Table I. Color, Yield, and Some IR (cm^{-1}) Bands

compound[a]	color	yield, %	in-plane ring defrmn mode
$[Cr(NO)(CN)_2(2\text{-}VPY)_2(H_2O)]$	yellow	50	1010[b]
$[Cr(NO)(CN)_2(4\text{-}VPY)_2(H_2O)]$	yellow	52	1025[b]
$[Cr(NO)(CN)_2(2\text{-}PYA)_2(H_2O)]$	yellow	50	650
$[Cr(NO)(CN)_2(3\text{-}PYA)_2(H_2O)]$	yellow	55	660
$[Cr(NO)(CN)_2(4\text{-}PYA)_2(H_2O)]$	yellow	58	662
$[Cr(NO)(CN)_2(PYAM)_2(H_2O)]$	brownish yellow	52	645

[a] VPY = vinylpyridine; PYA = pyridinaldoxime; PYAM = pyridin-2-amidoxime. [b] Pyridine ring breathing vibration.

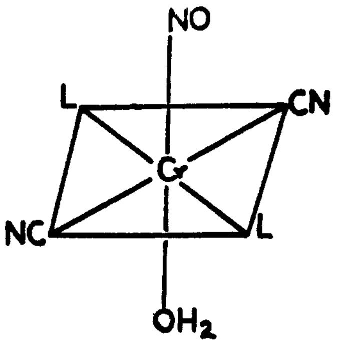

Figure 1. Proposed structure for $[CrNO(CN)_2(L)_2(H_2O)]$.

sured. The compounds were characterized on the basis of the following results.

(*I*) ***Infrared Spectra.*** Some infrared spectral bands for the complexes are given in Table I. The appearance of a very strong band in 1705–1720-cm^{-1} region and a strong band in the 2150–2190-cm^{-1} region are assigned to $\nu(NO)^+$ and $\nu(CN)$ modes, respectively, which are in accordance with the assignment made for the other reported compounds (*8*, *12*).

(***II***) ***Thermogravimetric Analysis.*** The weight loss observed by TGA at 120 ± 5 °C corresponds to the elimination of one molecule of water (*7*, *15*) and further supports the presence of one molecule of the coordinated water in the complexes.

(***III***) ***Magnetic Studies and ESR Spectra.*** The magnetic moments, 1.70–1.74 μ_B, at room temperature and g values, 1.982–1.986, of powdered samples, which are comparable to the observations made by Manoharan and Gray (*16*) and Meriwether et al. (*17*), consistent with a low-spin d^5 configuration of chromium(I).

The satisfactory analytical data and all the above results suggest the formulation of these complexes as $[Cr(NO)(CN)_2(L)_2(H_2O)]$ (Figure 1). Thus it is reasonable to propose an octahedral geometry (*4*, *7*) for these compounds.

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Registry No. $[Cr(NO)(CN)_2(2\text{-}VPY)_2(H_2O)]$, 112817-22-8; $[Cr(NO)(CN)_2(4\text{-}VPY)_2(H_2O)]$, 112817-23-9; $[Cr(NO)(CN)_2(2\text{-}PYA)_2(H_2O)]$, 112839-67-5; $[Cr(NO)(CN)_2(3\text{-}PYA)_2(H_2O)]$, 112839-68-6; $[Cr(NO)(CN)_2(4\text{-}PYA)_2(H_2O)]$, 112839-69-7; $[Cr(NO)(CN)_2(PYAM)_2(H_2O)]$, 112817-24-0; $K_3[Cr(NO)(CN)_5]$, 14100-08-4.

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Syntheses of 1-Phenyl-2-(4-pyrimidinyl)ethanone and Related Ethanones

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Eleven 1-phenyl-2-(4-pyrimidinyl)ethanones were synthesized by the condensation of 4-methylpyrimidine and the requisite methyl benzoate ester with sodium hydride as the condensing agent. Substituents in the 3- and 4-position of the phenyl ring were chloro, dimethylamino, methoxy, methyl, and trifluoromethyl.

In connection with our interest in enolizable ketones (*1*) we recently had need of some 1-phenyl-2-(4-pyrimidinyl)ethanones which carried substituents in the 3- or 4-position of the phenyl moiety, the substituents being chloro, dimethylamino, methoxy, methyl, and trifluoromethyl. The parent compound as well as the 3-chloro, 4-chloro, 3-methoxy, and 4-methoxy compounds have been prepared by Fauran et al. (*2*). The method of Rauch

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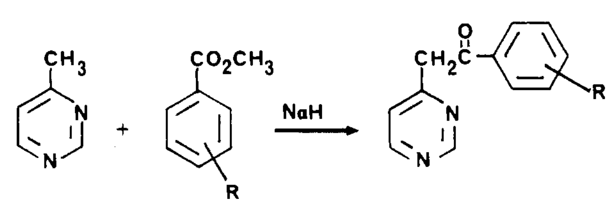

Figure 1.

Table I. 1-Phenyl-2-(4-pyrimidinyl)ethanones[a]

R	% yield	mp, °C	enol/keto ratio
H	79	92.5–93.5[b]	2.4
3-Cl	98	134–135[c]	4.6
4-Cl	78	108.5–110[d]	3.2
3-$(CH_3)_2N$	73	80.0–81.5	1.3
4-$(CH_3)_2N$	93	174.5–176.5	0.1
3-CH_3O	88	74.5–76.5[e]	2.5
4-CH_3O	83	96.5–97.5[f]	0.6
3-CH_3	49	63.5–65	2.5
4-CH_3	94	92.5–93.5	1.4
3-CF_3	89	105–106	9.7
4-CF_3	79	96.5–97.5	7.4

[a] Elemental analyses for C, H, N, F, and Cl in agreement with theoretical values were obtained and submitted for review. [b] Reported mp 96 °C (*2*). [c] Reported mp 134 °C (*2*). [d] Reported mp 109 °C (*2*). [e] Reported mp 134 °C (*2*). [f] Reported mp 88 °C (*2*).

et al. (*3*) was found to be a suitable procedure to produce the requisite ketones in adequate yield (Figure 1).

Table I lists the 1-phenyl-2-(4-pyrimidinyl)ethanones prepared as well as their melting points, yields, and enol/keto ratios.

Experimental Section

The 4-methylpyrimidine was obtained commercially. The substituted benzoic acids were obtained commercially and were converted into the individual methyl esters by the method of Clinton and Laskowski (*4*). Elemental analyses were performed by Huffman Microanalytical Laboratories, Wheatridge, CO 80033. Melting points were determined on a Thomas-Hoover melting point apparatus and were corrected. Yields represent single preparations and the yields increased as experience in the preparations was gained. The following example will illustrate the synthesis of 1-phenyl-2-(4-pyrimidinyl)ethanones.

For 1-(3-trifluoromethylphenyl)-2-(4-pyrimidinyl)ethanone, 15 mL of anhydrous toluene and 4.80 g (0.10 mol) of sodium hydride (50% oil dispersion) were placed in a stirred flask. 4-Methylpyrimidine, 1.88 g (0.02 mol) in 14 mL of anhydrous toluene, was added, and the reaction mixture was heated to 70 °C. A solution of 4.08 g (0.02 mol) of methyl 3-trifluoromethylbenzoate in 14 mL of anhydrous toluene was added dropwise while maintaining the temperature at approximately 70 °C. The reaction mixture was heated to reflux, refluxed overnight, and cooled in an ice bath. Acetic acid (3 mL) was cautiously added dropwise, followed by 6 mL of a 50–50 acetic acid–water mixture, added in a similar manner. With caution initially, 20 mL of water was then added to the reaction mixture. If at this point some of the sodium salt of 1-(3-trifluoromethylphenyl)-2-(4-pyrimidinyl)ethanone had not completely dissolved, it was dissolved by the addition of a small amount of acetic acid. The toluene layer was separated, washed with saturated $NaHCO_3$ solution, water, dried, and rotary evaporated resulting in the formation of the product. A total quantity of 4.74 g (89% yield) of 1-(3-trifluoromethylphenyl)-2-(4-pyrimidinyl)ethanone was obtained, which after several recrystallizations from toluene had a melting point of 105–106 °C. The NMR spectrum in $DCCl_3$ showed the following assignments: a multiplet at δ 8.65–6.77 for the aromatic protons: a singlet at δ 5.83 for the methine proton (enol); a singlet at δ 4.31 for the methylene proton (keto). Me_4Si was used as an internal standard; the chemical shifts are reported in parts per million relative to it in all cases. Several integrations of the methine signal and the methylene signal were performed, using the following formula: 2 × (area of enol proton)/(area of methylene protons) gave an enol/keto ratio of approximately 9.7. Elemental analysis for C, H, N, F, and Cl in agreement with theoretical values were obtained and submitted for review.

Registry No. PhC(O)OMe, 93-58-3; *m*-$ClC_6H_4C(O)OMe$, 2905-65-9; *p*-$ClC_6H_4C(O)OMe$, 1126-46-1; *m*-$Me_2NC_6H_4C(O)OMe$, 16518-64-2; *p*-$Me_2NC_6H_4C(O)OMe$, 1202-25-1; *m*-$MeOC_6H_4C(O)OMe$, 5368-81-0; *p*-$MeOC_6H_4C(O)OMe$, 121-98-2; *m*-$MeC_6H_4C(O)OMe$, 99-36-5; *p*-$MeC_6H_4C(O)OMe$, 5118-31-0; *m*-$CF_3C_6H_4C(O)OMe$, 2557-13-3; *p*-$CF_3C_6H_4C(O)OMe$, 2967-66-0; 1-phenyl-2-(4-pyrimidinyl)ethenol, 112815-91-5; 1-(3-chlorophenyl)-2-(4-pyrimidinyl)ethenol, 112815-92-6; 1-(4-chlorophenyl)-2-(4-pyrimidinyl)ethanol, 112815-93-7; 1-[3-(dimethylamino)phenyl]-2-(4-pyrimidinyl)ethenol, 112815-94-8; 1-[4-(dimethylamino)phenyl]-2-(4-pyrimidinyl)ethenol, 112815-95-9; 1-(3-methoxyphenyl)-2-(4-pyrimidinyl)ethenol, 112815-96-0; 1-(4-methoxyphenyl)-2-(4-pyrimidinyl)ethenol, 112815-97-1; 1-(3-methylphenyl)-2-(4-pyrimidinyl)ethenol, 112815-98-2; 1-(4-methylphenyl)-2-(4-pyrimidinyl)ethenol, 112815-99-3; 1-[3-(trifluoromethyl)phenyl]-2-(4-pyrimidinyl)ethenol, 112816-00-9; 1-[4-(trifluoromethyl)phenyl]-2-(4-pyrimidinyl)ethenol, 112816-01-0; 1-phenyl-2-(4-pyrimidinyl)ethanone, 36912-83-1; 1-(3-chlorophenyl)-2-(4-pyrimidinyl)ethanone, 36827-96-0; 1-(4-chlorophenyl)-2-(4-pyrimidinyl)ethanone, 36827-93-7; 1-[3-(dimethylamino)phenyl]-2-(4-pyrimidinyl)ethanone, 112816-02-1; 1-[4-(dimethylamino)phenyl]-2-(4-pyrimidinyl)ethanone, 112816-03-2; 1-(3-methoxyphenyl)-2-(4-pyrimidinyl)ethanone, 36827-97-1; 1-(4-methoxyphenyl)-2-(4-pyrimidinyl)ethanone, 36827-95-9; 1-(3-methylphenyl)-2-(4-pyrimidinyl)ethanone, 112816-04-3; 1-(4-methylphenyl)-2-(4-pyrimidinyl)ethanone, 112816-05-4; 1-[3-(trifluoromethyl)phenyl]-2-(4-pyrimidinyl)ethanone, 112816-06-5; 1-[4-(trifluoromethyl)phenyl]-2-(4-pyrimidinyl)ethanone, 112816-07-6; 4-methylpyrimidine, 3438-46-8.

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