The mixture was stirred for 2 h at 10—15°C and kept overnight, and then 30% H_2SO_4 was added at 5—10°C to pH 2.5. The precipitate that formed was separated, washed with toluene, and dissolved in ether. The solution was dried with $MgSO_4$ and concentrated, and the product was crystallized from ether to give 3.9g of acid **1**, m.p. 131—132°C (decomp.). IR, ν/cm: 1578, 1615 (C=C), 1682, 1703 sh. (C=O), 2233 (C≡N). ^{1}H NMR, δ: 6.00 (ddd, 1 H, H(3), $J_{H(3)H(2)}$= 10 Hz, $J_{H(3),H(4)}$= 1.4 Hz, $J_{H(3),H(1)}$= 0.6 Hz); 6.25 (ddd, 1 H, H(4), $J_{H(4),H(2)}$= 16.7 Hz, $J_{H(4),H(3)}$= 1.4 Hz, $J_{H(4),H(1)}$= 0.8 Hz); 6.89 (ddd, 1 H, H(2), $J_{H(2),H(4)}$= 16.7 Hz, $J_{H(2),H(1)}$= 11.4 Hz, $J_{H(2),H(3)}$= 10 Hz); 7.94 (ddd, 1 H, H(1), $J_{H(1),H(2)}$= 11.4 Hz, $J_{H(1),H(4)}$= 0.8 Hz, $J_{H(1),H(3)}$= 0.6 Hz); 9.51 (br.s, 1 H, COOH). Found (%): C, 58.51; H, 3.90; N, 11.33. $C_6H_5NO_2$. Calculated (%): C, 58.53, H, 4.09; N, 11.37.

2-Cyanopenta-(2*E*,4)-dienamide (2). Freshly distilled acrolein (4.2 g, 75 mmol) was added dropwise at 3—5°C to a solution of cyanoacetamide (4.2 g, 50 mmol) in 35 mL of 1 *M* aqueous K_3PO_4 (pH 7). The mixture was stirred for 2 h at 10—15°C and 1 h at 20°C. The precipitate that formed was separated, washed with cold water on a filter, and dried in a vacuum desiccator over P_2O_5 to give 2.4g of amide **2**, m.p. 140—145°C (decomp.) IR: 1392 (C—N), 1579, 1610 (C=O), 2223 (C≡N), 3407 (NH). ^{1}H NMR, δ: 6.31 (m, 2 H, H(3), H(4)); 7.08 (m, 1 H, H(2); 7.45 (br.s, 2 H, NH_2); 8.1 (d, 1 H, H(1), *J*= 12.0 Hz). Found (%): C, 58.84; H, 5.03; N, 23.10. $C_6H_6N_2O$. Calculated (%): C, 59.00; H, 4.95; N, 22.94.

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Regioselective synthesis and properties of 3-cyano-6-thienylpyridine-2(1*H*)-thiones

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Reactions of sodium derivatives of 2- and 3-thenoylacetaldehydes with cyanothioacetamide gave 2- and 3-cyano-6-thienylpyridine-2(1*H*)-thiones, which were used in the synthesis of substituted 2-alkylthiopyridines, thieno[2,3-*b*]pyridines, and other fused heterocycles.

Key words: cyanothioacetamide, β-oxoaldehydes, 6-thienylpyridine-2(1*H*)-thiones, thieno[2,3-*b*]pyridines.

Previously, reactions of sodium derivatives of aroyl- and nicotinoylacetaldehyde with cyanothioacetamide were studied.[1—3] It was found that these reactions occur highly regioselectively to give 6-aryl- or 6-(3-pyridyl)-3-cyanopyridine-2(1*H*)-thiones. The compounds obtained were then used in the syntheses of difficultly accessible annelated heterocycles.[2]

Taking into account that compounds of practical utility (pesticides, drugs, antioxidants, dyes, analytical reagents, *etc.*) have been found among substituted 3-cyanopyridine-2(1*H*)-thiones,[4] we have elaborated a convenient method for the synthesis of previously unknown 3-cyano-6-thienylpyridine-2(1*H*)-thiones and, on the basis of them, 2-alkylthiopyridines and fused pyridines. In addition, the study of the regioselectivity of reactions of cyanoacetic acid derivatives with 1,3-dicarbonyl compounds[1,5] was continued in this work.

Reactions of sodium derivatives of 2- and 3-thenoylacetaldehyde (**1a,b**) with cyanoacetamide (**2**) in ethanol in the presence of acetic acid occur regioselectively to give the corresponding 3-cyano-6-thienylpyridine-2(1*H*)-thiones **3a** and **3b**.

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