Short Communication

Oxidation by Polychromates

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The oligomeric chromates, potassium trichromate, $K_2Cr_3O_{10}$, (K3C), and potassium tetrachromate $K_2Cr_4O_{13}$, (K4C), are soluble in solvents such as acetone, acetonitrile, ethyl acetate, DMF and THF. Solutions of K3C or K4C in acetonitrile readily oxidized alcohols to the corresponding aldehydes or ketones in moderate to good yields.

Chromium(VI) reagents probably represent me most widely used group of oxidation agents in organic chemistry.[1] Despite the availability of a multitude of reagents for oxidation of organic molecules, chromium oxidation reagents still attract considerable interest in the continuing search for more efficient and selective oxidation agents.

Chromic acid is a common reagent usually formed from chromium trioxide, alkali chromates or dichromates. The structure of the active species in the chromic acid oxidation mixtures may vary with the reaction conditions.[2] The pH and concentration-dependent equilibria of Cr^{VI} in aqueous solution has been extensively studied.[3] The $CrO_4{}^{2-}$ ion exists above pH 8. In the pH range 2–6 the $HCrO_4{}^{-}$ and $Cr_2O_7{}^{2-}$ ions are in equilibrium. At lower pH the main species is H_2CrO_4 and at high Cr^{VI} concentrations, polychromates may be formed.[4] While many chromates and dichromates have been described, polychromates are far less numerous and appear to be limited to tri- and tetra-chromates. There is little evidence for more complex equilibria in aqueous solutions leading to the formation of polymeric chromate anions.[5] A number of tri- and tetra-chromates have been isolated and their structures determined.[6]

The mechanisms for Cr^{VI} oxidations have been extensively studied.[7] In oxidations with chromic acid, the simple chromic acid system, H_2CrO_4–$HCrO_4{}^{-}$, is usually assumed to be the active species. This may be a good approximation[8] which has also been reflected by most mechanistic studies. Oxidation with dichromates in aquous media is pH-dependent and usually performed under acidic conditions, although it has been reported that even alkali dichromates exhibit some reactivity under neutral conditions in aqueous solution.[9] Other chromium species

may be present and active in these reactions, particularly in aprotic solvents. However, to the best of our knowledge, polychromates have never been described to be of any significance for any of the reported Cr-oxidation reagents, either in papers dealing with synthetic applications or in mechanistic investigations of Cr^{VI}-species. Thus, the possibilities of their existence in the chromic oxidation agents were never discussed. As polychromate may exhibit reactivities, and mechanistic behaviour different from the monomeric species, we have initiated a study of the properties of *oligochromates*. We report here some of our findings dealing with synthetic application of $K_2Cr_3O_{10}$ and $K_2C_4rO_{13}$.

$K_2Cr_3O_{10}$ and $K_2Cr_4O_{13}$ (K3C and K4C). Potassium trichromate, K3C, and potassium tetrachromate, K4C, were prepared in good to moderate yields from aqueous solutions of $K_2Cr_2O_7$ and CrO_3 as described by Harbottle and Maddock[10] and Bauer.[11] The potassium salts were chosen as they exhibit no or little hygroscopicity in contrast with the corresponding sodium salts. As the presence of water may affect the reactivity, the anhydrous materials were also required and, in this connection, we have developed a new method for the synthesis of anhydrous potassium trichromate. For many purposes, however, K3C and K4C dried *in vacuo* over P_2O_5 work well. Chromate oligomers can be prepared by treatment of chromates with strong acids, e.g., concentrated nitric acid.[12] We found trifluoroacetic acid to be a suitable alternative. Thus, reacting potassium dichromate in trifluoroacetic acid containing 5–10 vol % of trifluoroacetic anhydride gave K3C as a red crystalline product in approx. 80% yield. An X-ray crystal structure analysis revealed indeed that the product was $K_2Cr_3O_{10}$, K3C. This compound has been studied before.[6] The polychromates were stored in closed containers at room temperature

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without any noticeable loss of activity. Surprisingly, the salts K3C and K4C were soluble in most of the high dielectric constant organic solvents, e.g., acetone, ethyl acetate, butyl acetate, acetonitrile, DMF, N,N-dimethylacetamide, TFA and nitromethane forming orange or deep red solutions. In some cases the crude anhydrous K3C reacted violently with DMSO and DMF, THF and even acetone. This is probably due to formation of some CrO_3 in TFA. The reagents were insoluble in non-polar solvents such as benzene, hexane, chlorobenzene, tetrachloromethane, chloroform and dichloromethane. The anhydrous reagent, K3C(anh), was slightly more soluble in organic solvents than either of the products from the aqueous procedures, [solubilities in acetonitrile: K3C(anh) ca. 0.20 gm l^{-1}, K3C ca. 0.08 gm l^{-1} and K4C ca. 0.11 gm l^{-1}].

Oxidation with polychromates. To the best of our knowledge the oligochromates K3C and K4C have not previously been reported as oxidizing agents in organic chemistry. Acetonitrile, ethyl acetate or acetone were found to be suitable solvents for the oxidation of alcohols. However, even in poor solvents such as chloroform, dichloromethane, hexane or benzene some oxidations took place. Oxidation of benzyl alcohol with K3C at room temperature for 2 h in a series of solvents gave the following conversions to benzaldehyde: acetonitrile (100%), ethyl acetate (100%), acetone (84%), diethyl ether (54%), heptane (44%), dichloromethane (9%) benzene (6%). Acetonitrile became the solvent of choice owing to its convenient solvent properties and because of its relative resistance to oxidation.

The performance of K3C and K4C as oxidizing agents were tested with a series of alcohols. Representative ex-

amples are shown in Table 1. The molar ratio between the organic substrate and the oxidation agent is an important parameter with respect to the practical value of an oxidation reagent. In the polychromate oxidations, we have reason to assume that the oxidation state of the chromium reagents goes from VI to IV. An X-ray spectroscopic (ESCA) study of this problem is in progress and will be reported later. In this study an approximately $0.6:1$ molar ratio between oxidant and the organic substrates for K3C was used and $0.45:1$ for K4C. In both cases this corresponded to an approximately 90% excess of the Cr-reagent.

Benzyl alcohols were readily oxidized to the aldehydes in good to moderate yields. Primary alcohols were oxidized to the corresponding aldehydes, unfortunately in moderate yields at best, although reactions were fairly clean as indicated by GLC analyses. Low yields of aldehydes may also be due to formation of Cr-salt or complexes with the substrate or product molecules. A preliminary X-ray spectroscopic investigation of the inorganic reaction products gave some indication of organo-chromium species. Geraniol (entry 7) upon oxidation gave 55% conversion into citral, but few by-products. Nerol, in a slower reaction, yielded a similar product mixture, showing that double bond Z–E isomerization can take place on oxidation of allylic alcohols. Citral was also obtained in 61% yield upon oxidation of linalool (entry 8), indicating that tertiary allylic alcohols may undergo oxidative transposition reactions. GLC analyses indicated only negligible over-oxidation to the corresponding carboxylic acids. Secondary alcohols gave consistently high yields of the corresponding ketones. Side-reactions, e.g., retro-condensation reactions, entry 6, may take place. K3C oxidized adamantane to 1-adamantanol.

Table 1. Oxidations with polychromates in acetonitrile.

Entry	Substrate	Oxidant	Molar ratio subst./Cr^{VI}	t/h	Product (yield, %)
1	4-Chlorobenzyl alcohol	K3C	1:0.64	2	4-Chlorobenzaldehyde (77)[a]
2	Benzyl alcohol	K4C	1:0.48	2	Benzaldehyde (79)[b]
3	4-Methoxybenzyl alcohol	K4C	1:0.66	2	4-Methoxybenzaldehyde (81)[b]
4	1-Phenylethanol	K3C	1:0.61	2	Acetophenone (99)[b]
5	Citronellol	K3C	1:0.65	2	Citronellal (62)[b]
6	Cinnamyl alcohol	K3C	1:0.65	2	Cinnamaldehyde (42)[a] Benzaldehyde (25)
7	Geraniol	K3C	1:0.65	6	Citral (55)[b]
8	Linalool	K3C	1:1	24	Citral (61)[c]
9	4-*tert*-Butylcyclohexanol	K3C	1:0.64	2	4-*tert*-Butylcyclohexanone (83)[b]
10	Fenchyl alcohol	K3C	1:0.66	2	Fenchone (76)[b]
11	Isoborneol	K3C	1:0.66	2	Camphor (99)[a]
12	Menthol	K4C	1:0.47	2	Menthone (84)[b]
13	Verbenol	K4C	1:0.48	2	Verbenone (77)[b]
14	4-Methyl-3-hexanol	K4C	1:0.48	2	4-Methyl-3-hexanone (82)[b]
15	α-Cyclopropyl-(4-chlorobenzyl) alcohol	K3C	1:1	2	4-Chlorophenyl cyclopropyl ketone (98)[a]
16	Adamantane	K3C	1:1.3	6	1-Adamantanol (53)[b]
17	Anthracene	K3C	1:2.6	6	Anthraquinone (83)[b]
18	Phenylmethanethiol	K3C	1:0.66	8	Dibenzyl disulfide (89)[b]

[a] GLC-yield using C_{14}-alkane as an internal standard. [b] Isolated yield. [c] The yield was based on 48% conversion.

Anthracene was converted in high yield into anthra-quinone and sulfides were oxidized cleanly to disulfides, e.g, entry 18.

In conclusion, the performance of the polychromates as oxidants were, in many cases, comparable to those of popular Cr-oxidation reagents such as PCC and PDC. However, the polychromates are considerably less expensive, the reactions are easy to handle and experimentally they are more convenient than classical reagents such as the Collins, Sarrett and chromic acid reagents.

Experimental

General. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX400 FT NMR SYSTEM NMR spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard. IR and GC–IR spectra were obtained on a Nicolet 20-SXC FT-IR (GC Carlo Erba 5160, 25 m, CP-Sil-5 CB). Mass spectra were recorded on a AEI MS-902 spectrometer at 70 eV (IP) and 200°C inlet temperature. GC measurements were performed on a Varian 3700 gas chromatograph equipped with a BP-1 capillary column (25 m).

Anhydrous K3C was prepared by adding 25 g of potassium dichromate in portions to a well stirred solution containing 75 ml of trifluoroacetic acid and 5 ml of trifluoroacetic anhydride over a 30 min period. An exothermic reaction took place. The reaction mixture was stirred overnight and the resulting deep red precipitate isolated by filtration. The anhydrous K3C formed was dried under vacuum until constant weight. The yield was 19.0 g, 85%. IR (KBr): 948, 903, 884, 827, 777, 755, 555, 520 cm^{-1}. UV–VIS (acetonitrile): λ_{max} 285 nm (ε 3200), 380 (ε 2700).

Depending on the reaction conditions the product melted in the range 200–220°C with decomposition. The melting point reported in the literature for authentic K3C was 210–215°C, (Ref. 12).

Oxidation with K3C and K4C. General procedure. To a solution containing 0.20 g, 0.5 mmol, of K3C or 0.19 g, 0.38 mmol, of K4C in 9 ml of dry acetonitrile was added dropwise a solution containing 0.8 mmol of the alcohol in 1 ml of the solvent. The reaction mixture immediately

turned dark brown and a precipitate was formed. The reaction was allowed to continue for another 2–4 h and the solvent was then removed under reduced pressure. The resulting semi-solid was then extracted with dichloromethane. The organic extract was filtered through a short column of silica gel, and concentrated under reduced pressure. Bulb-to-bulb distillation or recrystallization yielded the pure products. In all cases the chromatographic and spectroscopic properties were in total agreement with those of the authentic compounds.

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