temperature increases to 200 °C, the weight loss of NH_4 nitrolite reaches its limit value, at which the reversible water adsorption is maximum (100%). As seen in Fig. 2, at temperatures above 200 °C, NH_4 natrolite begins to lose its adsorption (rehydration) ability, and the initial natrolite remains thermally stable up to 650 °C.[8]

The values of heats of immersion of NH_4 and Na natrolite[8] evacuated at 200 °C are maximum and equal to 415 and 330 J g^{-1}, respectively. However, over the temperature range from 200 to 400 °C, the Q_i value for the initial natrolite remains constant,[8] and the Q_i *vs.* T curve for the NH_4 natrolite has a maximum as in the case of calcium-containing zeolites, *i.e.*, scolecite, mesolite, and thomsonite.[9] The $Q_i = f(T)$ curve over the temperature range from 200 to 500 °C can be arbitrarily divided in two portions: 200—350 °C and 350—500 °C. In the first portion, the heat of immersion sharply decreases, and in the second portion, it remains almost constant. The curve of the relative amount of absorbed water changes with the temperature in parallel with the Q_i *vs.* T curve.

Thus, in the course of formation of the hydroxyl groups in natrolite, the irreversible deformation of its structure occurs, *i.e.*, the ammonium form of natrolite is thermally unstable.

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Condensation of nitriles of polyhalogenated carboxylic acids and benzonitrile with 2-hydroxy-4,6-dimethylacetophenone

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Condensation of 2-hydroxy-4,6-dimethylacetophenone with trifluoro- and trichloroacetonitriles gives 2-amino-5,7-dimethyl-2-trifluoro(trichloro)methyl-4-chromanones. The condensation with 2,2,3,3-tetrafluoropropionitrile, perfluorovaleronitrile, and benzonitrile stops at the stage of formation of the corresponding enamines.

Key words: condensation, nitriles of polyhalogenated carboxylic acids, 2-hydroxy-4,6-dimethylacetophenone, ring-chain isomerism; enaminones, chromanones, chromones.

We have previously shown[1] that 2-hydroxyacetophenone reacts with trifluoro- and trichloroacetonitriles in the presence of *N*-ethylanilinomagnesium bromide to form enaminones in the form of *Z*-isomers with coplanar *s-cis*-conformation stabilized by intramolecular hydrogen bonds. 2-Acetyl-1-naphthol reacts similarly, and in this case, the reaction is accompanied by partial cyclization of the resulting enaminone to 2-amino-2-trifluoro(trichloro)methyl-5,6-benzo-4-chromanones.[2]

We found a new example of ring-chain isomerism in the aromatic β-hydroxyenaminone series, when we studied the reaction of nitriles of halogenated carboxylic acids with 2-hydroxy-4,6-dimethylacetophenone. Condensation of this ketone with trifluoroacetonitrile gave a mixture (approximately 1 : 1) of ring-chain isomers, 3-amino-1-(2-hydroxy-4,6-dimethylphenyl)-4,4,4-trifluorobut-2-en-1-one (**1a**) and 2-amino-5,7-dimethyl-2-trifluoromethyl-4-chromanone (**2a**), in a total yield of

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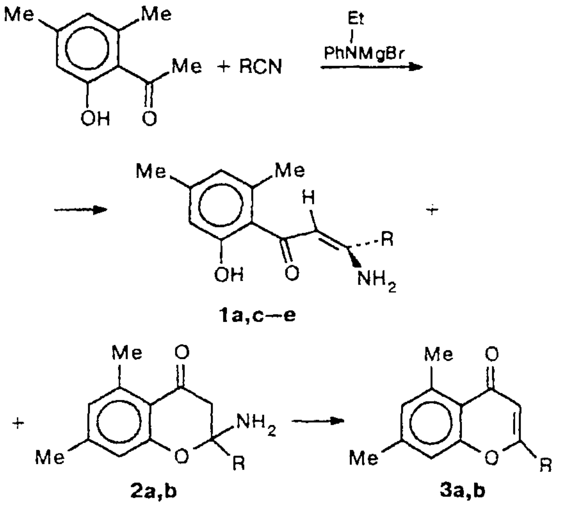
40%, which were separated by recrystallization from ethanol. The product of the reaction of 2-hydroxy-4,6-dimethylacetophenone with trichloroacetonitrile cyclizes much faster, and we isolated it only in the form of aminochromanone (**2b**) in 33%. When gaseous HCl was passed through ether solutions of aminochromanones **2a,b**, chromones **3a,b** were formed in almost quantitative yields.



R = CF_3 (**a**), CCl_3 (**b**), $(CF_2)_2H$ (**c**), C_4F_9 (**d**), C_6H_5 (**e**)

Cyclization of the initially formed enaminones **1a,b** to chromanones **2a,b** is attributed to the fact that in this case the formation of the conformers in which the enone moiety is coplanar to the benzene ring is impossible because of interaction of the *ortho*-methyl group with the hydrogen atom at the C=C bond of the enamine moiety. This causes weakening of an intramolecular hydrogen bond in the hydroxyketone moiety and favors the cyclization.

The length of the polyfluoroalkyl substituent at the double bond of compounds of the type **1** is also of great importance, because the reaction of 2-hydroxy-4,6-dimethylacetophenone with 2,2,3,3-tetrafluoropropionitrile gives only enaminone **1c** in 46% yield, which is stable on storage and is not transformed spontaneously into the corresponding chromanone. The reactions with perfluorovaleronitrile and benzonitrile also give only compounds **1d,e**, but in very low yield (3—5%).

Experimental

IR spectra were obtained on an IKS-29 instrument in Nujol. ^1H NMR spectra were recorded on a Tesla BS-567A spectrometer (100 MHz) in $CDCl_3$ with $SiMe_4$ as the internal standard.

Yields, elemental analysis, and spectral data of the synthesized compounds are presented in Table 1. The condensation of 2-hydroxy-4,6-dimethylacetophenone with nitriles was carried out according to a known procedure[3] using twice the

Table 1. Yields, melting points, elemental analysis, ^1H NMR, and IR spectra data for compounds **1a,c—e**, **2a,b**, and **3a,b**

Compound	Yield (%)	M.p./°C	Molecular formula	Found/Calculated (%)		^1H NMR, δ (J/Hz)	IR, ν/cm^{-1}
				C	H		
1a	21	86—87	$C_{12}H_{12}F_3NO_2$	55.66 55.60	4.78 4.67	2.25 (s, 3 H, CH_3); 2.48 (s, 3 H, CH_3); 5.94 (s, 1 H, =CH); 6.54, 6.60 (both s, 2 H, C_6H_2); 7.3 (br.s, 2 H, NH_2); 11.11 (s, 1 H, OH)	3410, 3305, 1620, 1565, 1540
1c	46	91—92	$C_{13}H_{13}F_4NO_2$	53.54 53.61	4.62 4.50	2.25 (s, 3 H, CH_3); 2.47 (s, 3 H, CH_3); 5.83 (s, 1 H, =CH); 5.87 (tt, 1 H, CHF_2, $^2J_{H,F}$ = 53.6, ^3J = 3.0); 6.54, 6.60 (both s, 2 H, C_6H_2); 7.5 (br.s, 2 H, NH_2); 11.16 (s, 1 H, OH)	3405, 3300, 3195,1670, 1625, 1570, 1555
1d	3	98—99	$C_{15}H_{12}F_9NO_2$	43.78 44.01	3.23 2.96	2.21 (s, 3 H, CH_3); 2.24 (s, 3 H, CH_3); 6.14 (s, 1 H, =CH); 6.75, 7.36 (both s, 2 H, C_6H_2); 7.5 (br.s, 2 H, NH_2); 12.46 (s, 1 H, OH)	3475, 3440, 3280, 1640, 1575, 1540
1e	5	139—140	$C_{17}H_{17}NO_2$	76.61 76.38	6.58 6.41	2.25 (s, 3 H, CH_3); 2.54 (s, 3 H, CH_3); 5.80 (s, 1 H, =CH); 6.54, 6.61 (both s, 2 H, C_6H_2); 7.4—7.6 (m, 5 H, C_6H_5); 5.6, 10.3 (br. s, 2 H, NH_2); 11.4 (br.s, 1 H, OH)	3455, 3400, 3280, 1600, 1570, 1540
2a	19*	103—104	$C_{12}H_{12}F_3NO_2$	55.81 55.60	4.49 4.67	2.30 (s, 3 H, CH_3); 2.59 (s, 3 H, CH_3); 2.27 (s, 2 H, NH_2); 2.74, 3.14 (both d, 2 H, CH_2, J = 16.0); 6.69 (s, 2 H, C_6H_2)	3430, 3340, 3255, 1685, 1625, 1575
2b	33	162—163	$C_{12}H_{12}Cl_3NO_2$	46.84 46.71	4.05 3.92	2.32 (s, 3 H, CH_3); 2.62 (s, 3 H, CH_3); 2.43 (s, 2 H, NH_2); 2,97, 3.51 (both d, 2 H, CH_2, J = 16.0); 6.71, 6.76 (both s, 2 H, C_6H_2)	3460, 3360, 1695, 1620, 1575
3a	94	104—105	$C_{12}H_9F_3O_2$	59.44 59.51	3.82 3.75	2.43 (s, 3 H, CH_3); 2.79 (s, 3 H, CH_3); 6.59 (s, 1 H, =CH); 7.01, 7.16 (both s, 2 H, C_6H_2)	1675, 1650, 1620
3b	96	174—175	$C_{12}H_9Cl_3O_2$	49.30 49.43	3.14 3.11	2.44 (s, 3 H, CH_3); 2.80 (s, 3 H, CH_3); 6.86 (s, 1 H, =CH); 7.00, 7.22 (both s, 2 H, C_6H_2)	1660, 1635, 1620

* Compound **2a** contains 4% chromone **3a** (according to ^{19}F NMR spectral data).

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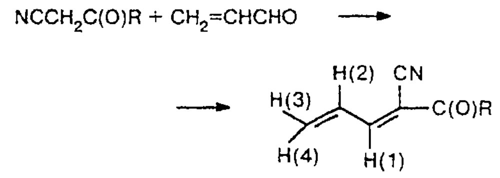
Knoevenagel condensation of acrolein with $NCCH_2COOK$ or $NCCH_2CONH_2$ in 1 *M* aqueous solutions of K and Na phosphates gave 2-cyanopenta-(2*E*,4)-dienoic acid and its amide, respectively.

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).



1, 2

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