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HIGH VALENT CHROMIUM HETEROCYCLIC COMPLEXES-II: NEW SELECTIVE AND MILD OXIDANTS

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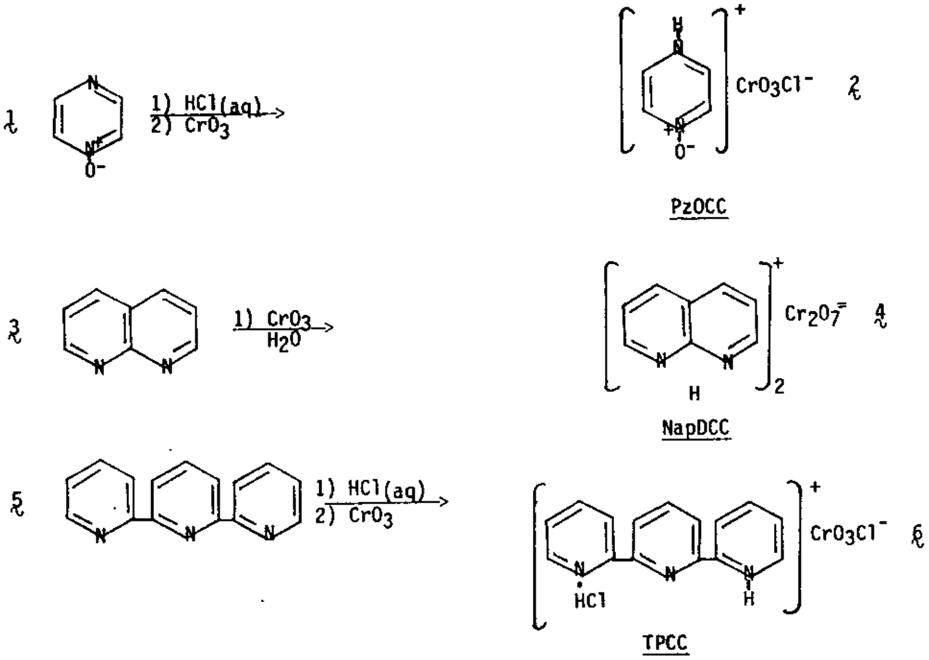
Abstract — The new mild oxidizing agents, pyrazinium-N-oxide chlorochromate (PzOCC), tripyridinium hydrochloride chlorochromate (TPCC), and naphthyridinium dichromate (NapDC) have been prepared and characterized. A study of the oxidative behavior of these new compounds relative to pyridinium chlorochromate (PCC) and bipyridinium chlorochromate (BPCC) with selected primary and secondary alcohols is reported.

Since the report by Corey and Saggs[1] of the pyridinium chlorochromate complex (PCC) and its ability to oxidize alcohols to carbonyl compounds, many reports of new chlorochromate and dichromate complexes have appeared in the literature.[2] The major focus of these investigations is concerned with the preparation of oxidizing agents which (i) produce high yields of the desired product, (2i) are stereoselective for a particular alcohol function in a multifunctional molecule, and (3i) are easily separable in the active and inactive forms from the desired product. Current approaches to achieving these goals involve the use of different organic cations to potentially impart a greater degree of stereoselectivity, the use of different solvents to enhance desirable solvent effects, and the use of polymer supported chromate complexes which provide for easy separation of the chromium species irrespective of the solvent system used.[3] All of these studies have contributed to enhancing and diversifying the applicability and usefulness of hexavalent chromium species as oxidizing agents.

We recently reported two new chlorochromate complexes, naphthyridinium chlorochromate (NapCC) and pyrazinium chlorochromate (PzCC).[2a] Both of these species, like PCC, are easily prepared, quite stable when stored dry and in the absence of light, and are active as oxidizing agents for the conversion of alcohols to carbonyl compounds.

In this paper we report three new chromate complexes, pyrazinium-N-oxide chlorochromate, (PzOCC)(**2**), naphthyridinium dichromate (NapDC)(**4**), and tripyridinium hydrochloride chlorochromate (TPCC)(**6**).

As found for the PCC, NapCC, and PzCC complexes, the three new chromate complexes are produced in good yields as orange crystalline precipitates by the addition of aqueous solutions of CrO_3 to the heterocycle; the use of 6M HCl with CrO_3 causes the formation of the chlorochromate species, while the dichromate species is formed when distilled water is used.



Both TPCC and NapDC are stable for prolonged periods of time when stored dry and in the absence of light, while PzOCC is much less stable, decomposing slowly over a two month period. All of these compounds are nonhygroscopic.

Solubility tests of PzOCC, TPCC, and NapDC in various solvents show that the three complexes are moderately to highly soluble in water and pyridine, but are insoluble in low dielectric solvents, ($(CH_3CH_2)_2O$ and CH_2Cl_2). These results are indicative of the ionic nature of PzOCC, TPCC, and NapDC, and are in good agreement with the results obtained from uv/vis and ir spectroscopic studies.

The ir absorption frequency for PzOCC at 939 cm^{-1} is attributable to the ν_{as} Cr=O stretching mode, and the bands at 901 and 437 cm^{-1} are attributable to ν_{sym} Cr=O and ν Cr-Cl, respectively. TPCC shows absorption frequencies at 940, 899, and 431 cm^{-1} attributable to ν_{as} Cr=O, ν_{sym} Cr=O, and ν Cr-Cl, respectively. For both PzOCC and TPCC, these values are in good agreement with those found for the CrO_3Cl^- anion in $KCrO_3Cl$,[4] NapCC, or PzCC.[2a]

In addition to the characteristic ir frequencies due to CrO_3Cl^-, TPCC has a broad absorption at 2740 cm^{-1} attributable to the ν NH-Cl stretching mode.[5] The ir spectrum of NapDC shows an absorption at 930 cm^{-1} attributable to ν_{as} CrO_3, while absorptions at 902 and 883 cm^{-1} are attributable to ν_{sym} CrO_3. The bands at 785 and 751 cm^{-1} are attributable to ν_{as} Cr-O-Cr, while the bands at 370 and 358 cm^{-1} are assigned as δ CrO_3. These results are in close agreement with that found for the dichromate ion in $(NH_4)_2Cr_2O_7$.[6]

The uv/vis spectra of PzOCC, TPCC, and NapDC fully support the ir spectral interpretations. For example, salts containing the CrO_3Cl^- anion typically show three distinct bands in the visible and ultraviolet regions between 450 and 300 nm.[7] Indeed, for PzOCC and TPCC, two of the three bands are found in the regions 454-455 and 359-357 nm. The third band, which is overlapped by a ligand band, is broad and extends into the ultraviolet region. For PzOCC, TPCC, and NapDC the organic heterocycle is protonated and serves as the cation.

A study was undertaken to determine the ability of PzOCC, TPCC, and NapDC to oxidize primary and secondary alcohols. The results were compared to those obtained using bipyridinium chlorochromate (BPCC), and the well known pyridinium chlorochromate (PCC). The results are presented in Table I, and show that the time required to reach 50% conversion (alcohol to respective carbonyl compound) is identical for PzOCC and PCC, but that the time required to accomplish the complete conversion is less for PCC. In general, our investigation shows that the order of decreasing oxidizing strength is PCC ≈ PzOCC > BPCC > NapDC >> TPCC.

It is interesting to note that PCC is a stronger oxidizer than BPCC which in turn is far superior to TPCC. It appears, in fact, that a limit is reached for TPCC in which the steric requirements of the large tripyridine ligand effectively prevents electron transfer and thus oxidation of the alcohol.

All of the chromate complexes show some decrease in the rate of oxidation of the alcohol with time; for NapDC this decrease in activity is much more pronounced than for the chlorochromates PCC, PzOCC, and BPCC. This is to be expected in any heterogeneous reaction as the active reaction surface of the solid reagent becomes increasingly diminished with time, thus decreasing the reaction rate. The 50% conversion times are intended to illustrate a realistic comparison of the effectiveness of the various oxidizing agents since it is likely that a fair number of active surface sites remain at that point.

Our studies have shown that NapDC converts only 17% of initial menthol to menthone, and only 18% of cyclohexanol to cyclohexanone during the time in which 60% of initial benzyl alcohol is converted to benzaldehyde. Furthermore, the 1° alcohol heptanol is only 12% oxidized during the time in which benzyl alcohol is 53% converted to the aldehyde. The new dichromate complex, NapDC, therefore is a mild, but quite selective oxidizing agent for the oxidation of benzyl alcohol to benzaldehyde.

The recently reported 4-(dimethylamino)pyridinium chlorochromate complex shows similar selectivity towards benzylic and allylic alcohols, but suffers to a limited degree from its inherent acidic character.[2c] By analogy to the pyridinium dichromate complex,[2d] NapDC may be especially useful for oxidizing benzylic alcohols which contain acid labile substituents. Work is currently in progress to determine if NapDC also shows some selectivity towards allylic alcohols, and to a wide range of benzylic alcohols.

PzOCC and NapDC failed to oxidize the aldehydes or ketones to acids, and also failed to oxidize carbon-carbon double bonds.

In addition, we have found that pyrazine and chromium trioxide in methylene chloride form a 1:1 complex, $C_4H_4N_2 \cdot CrO_3$. Preliminary experiments with this complex show it to have some oxidizing activity.

EXPERIMENTAL

Chemicals and Equipment - Chromium trioxide, purchased from Baker Chemical Company, was dried under vacuum ($\approx 10^{-3}$ torr) at 150°C for 4 h prior to its use. 1,8-Naphthyridine was prepared by literature methods.[8] Tripyridine was obtained from the G. Frederick Smith Chemical Company and was used as received. Pyrazine-N-oxide was prepared by the oxidation of pyrazine (Aldrich Chemical Company) with 30% H_2O_2 in glacial acetic acid; the crude product containing acetate ion was dissolved in NaOH solution and crystallized out of this solution; mp 109-111°C. Benzyl alcohol was obtained from Eastman Organic Company, heptanol was obtained from Matheson Coleman and Bell and was distilled prior to its use; cyclohexanol and acetonitrite (Chrom AR) were obtained from Mallinkrodt Chemical Works; menthol was obtained from the Blumauer-Frank Company and was found to be pure.

IR spectra were recorded on a Perkin Elmer 467 spectrophotometer. UV/VIS spectra were recorded in acetonitrile or water using a Cary 14 spectrophotometer. Product analysis and percent conversion were obtained via the 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 mm. A split ratio of 90 to 1 was needed for a typical sample injection of 0.6 μl. The column temperature was adjusted to give the best possible separation within a 15 min run time. Melting points (uncorrected) were obtained in sealed capillary tubes using a Mel-Temp apparatus. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Preparation of $C_4H_4N_2OHCrO_3Cl$. A solution containing 499.7 mg (5.2 mmol) $C_4H_4N_2O$ in 2 ml 6N HCl (12 mmol) at room temperature was added dropwise with stirring to a solution containing 1,350 mg (13.5 mmol) CrO_3 in 2 ml 6N HCl (12 mmol). An orange solid was formed and collected on a sintered glass funnel. The filtrate was collected and cooled to -10°C resulting in the formation of more orange solid; the solid formed was subsequently collected in the same manner. The combined solid was dried under vacuum ($\approx 10^{-3}$ torr) for 12-15 h. Yield, 851 mg (70%); mp 94°C.

The ir spectrum has bands (cm^{-1}): 3155 (m), 3080 (m, b), 3037 (m, sh), 1644 (m), 1563 (m), 1528 (w), 1503 (mw), 1464 (vs), 1349 (s), 1268 (w), 1207 (mw), 1182 (ms), 1076 (w), 1065 (mw), 1020 (mw), 939 (vs,b) 901 (s), 865 (m), 808 (s), 700 (mw), 658 (w), 544 (m), 521 (m), 491 (mw), 437 (m). The uv/vis spectrum (CH_3CN) shows peaks (nm) at 454, 359, 282 and a broad set of overlapping peaks centered at 255.

Anal. Calcd. for $C_4H_5N_2O_4ClCr$: C, 20.66; H, 2.15; N, 12.04; Cl, 15.25; Cr, 22.36. Found: C, 20.70; H, 2.34; N, 12.08; Cl, 15.46; Cr, 22.11.

Preparation of $[C_{15}H_{11}N_3H\cdot HCl]CrO_3Cl$. A solution containing 489.8 mg (2.1 mmol) tripyridine in 1 ml 6N HCl (6 mmol) at room temperature was added dropwise to a solution containing 210 mg (2.1 mmol) CrO_3 in 1 ml 6N HCl (6 mmol) over a 0.17 h period. The resulting orange solid was collected on a sintered glass funnel by suction filtration. Recrystallization from boiling H_2O yielded a bright orange solid. The solid product was dried under vacuum ($\approx 10^{-3}$ torr) for 24 h. Yield, 720 mg (85%); mp 167-169°C dec.

The ir spectrum has bands (cm^{-1}): 3096 (m), 3050 (w), 2740 (m, b), 1607 (s), 1587 (s), 1523 (s), 1468 (mw), 1446 (m), 1408 (mw), 1363 (w), 1330 (vw), 1295 (ms, sh), 1288 (s), 1257 (mw), 1237 (m), 1206 (vw), 1188 (w), 1170 (vw), 1154 (vw), 1090 (w), 1029 (w, b), 996 (mw), 940 (vs), 899 (m), 794 (w), 777 (s), 643 (vw), 612 (vw), 518 (vw), 431 (mw), 399 (vw), 380 (vw). The uv/vis spectrum (CH_3CN) shows a distinct peak (nm) at 455, overlapping peaks at 281.2, 252.4, and 226.1. A multiplet peak is centered at 357.6 and is overlapped by the very strong absorptions at 281.2 and 252.4.

Anal. Calcd. for $C_{15}H_{13}N_3O_3Cl_2Cr$: C, 44.35; H, 3.23; N, 10.34; Cl, 17.46; Cr, 12.80. Found: C, 44.93; H, 3.06; N, 10.08; Cl, 17.08; Cr, 12.94.

Preparation of $(C_8H_6N_2H)_2Cr_2O_7$. A solution containing 827 mg (0.827 mmol) CrO_3 in 1 ml H_2O was added dropwise to a rapidly stirring solution at 0°C containing 102.4 mg (0.787 mmol) $C_8H_6N_2$ in 1.5 ml H_2O. The formation of the orange solid was initially slow but increased very rapidly with time. After 2 h at 0°C the solution was filtered. The solid was then collected on a sintered glass funnel by suction filtration, and was recrystallized twice from H_2O. The resulting clean orange needle-like crystals were dried under vacuum ($\approx 10^{-3}$ torr) for 5 h. Yield: 111.6 mg (59%); mp 140-142 dec.

The ir spectrum shows bands (cm^{-1}): 3100 (mw), 3064 (mw), 3055 (mw), 3020 (w,b), 1625 (ms), 1600 (s), 1544 (ms), 1454 (mw), 1404 (m), 1373 (ms), 1350 (m), 1286 (w), 1270 (vw), 1257 (w), 1199 (m), 1147 (m), 1129 (m), 1048 (w), 1032 (mw), 1000 (w), 930 (vs, b), 902 (s, sh), 883 (s), 818 (vs, b), 785 (s), 751 (vs), 603 (m), 533 (m), 477 (w), 466 (m), 387 (m), 370 (ms), 358 (ms). The uv/vis spectrum (H_2O) (nm) shows a multiplet at 382.4, and additional peaks at 307.9, 301.2, 294.7, and 274.7.

Anal. Calcd. for $C_{16}H_{14}N_4O_7Cr_2$: C, 40.19; H, 2.93; N, 11.71; Cr, 21.75. Found: C, 40.74; H, 2.82; N, 11.81; Cr, 22.47.

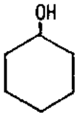
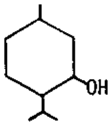
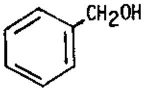
Preparation of $C_4H_4N_2 \cdot CrO_3$. 505.7 mg (5.06 mmol) CrO_3 and 499.4 mg (6.24 mmol) $C_4H_4N_2$ were placed in a single neck 50 ml round bottom flask equipped with a Teflon coated magnetic stir bar. Dry CH_2Cl_2 (20 ml) was vacuum distilled into the flask, and 1 atm N_2 was placed in the vessel. Upon removal from the vacuum line, a drying tube filled with indicator Drierite was fitted into the 19/22 ground glass joint. The solution was allowed to warm briefly to room temperature before being placed in a 0°C ice bath; the solution was stirred for 3.75 h at 0°C during which the yellow complex formed. After remaining at -78°C overnight, the solution was rapidly filtered on a sintered glass funnel and dried under vacuum ($\approx 10^{-3}$ torr), resulting in a bright yellow light sensitive solid. Yield: 502.7 mg (55%); mp > 350°C.

The ir spectrum shows bands (cm^{-1}): 3095 (m), 3042 (m), 1422 (s), 1403 (m), 1372 (w), 1172 (s), 1114 (ms), 1062 (m), 1011 (w), 928 (vs), 902 (s), 825 (ms), 767 (m), 500 (mw), 312 (s), 302 (s), 280 (ms). The uv/vis spectrum shows peaks (nm) at 382.4, 267.6, 261.8, and 255.4.

Anal. Calcd. for $C_4H_4N_2O_3Cr$: C, 26.68; H, 2.24; N, 15.56; Cr, 28.87. Found: C, 24.11; H. 2.14; N, 14.46; Cr, 30.24.

Oxidation Reactions Employing PzOCC, TPCC, NapDC, PCC, and BPCC. In a typical reaction, 1.5 ml of CH_2Cl_2 was added to 50 mg of the chromium complex (all complexes were insoluble in CH_2Cl_2). To this mixture an amount of alcohol was added (with stirring) such that the molar ratio of the chromium complex to alcohol was always 4:1, except for NapDC with heptanol and methanol (5:1); the starting time for the reaction coincided with the addition of the alcohol. Identification of organic products was accomplished by comparison of sample retention times to experimentally measured retention times of known standards.

TABLE I

REACTANT	PzOCC		TPCC		NapDC		PCC		BPCC	
	% Conv	Hour Time	% Conv	Hour Time	% Conv	Hour Time	% Conv	Hour Time	% Conv	Hour Time
$CH_3(CH_2)_5CH_2OH$	92.9	0.55 (0.1)	0.0	22.5	38.2	22	97.8	0.65 (0.06)	66.6	0.63 (0.3)
	100	0.62 (0.22)	0.0	22	18.1	6.5	97	<0.33 (0.23)	66.9	0.66 (0.3)
	97.4	0.48 (0.1)	0.0	27	78	32.2 (17.7)	90	0.23 (0.1)	93.7	2.66 (0.54)
	99	0.87 (0.09)	0.0	22	60.4	7.1 (3.2)	100	<0.17 (0.09)	73.3	0.53 (0.21)

All chromate complexes listed failed to oxidize cyclohexene.

Numbers in parentheses refer to the time elapsed to accomplish 50% conversion; these times were estimated from graphs of % conversion vs time for each alcohol. NapDC with heptanol and cyclohexanol failed to achieve 50% conversion. The $C_4H_4N_2 \cdot CrO_3$ complex readily oxidizes benzyl alcohol to benzaldehyde, 93% conversion (0.65 h).

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