

HIGH VALENT CHROMIUM HETEROCYCLIC COMPLEXES-I NAPHTHYRIDINIUM AND PYRAZINIUM CHLOROCHROMATES

Harry B. Davis, Roger M. Sheets, Jeanne M. Brannfors, William W. Paudler
and Gary L. Gard*

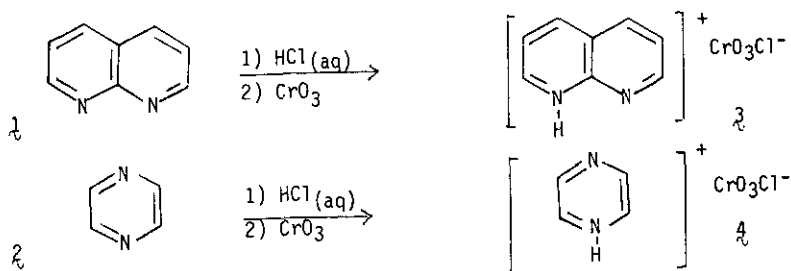
Department of Chemistry, Portland State University, Portland, Oregon 97207

Abstract -- The new mild oxidizing agents, 1,8-naphthyridinium chlorochromate (NapCC) and pyrazinium chlorochromate (PzCC) have been prepared and characterized. A study of the oxidative behavior of NapCC and PzCC relative to pyridinium chlorochromate (PCC) with primary and secondary alcohols is reported.

There are currently a large number of oxidizing agents available for the conversion of alcohols to carbonyl compounds. A major interest in this area has involved the preparation and use of oxidizing agents which function as mild oxidants and afford easy separation of the unreacted and reacted oxidizing agent from the desired products. The dipyridine-chromium(VI) oxide complex¹ and the pyridinium chlorochromate complex (PCC)² have been studied extensively for such purposes. More recently the 2,2-bipyridinium chlorochromate complex has been utilized as a convenient oxidizing agent.³

We wish to report two new chlorochromate complexes, 1,8-naphthyridinium chlorochromate ($C_8H_6N_2HCrO_3Cl$) (**3**) and pyrazinium chlorochromate ($C_4H_4N_2HCrO_3Cl$) (**4**). These mild oxidizing agents are easily prepared and readily separable from the desired organic products and are milder oxidants than PCC.

The naphthyridinium chlorochromate (NapCC) (**3**) and pyrazinium chlorochromate (PzCC) (**4**) complexes are formed as solid crystalline precipitates upon addition of an aqueous solution of CrO_3 , containing at least a molar equivalent of HCl, to an aqueous solution at 0°C containing one molar equivalent of HCl and 1,8-naphthyridine (**1**) or pyrazine (**2**), respectively.



Both of these new solid products (3,4) are stable, non-hygroscopic, and have shelf lives of at least three months when stored in the dark.

NapCC and PzCC are insoluble in CH_2Cl_2 , CCl_4 , and $(\text{CH}_3\text{CH}_2)_2\text{O}$. NapCC is soluble in pyridine, $(\text{CH}_3)_2\text{SO}$, CH_3CN , and H_2O and while PzCC is soluble in H_2O and CH_3CN , it readily exchanges with pyridine forming the corresponding pyridinium chlorochromate and free pyrazine.

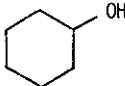
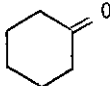
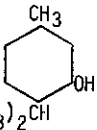
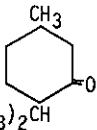
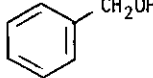
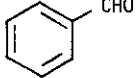
The infrared absorption frequencies for the chlorochromate group at 937 , 898 and 419 cm^{-1} in naphthyridinium chlorochromate and at 938 , 901 and 423 cm^{-1} in pyrazinium chlorochromate are attributable to ν asym (Cr-O), ν sym (Cr-O), and ν (Cr-Cl), respectively. These assignments are in accord with those found for KCrO_3Cl .⁴

Further verification for the presence of the CrO_3Cl^- group in these compounds is shown by their characteristic uv/vis spectrum. We have found for both new compounds a weak band at about 450 nm , strong bands which extend beyond 300 nm and an intervening band with a partially resolved vibrational spectrum. These results are in close agreement for other systems containing the chlorochromate group.⁵ For example, salts containing the ClCrO_3^- group typically display three distinct bands in their visible and near-ultraviolet spectra - there is a weak band at about 450 nm and the edge of a very strong, broad band which extends beyond 300 nm ; the intervening band (oxygen to chromium charge transfer) exhibits a partially resolved vibrational progression due to excitation of a symmetric stretching mode in the CrO_3 group. Also, it has been found that the CrO_3Cl^- group shows a total lack of spectral dependence on the cation.⁵

The infrared and uv/vis spectra for both chlorochromate complexes show the presence of the ClCrO_3^- anion. The corresponding cations would be $\text{C}_8\text{H}_6\text{N}_2\text{H}^+$ and $\text{C}_4\text{H}_4\text{N}_2\text{H}^+$, respectively. The uv spectrum, below 300 nm , of $\text{C}_8\text{H}_6\text{N}_2$ and HCl in CH_3CN is similar to that found for $\text{C}_8\text{H}_6\text{N}_2\text{HCrO}_3\text{Cl}$ in CH_3CN and strongly supports the presence of the $\text{C}_8\text{H}_6\text{N}_2\text{H}^+$ cation. The uv spectrum, below 330 nm , for $\text{C}_4\text{H}_4\text{N}_2\text{HCrO}_3\text{Cl}$ in CH_3CN is essentially that found for pyrazine in CH_3CN and is attributable to the weakly basic nature of pyrazine, (pK_a 0.65).

A study of the oxidative behavior of NapCC and PzCC relative to pyridinium chlorochromate (PCC) with primary and secondary alcohols was undertaken. The results, which are presented in Table I, show that PzCC is a much milder oxidant than PCC and that NapCC is milder than PzCC. Treatment of primary or secondary alcohols with either NapCC or PzCC in CH_2Cl_2 yields the corresponding aldehyde or ketone, respectively. No evidence was found for the further oxidation of an aldehyde to the corresponding carboxylic acid.

TABLE I
OXIDATION REACTIONS OF SOME SELECTED ALCOHOLS

REACTANT	PRODUCT	NapCC		PzCC		PCC	
		%	hr	%	hr	%	hr
		<u>conv time</u>		<u>conv time</u>		<u>conv time</u>	
CH ₃ CH ₂ CH ₂ OH	CH ₃ CH ₂ CHO	84	23.5 (5.7) ^a	100	5.3 (1.8)	86	0.08 (<0.1)
		38	6.0 (9.8)	96.6	7.6 (3.2)	97	0.67 (0.4)
		67	7.3 (4.7)	82	6.7 (3.1)	90	0.23 (0.1)
		81	6.25 (1.8)	91.5	2.8 (1.2)	100	0.17 (<0.1)
CH ₂ =CHCH ₂ OH*	CH ₂ =CHCHO	71	4.7 (2.9)	97	5.6 (2.9)	57	0.08 (<0.1)

* NapCC failed to oxidize cyclohexene and allyl benzene.

a Numbers in parentheses refer to time elapsed to accomplish 50% conversion.

EXPERIMENTAL

Chemicals and Equipment -- Chromium trioxide purchased from Baker Chemical Company was dried under vacuum ($\sim 10^{-3}$ torr) at 150°C for 4 h prior to its use. Pyrazine and allyl alcohol were obtained from Aldrich Chemical Company. 1,8-Naphthyridine was prepared by literature methods.⁶ Benzyl alcohol was obtained from Eastman Organic Chemicals; 1-propanol, cyclohexanol, and acetonitrile (ChromAR) were obtained from Mallinkrodt Chemical Works. Menthol was obtained from the Blumauer-Frank Drug Company and was found to be pure.

Infrared spectra were recorded on a Perkin Elmer 467 spectrometer. UV/Vis spectra were recorded in acetonitrile using a Carey - Model 14 spectrometer. Product analysis and percent conversion were obtained via use of a Varian 3700 Gas Capillary Chromatograph. The capillary

column used was a 30 meter SE-54 with an O.D. of 0.8 nm. A split ratio of 90 to 1 was needed for a typical sample injection of 0.6 μ l. Column temperature was adjusted to give best possible separation within a 15 min run time. Melting points were obtained in sealed capillary tubes using a Mel-Temp apparatus. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Preparation of $C_8H_6N_2HCrO_3Cl$ -- A solution containing 170.2 mg (1.70 mmol) CrO_3 and 0.35 ml 6 M HCl (2.1 mmol) in 2 ml H_2O at room temperature, was added dropwise to a 0°C solution containing 209.1 mg (1.60 mmol) of $C_8H_6N_2$ and 0.17 ml 12 M HCl (2.04 mmol) in 1 ml H_2O . Formation of an orange material was immediate, and an additional 1-2 ml H_2O was added during the first 10 min of reaction time. The solution was then cooled to 0°C for 1 h, filtered onto a sintered glass funnel, and the collected solid was twice recrystallized from a minimum amount of acidified H_2O . The resulting fine needle-shaped crystals were dried for 48 h under vacuum ($\sim 10^{-3}$ torr). Yield, 0.3535 g (67.3%); mp 137-139°C.

The infrared spectrum has bands (cm^{-1}): 3070(w), 3033(w), 1652(mw), 1609(s), 1478(mw), 1412(mw), 1376(m), 1282(mw), 1209(mw), 1140(m), 1059(w), 942(vs), 899(s), 838(s), 784(s), 626(m), 533(w), 464(w), 422(m). The uv/vis spectrum (CH_3CN) showed peaks at 455 nm(w,b), multiplet with band center at 365 nm(m), 308 nm(s), 301 nm(s).

Anal. Calcd. for $C_8H_7N_2O_3ClCr$: C, 36.04; H, 2.65; N, 10.51; Cl, 13.30; Cr, 19.50. Found: C, 36.08; H, 2.71; N, 10.46; Cl, 13.25, Cr, 19.48.

Preparation of $C_4H_4N_2HCrO_3Cl$ -- A solution containing 230.7 mg (2.31 mmol) CrO_3 and 0.2 ml 12 M HCl (2.4 mmol) in 2 ml H_2O at room temperature was added dropwise with stirring to a solution containing 179.4 mg (2.24 mmol) $C_4H_4N_2$ and 0.19 ml 12 M HCl (2.28 mmol) in 4 ml H_2O . An orange material formed immediately upon contact of the two solutions. After addition of half of the CrO_3 solution, the 0°C solution was stirred for 5 min and the remaining CrO_3 solution was added. The solution was then stirred for 0.33 h at 0°C. The separated solid was collected on a sintered glass funnel and the material was recrystallized twice from a minimum amount of acidified H_2O . The resulting bright-orange crystals were dried under vacuum ($\sim 10^{-3}$ torr) at room temperature for 24 h. Yield, 0.2938 g (61%); mp 148-150°C.

The infrared spectrum has bands (cm^{-1}): 3120(w), 3082(mw), 3054(m), 2960(w), 2700(w,b), 2080(w), 1618(m), 1501(m), 1376(m), 1316(w), 1164(s), 1116(w), 1054(w), 1023(m), 938(vs), 901(s), 782(s), 772(s), 613(s), 423(s). The uv/vis spectrum showed peaks at 454 nm(m,b), multiplet with band center at 364 nm(m), 312 nm(m,b), 267 nm(s), 261 nm(s), 255 nm(s), 248 nm(s,sh).

Anal. Calcd. for $C_4H_5N_2O_3ClCr$: C, 22.19; H, 2.33; N, 12.94; Cl, 16.37; Cr, 24.01. Found: C, 22.32; H, 2.34; N, 13.00; Cl, 16.27; Cr, 24.05.

Oxidation Reactions Employing $C_8H_6N_2HCrO_3Cl$ and $C_4H_4N_2HCrO_3Cl$ -- In a typical reaction using 1 mmol of the alcohol and 4 mmol of the chlorochromate complex in 5 ml CH_2Cl_2 , the organic product was obtained by washing the final reaction mixture with four 5 ml (193 mmol) volumes of diethyl ether; the decanted liquid fractions were filtered, yielding a pale yellow solution. The yellow solution was extracted twice with 5 ml (556 mmol) volumes of water to remove the soluble chromium species. Finally, the desired carbonyl compound was obtained by vacuum distillation. Identification of all products was achieved by gas chromatography.

ACKNOWLEDGEMENT

We wish gratefully to acknowledge the support of the donors of the Petroleum Research Fund administered by the American Chemical Society.

REFERENCES

1. J.C. Collins, W.W. Hess, and F.J. Frank, Tetrahedron Lett., 1968, 3363.
2. E.J. Corey and J.W. Suggs, Tetrahedron Lett., 1975, 2647.
3. F.S. Guziec, Jr. and F.A. Luzzio, Synthesis, 1980, 691.
4. H. Stammreich, O. Sala, and K. Kawai, Spectrochim Acta, 1961, 17, 226.
5. D.C. McCain, J. Phys. Chem., 1975, 79, 1102.
6. W.W. Paudler and T.J. Kress, J. Org. Chem., 1967, 32, 832.

Received, 30th May, 1983