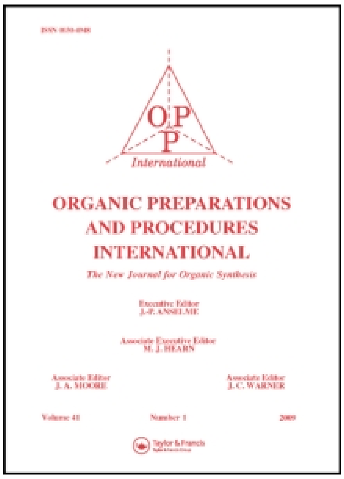

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3-CARBOXYPYRIDINIUM TRIFLUOROACETATOCHROMATE AND 3-CARBOXYPYRIDINIUM TRICHLOROACETATOCHROMATE, TWO NEW AND EFFICIENT REAGENTS FOR THE OXIDATION OF ALCOHOLS, BENZYLIC HYDROCARBONS AND POLYCYCLIC AROMATIC COMPOUNDS

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3-CARBOXYPYRIDINIUM TRIFLUOROACETATOCHROMATE AND 3-CARBOXYPYRIDINIUM TRICHLOROACETATOCHROMATE, TWO NEW AND EFFICIENT REAGENTS FOR THE OXIDATION OF ALCOHOLS, BENZYLIC HYDROCARBONS AND POLYCYCLIC AROMATIC COMPOUNDS

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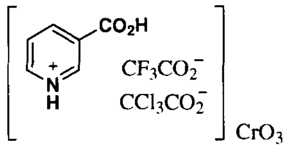
Chromium(VI) reagents are widely used for the oxidation of alcohols to carbonyl compounds.[1-9] Several oxidizing agents supported on silica gel,[10] montmorillonite K10[11] and polymer[12] are known. The application of oxochromium amine complexes as oxidants in organic synthesis was reported by Luzzio and Guziec.[13] Some of the reported reagents suffer from disadvantages such as instability, hygroscopicity, low selectivity, long reaction times, difficulty of preparation or need for a large excess of the reagent. Thus, a mild, more selective and inexpensive reagent is still in demand. We have recently introduced 3-carboxypyridinium trichloroacetatochromate (CPTCAC) as an efficient reagent for oxidation of thiols to disulfides.[14] We now report 3-carboxypyridinium trifluoroacetatochromate (CPTFAC) and CPTCAC as useful oxidizing agents for the conversion of primary, secondary and benzylic alcohols to the corresponding carbonyl compounds. They can also oxidize various benzylic hydrocarbons such as indan, tetralin, diphenylmethane, toluene, fluorene and polycyclic aromatic compounds such as anthracene and phenanthrene.



CPTFAC and CPTCAC

3-Carboxypyridinium trichloroacetatochromate (CPTCAC) was synthesized as previously described.[14] 3-Carboxypyridinium trifluoroacetatochromate (CPTFAC) was readily prepared as a stable orange compound by the addition of nicotinic acid to a solution of an equimolar amount of CrO_3 and trifluoroactic acid at 0°C. It is soluble in polar solvent such as water, dimethylformamide, dimethyl sulfoxide, acetone, ethyl acetate, acetonitrile, but insoluble in dichloromethane, benzene, carbon tetrachloride and ether. The molar conductance of CPTFAC in water at 25°C is 136 Ω^{-1} cm^2 mol^{-1} and its acidity (pH of a 0.01 M solution is 2.46) is less than both CPTCAC (pH of 0.01 M solution is 1.91)[14] and PCC (pH of a 0.01 M solution 1.75).[3] Its structure was established by infrared spectra and elemental analysis. The amount of chromium(IV) was determined by colorimetric methods using diphenylcarbazide solution.[15]

As seen from *Table 1,* the oxidation of various substrates were tested with both CPTCAC and CPTFAC. They readily oxidize alcohols (*Entries 1-11*) to the corresponding

Table 1. Oxidation of Alcohols, Benzylic Hydrocarbons and Arenes to Aldehydes and Ketones with **CPTFAC** and **CPTCAC**

Entry	Substrate	Product	Substrate to oxidant	Time (hr)	Yield (%) CPTCAC	Yield (%) CPTFAC	Yield(%) (oxidant)[d] Time[Lit]
1	*n*-Butanol	Butanal	1:1	1	90[b]	97[b]	95(QFC) 1.5 h[5]
2	*Iso-A*myl alcohol	3-Methylbutanal	1:1	1	82[b]	90[b]	----
3	1-Octanol	Octanal	1:1	2	78[b]	86[b]	75(*QnFC)* 4 h[23]
4	Benzyl alcohol	Benzaldehyde	1:1	1	85[b]	92[b]	100(PCC) 0.17 h[25]
5	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	1:1	1	80[c]	90[c]	74(*QnFC)* 3 h[23]
6	Benzoin	Benzil	1:1	1	90[c]	95[c]	98(QFC) 2 h[5]
7	2-Pentanol	2-Pentanone	1:1	1	80[b]	88[b]	----
8	Benzhydrol	Benzophenone	1:1	2	77[c]	85[c]	84(*QnFC)* 3 h[23]
9	Cyclohexanol	Cyclohexanone	1:1	2	83[b]	90[b]	72(PDC) 4 h[25]
10	Cholesterol	3-Oxocholesterol	1:1	2	65[c]	76[c]	96(PFC) 6 h[24]
11	1-Menthol	1-Menthone	1:1	1.5	72[c]	78[c]	92(PFC) 6 h[24]
12	Indan	1-Indanone	1:3	4.5	62[c]	71[c]	80(PCC) 7 h[25]
13	Tetralin	Tetralone	1:3	4.5	63[c]	69[c]	83(PCC) 8 h[25]
14	Diphenylmethane	Benzophenone	1:3	4.5	58[c]	64[c]	88(PCC) 10 h[25]
15	Fluorene	9-Fluorenone	1:3	3.0	57[c]	62[c]	89(PCC) 10 h[25]
16	Toluene	Benzaldehyde	1:3	4.5	48[b]	53[b]	89(PCC)[22]
17	Anthracene	9,10-Anthraquinone	1:3	1.5	81[c]	86[c]	72 (QFC) 3.5 h[5]
18	Phenanthrene	9,10-Phenanthrenequinone	1:3	3.0	75[c]	78[c]	60(QFC) 4 h[5]

a) Oxidations were carried out in dichloromethane at room temperature. b) Yields refer *2,4-DNP* derivatives identified by melting points. c) Yields refer to solid products whose melting points were compared with those of authentic samples (IR, TLC and NMR). d) QFC = quinolinium fluorochromate; QnFC = quinaldinium fluorochromate; PCC = Pyridinium chlorochromate; PDC = Pyridinium dichromate; PFC = Pyridinium fluorochromate.

carbonyl compounds in excellent yields as well the benzylic carbon of indane, tetralin,[16] diphenyl-methane and fluorene *(Entries 12-15)* to the ketones in good yields; toluene *(Entry 16)* was converted to the benzaldehyde, albeit in poor yield. In order to ascertain the scope of the reagents, anthracene and phenanthrene were oxidized[17] to 9,10-anthraquinone and 9,10-phenanthrenequinone in good to excellent yields using substrate/oxidant ratio, 1:3 (*Entries 17 and 18*). All products were characterized by NMR and IR spectra and comparison of their physical constants with literature data.[18] Because CPTFAC is less acidic than CPTCAC, it is not only a milder oxidizing agent but also a more powerful one.

In conclusion, we have developed a practical procedure for the oxidation of alcohols and of benzylic carbons to corresponding carbonyl compounds and of arenes to the quinones with CPTFAC and CPTCAC.[19-25] Because of the granular nature of filter cake containing reduced chromium, work-up using filtration and extraction processes is very easy.

EXPERIMENTAL SECTION

Melting points were determined with Electrothermal 9100® apparatus. IR spectra were recorded on a PERKIN ELMER Spectrum BX® model spectrophotometer. ^{1}H-NMR spectra were obtained using a 400 MHz Bruker DPX® instrument. Chromium analyses were performed using UV-1601 Shimadzu®. All products are known compounds; they were identified by comparison of their physical and spectral data with those of authentic samples. All reagents and solvents were of analytical grade apurchased from the Aldrich Chemical Company Inc. (Milwaukee, WI).

Synthesis of 3-Carboxypyridinium Trifluoroacetatochromate.- To a stirred (magnetic stirrer) solution of chromium trioxide (10.0 g, 0.1 mol) in 25 mL water was added trifluoroacetic acid (11.4 g, 0.1 mol) at 0°C. To the resultant orange red solution cooled in an ice bath, nicotinic acid (12.3 g, 0.1 mol) were added portionwise as a solid with continuous mixing. Within five minutes, the mixture became viscous and the precipitated orange solid was allowed to stand for 1 hour at 0°C. It was then collected on a sintered glass funnel and dried in vacuum desiccator over P_2O_5 to yield 30.32 g (90%), mp. 118-119°C (dec.). IR (KBr pellet): 3449, 3080, 1626, 1346, 840, 703 cm^{-1}.

Anal. Calcd. for $C_8H_6CrF_3NO_7$: C, 28.50; H, 1.79; N, 4.15, Cr, 15.43.
Found: C, 28.43, H, 1.72; N, 4.09; Cr,15.34.

General Procedure for the Oxidation by 3-Carboxypyridinium Trifluoroacetato chromate, CPTFAC in Dichloromethane.- A solution of the organic compound (10 mmol) in 10 mL dichloromethane was added to solid CPTFAC (1:1 ratio; 3.37 g, 10 mmol or 1:3 ratio; 10.11 g, 30 mmol). The mixture was stirred at ambient temperature until the complete consumption of the substrate as shown by TLC. After completion of the reaction, 50 mL of water was added to the reaction mixture and the solid material containing reduced chromium salt was removed by vacuum filtration and washed with dichloromethane (2 x 10 mL). The combined filtrate was extracted with ether (3 x 20 mL). The organic phase was dried over $MgSO_4$ and evaporated on a rotary evaporator under reduced pressure to give the product which was chromatographed over silica gel using ethyl acetate-hexane (1:4) as the eluent to separate the product. After the evaporation of the solvent, the solid products were obtained in fairly pure form. The liquid carbonyl compounds were derivatized as the 2,4-dinitrophenyl-hydrazones.

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