

QUINALDINIUM AND POLY(2-VINYLBINYLQUINOLINIUM) DICHROMATES AS NEW MONOMERIC AND POLYMERIC OXIDIZING REAGENTS

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Abstract

Preparation and uses of quinaldinium dichromate and its polymeric analogue poly (2-vinylquinolinium) dichromate as the new monomeric and polymeric oxochromium-amine complex reagents for oxidizing various organic compounds, with emphasis on the latter, are described.

Introduction

Continuing interest in the development of new methods for the mild and selective oxidation of alcohols has prompted reports of many new monomeric and polymeric reagents which are effective in accomplishing this transformation. Many monomeric oxochromium-amine complexes such as chromium trioxide-pyridine complex [1], pyridinium chlorochromate [2], bipyridinium chlorochromate [3], pyridinium dichromate [4], tetrabutylammonium dichromate [5] and recently tetrakis (pyridine) silver dichromate [6], have been synthesized and used as oxidizing reagents. It has been shown that varying the amine ligand associated with the oxochromium species can change the properties and selectivities of these oxidizing reagents [7].

Several polymeric analogues of these reagents have also been developed for use in organic synthesis. These are polymer bound chromate based on commercial Amberlyst A-26 resins [8], polyvinylpyridinium chlorochromate [9], polyvinylpyridinium dichromate [10, 11], polymer supported quaternary ammonium complex chromate [12], and recently polyvinylpyridine supported silver dichromate [13], which have been used mainly for the oxidation of different types of alcohols.

These polymeric reagents are generally used in a single step reaction. Their main advantage over the

monomeric reagents is their insolubility in the reaction medium and consequently the easier separation of the products from the reaction mixture, in most cases just by a mere filtration. They are milder and often more selective than the monomeric reagents. The reactions can be driven to completion by using excess of these reagents without the fear of separating the unspent reagents or the polymeric by-products from the desired reaction products. In addition the spent polymeric reagents can usually be recovered quantitatively at the end of the reactions, and in ideal cases, they can be regenerated to their initial activities.

This paper describes the preparation and uses of quinaldinium dichromate and its polymeric analogue poly (2-vinylquinolinium) dichromate as the new monomeric and polymeric oxochromium-amine complex reagents for oxidizing various organic compounds.

Results and Discussion

Poly (2-vinylquinoline) [P2-Q] was prepared by free radical bulk polymerization of 2-vinylquinoline monomer. The monomer was synthesized by dehydration of 2-(2-hydroxyethyl) quinoline according to the methods reported in the literature [14, 15]. In the first method quinaldine was heated with phenyllithium and then condensed with formaldehyde to give the alcohol after acidification. This procedure was tedious and the alcohol could not be obtained in good yield. However, using the second method, the alcohol could be prepared easily by just refluxing a mixture of quinal-

Key words: Oxidizing reagents, Quinaldinium dichromate, poly (2-vinylquinolinium) dichromate

dine, ethanol, water and formaline for a long time. We modified this procedure by adding a few drops of piperidine to the mixture and it improved the yield and reaction time considerably.

Fixation of the dichromate anion onto the quinaldine and its polymeric analogue [P2-Q] was done by adding the latter compounds to excess of aqueous chromic anhydride solutions (> 0.05 M), according to methods reported for preparation of pyridinium dichromate and its insoluble polymeric analogue [4, 10]. In the case of [P2-Q], however, the method was modified due to the solubility behavior of this polymer. The capacity of poly (2- vinylquinolinium) dichromate [P2-QDC] was determined by atomic absorption technique and the standard iodometric titration procedure [16] and was found to be 72 mmole $\text{Cr}_2\text{O}_7^{=}$ per gram of the reagent (calculated value 1.76).

Quinaldinium dichromate [Q-DC] was soluble in DMF and slightly soluble in CH_2Cl_2 . It was completely insoluble in cyclohexane and toluene. DMF was found to be a suitable solvent for the oxidation reactions at room temperature, however the work-up of the reaction mixture was not easy. In comparison toluene was a good medium for oxidation at high temperature and the work-up of the reaction mixture was much easier due to the insolubility of the reagent. As shown in Table I, when oxidation of alcohols are carried out in DMF at room temperature or in refluxing toluene the corresponding carbonyl compounds are obtained. In the case of DMF, longer reaction times at room temperature or higher temperatures led to overoxidation. No overoxidation was obtained in refluxing toluene. In general, our preliminary studies on the efficiencies of the well known pyridinium dichromate [P-DC] with [Q-DC] showed that the latter is more stable and milder than the former.

Toluene was the solvent of choice in the case of polymeric reagent [P2-QDC], and all of the oxidation reactions were done in this medium. The chromium ions remained firmly bound to the insoluble polymer support after the oxidation reactions, a fact which makes this reagent advantageous over most monomeric reagents. The product isolation and purification were easy, simply by filtration of the reaction mixture, evaporation of the solvent and if necessary further separation of the unreacted starting material by column chromatography. As shown in table II, [P2-QDC] was effective in the oxidation of various types of hydroxy compounds such as primary and secondary benzylic and allylic alcohols and acylols to their corresponding carbonyl compounds. The reagent

selectively oxidized the benzylic hydroxy group. It could change hydroquinone to its corresponding quinone. No product of overoxidation was detected in the reaction mixture at the end of oxidation reactions (Table II).

Deoximation of several oximes to their carbonyl compounds and oxidation of thiols to their disulfides were also performed by this polymeric reagent with good yields (Table II).

In comparison to the already reported chromium (VI) based polymeric oxidants used for oxidation of alcohols, this reagent can be used in equimolar amounts with respect to the substrates [9-11]. It is non-acidic and useful for oxidation of acid sensitive compounds. No wetting of the reagent is needed prior to oxidation reactions, a fact which was reported essential in the use of polyvinylpyridinium dichromate [10]. This makes it suitable for oxidation of water sensitive compounds. Finally, our preliminary studies on crosslinked [P2-QDC], which will be reported elsewhere, has shown almost the same kind of behavior and efficiency as the linear one in oxidation of alcohols and several other organic compounds with the advantage that the spent reagent can be regenerated easily and reused several times.

Experimental Section

Quinaldin a commercial product obtained from fluka A. G. Poly (2- vinylquinoline) was prepared by free radical bulk polymerization of 2- vinylquinoline obtained from dehydration of 2- (2- hydroxyethyl) quinoline. Capacity of the polymeric reagent was determined by a standard iodometric titration procedure and atomic absorption technique using Philips Atomic Absorption Instrument. All oxidation products were known compounds and were identified by comparison of their spectra and physical data with those of the authentic sample. IR spectra were run on a Perkin Elmer IR. 157-G spectrophotometer. NMR spectra were run on a Hitachi R21-60 MHz. Melting points were determined in open capillaries with a Galen Kamp Melting Point Apparatus. The progress of reactions were followed by T. L. C. on silica gel polygram SIL G/UV 254 plates, and separation of the products were conducted on silica gel column.

2- (2- hydroxyethyl) quinoline

2- Methylquinoline (quinaldine) (200 g, 1.4 moles), formaline (180 g., 2.4 moles of formaldehyde), 2 drops of piperidine, ethanol (100 ml) and water (100 ml) were heated for 24 hrs. on a steam-bath. The solvent distilled

off, and the residue was distilled at 2-3 mm. pressure to give 2- (2- hydroxyethyl) quinoline, 140 g. (70%). m. p. 103-105°C (102-104°C) [17]. NMR (CDCl₃): 7.2-8.5 (m; 6H), 4.74 (s; 1H), 4.1-4.3 (t; 2H), and 3.9-3.3 ppm (t; 2H). IR: 3050- 3200 (b), 2900- 3100 (b), 1600 (w), 1450 (s), 1120 (w), 810 (s) and 760 cm⁻¹ (s).

2- Vinylquinoline

2 (2- Hydroxyethyl) quinoline (10g. 0.57 mole) was heated with sodium hydroxide (15g.) and N-phenyl- 2- naphthylamine (0.1g.), at 1-2 mm. Hg pressure, to give distillate of 2- vinylquinoline, 6.7g (75%). b_p 108°C/ 2mm. (120-125°C/ 7mm) [15]. NMR (CDCl₃): 8.4 (m; 8-H), 7.57 (m; 3-H, 4-H, 5-H, 6-H, 7-H), 7.23 (q; H^c), 6.33 (dd; H^b) and 5.55 ppm (dd; H^a). IR: 2200-3100 (b) 1580 (s), 1480 (s), 1300 (s), 900-100 (s), 820 (s) and 750 cm⁻¹ (s).

Poly (2- vinylquinoline) [P2-Q]

Freshly distilled 2- vinylquinoline (10.5 g, 0.1 mole) and azobisisobutyronitrile (AZBN) (0.05%), were placed in a polymerization tube. The tube was flushed with dried nitrogen and sealed under vacuum. It was then heated at 70-80°C for 24 hrs. The solid polymer was dissolved in aqueous HCL (5%) and precipitated in ammonia solution, and then was purified using chloroform / petroleum benzene, as solvent / precipitant system. The polymer was dried in vacuum at 40-50°C for 12 hrs. to give a cream coloured powder, 8.5 g (80%). Softening point 190-195°C. NMR (CDCl₃): 6.4-7 (bs; 3-4, 4-H, 5-H, 6-H, 7-H, 8-H) and 1.4-2.5 ppm (bm; -CH-CH₂-).

Poly (2- vinylquinolinium) Dichromate [P2-QDC]

Poly (2- vinylquinoline) (20g., 0.13 mole), dissolved in chloroform (30 ml) and added dropwise to a well stirred solution of chromium trioxide (30 g., 0.3 mole) in a minimum amount of water which had been diluted slowly by acetone (200 ml) at 0-5°C. The mixture was stirred for 2-3 hrs. and then refrigerated overnight. The orange precipitate was collected by simple filtration

and washed repeatedly with water until the filtrate was colourless. The reagent can be used directly without drying or can be stored in dry form 27g. (80%). The IR spectrum showed bands at 765 and 930 cm⁻¹ characteristics of dichromate ion [19]. Capacity of the reagent determined by titration and atomic absorption technique was 1.72 mmole Cr₂O₇⁼ / gram of polymer.

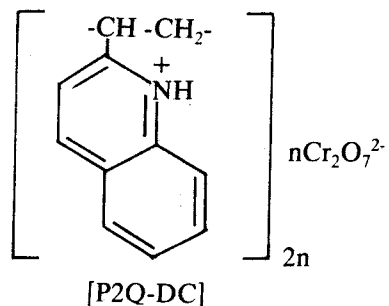
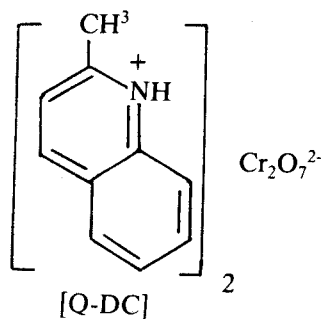
Quinaldinium dichromate [Q-DC]

2- Methylquinoline (quinaldine) (20.2 ml, 0.15 mole) is gradually added to cold solution of chromium trioxide (25g, 0.25 mole) in water (50 ml), keeping the reaction temperature under 10°C. The solution is then diluted with acetone (200 ml) and cooled to -10°C. After 2-3 hrs. the orange crystals were collected, washed with ether and dried *in vacuo*. 33 g. (88%). The IR spectrum showed bands at 765 and 930 cm⁻¹ characteristics of Cr₂O₇⁼¹⁹. This reagent was soluble in water, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) and insoluble in hexane, toluene and diethyl ether.

General procedure for oxidation of alcohols with [Q-DC]

To a solution of alcohol (2 mmole) in DMF (20 ml) in 50 ml round-bottomed flask equipped with a condenser and a magnetic stirrer, [Q-DC] (1-2 g) was added and stirred at room temperature for (1.5-5 hrs). The progress of reaction was monitored by TLC (eluent: n-hexane- ether). The reaction mixture was poured into 7-10 volumes of water and extracted with ether or ether- pentane mixture. Last traces of Cr species were easily removed by filtering an ethereal solution through a small amount of anhydrous magnesium sulfate of silica gel. The filtrate was purified on silica gel plate with appropriate eluent. Evaporation of the solvent afforded pure carbonyl compounds. (Table I).

The procedure for oxidation of alcohols with [Q-DC] in toluene was the same as above, except that the reagent is insoluble in this solvent and no extraction is needed.



General procedure for oxidation of alcohols, thiols and oximes with [P2-QDC]

To a solution of the substrate (1-3 mmole) in toluene (20 ml) in a 50 ml round-bottomed flask equipped with a condenser and a magnetic stirrer, [P2-QDC] (1-6 gr) was added and refluxed. The refluxed time was varied according to the substrate used.

The progress of reaction was monitored by TLC (eluent: n-hexane-ether). The reaction mixture was cooled to room temperature and filtered with suction.

The solid material was washed several times, once with toluene and three times with dichloromethane. The resulting material was purified on a silica gel column (or silica gel plate) with appropriate eluent. Evaporation of the solvent afforded the pure product. (Table II).

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Table I. Oxidation^(a) of different hydroxy compounds with Quinaldinium Dichromate [Q-DC] to corresponding carbonyl compounds.

No.	Substrate	Product	Time(min)	Yield%
1	Benzyl alcohol	Benzaldehyde	90 ^(b)	100
2	P-Methoxybenzyl alcohol	P-Methoxybenzaldehyde	150 ^(b)	95-100
3	1-phenyl ethanol	Acetophenone	20 ^(c)	90
4	Benzhydrol	Benzophenone	5 ^(c)	95
5	Cinnamyl alcohol	Cinnamaldehyde	240 ^(b)	90
6	Benzoine	Benzil	45 ^(c)	80
7	Piperonal	Piperonal	25 ^(c)	80
8	Mandelic Acid	Benzaldehyde	300 ^(b)	90

(a): Molar ratio of oxidant to substrate, 1:1.

(b): DMF as solvent at room temperature.

(c): In refluxed toluene.

Table II: Oxidation of different hydroxy compounds, oximes and thiols with Poly (2-vinylquinoldinium) Dichromate [P2-QDC]

No.	Substrate	Product	Oxidant/substrate	Time(hr)	Yield%
1	Benzyl alcohol	Benzaldehyde	1	0.66	90
2	Hydroquinone	Quinone	1	2	80
3	Cinnamyl alcohol	Cinnamaldehyde	1	3	75
4	Furfuryl alcohol	Forfural	1	2	80
5	4,4'-Dibromobenzoin	4,4'-Dibromobenzil	1	4	50-55
6	Furoin	Furil	1	3	75
7	1-Phenylethanol	Acetophenone	1	1.5	90
8	Benzoine	Benzil	1	4	75-80
9	Piperonal	Piperonal	1	3	70
10	Acetophenone Oxime	Acetophenone	3	10	80
11	Benzophenone Oxime	Benzophenone	3	8	90
12	Piperonaloxime	Piperonal	4	9	80-85
13	P-Methoxy benzaldoxime	P-Methoxy benzaldehyde	3	8	85
14	Ph-CH ₂ -CH ₂ -C(=NOH)-CH ₃	Ph-CH ₂ -CH ₂ -C(=O)-CH ₃	5	24	20
15	P-chlorobenzaldoxime	P-chlorobenzaldehyde	5	10	70
16	Salicylaloxime	Salicylaldehyde	3	8	80-85
17	α-Benzoin Oxime	Benzoine and Benzil	5	10	50,50
18	Benzylthiol	Benzyldisulfide	1	1.33	90
19	Thiophenol	Phenylsulfide	1	1	95
			1	1.25	85-90

(a) In refluxed toluene.

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