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3,4-Dihydroisoquinolinium Chlorochromate: A Mild and Effective Reagent for the Oxidation of Alcohols to Carbonyl Compounds and Arenes to Quinones

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A new chromium(VI) reagent, 3,4-dihydroisoqinolinium chlorochromate (DIQCC) was prepared and characterized. This reagent is suitable to oxidize various primary and secondary alcohols to the corresponding carbonyl compounds and antracene to anraquinone in a good yields.

Key Words: Dihydroisoquinolinium chlorochromate, Oxidation, alcohols, Carbony compounds, Quinones.

INTRODUCTION

Oxidation of alcohols to the corresponding carbonyl compounnds is one of the most important of all chemical transformations[1]. The represantative chromium-based reagents play a vital role in organic chemistry as oxidants for alcohols[2]. For instance, the Collins reagent[3], pyridinium chlorochromate[4], pyridinium bromochromate[5], cerium(III) bromate[6], quinolinium fluorochromate[7] have been developed for this purpose. There are several examples using supported organic molecules on solid support as a oxidizing agents such as silica gel, montmorillonite[8] K 10. Some of the reported reagents suffer from disadvantages such as instability, hygroscopicity, low selectivity, long reaction time, difficulty of preparation and need for a large excess of the reagent. Thus, a mild, a more selective and inexpensive reagent is still in demand.

Recently, we have introduced 3-carboxypyridinium trichloroacetatochromate as an efficient reagent for oxidation of thiols to disulfides[9].

In continuation of our study, we wish to report, 3,4-dihydroisoquinolinium chlorochromate a facile oxidation of primary, secondary and benzylic alcohols to their corresponding carbonyl compounds. At the same time, this reagent was used for oxidizing various arenes such as indane, tetraline, antracene, pheneanthrene compounds.

EXPERIMENTAL

Melting points were determined on Electrothermal 9100® apparatus. IR spectra were recorded on a Win First Satellite® 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 comparision of their physical and spectral data with those of authentic samples. All reagent and solvents are of reagent grade. 3,4-Diydroisoquinoiline was prepared according to literature[9].

Preparation of 3,4-dihydroisoqunolinium chlorochromate (DIQCC): A solution of CrO_3 (10 g, 0.1 mol) in 18.4 cm^3 of 6 N HCl (0.10 mol) was cooled to 0ºC and to this 3,4-dihydroisoquinoline (26.73 g, 0.10 mol) were added dropwise during 0.5 h. In five min time, red-orange solid was precipated and allowed to stand for 1 h. The cold mixture was filtered on a sintered glass funnel and the red-orange solids were collected. The product was dried in vacuum desicator over P_2O_5 to give DIQCC in 90 % yield. (m.p. 58-59ºC). IR (KBr pellet) cm^{-1} 3450, 3070, 1650, 1300, 950, 930. Anal. Calcd. for $C_9H_{10}NO_3ClCr$: C, 40.39; H, 3.77; N, 5.23. Found: C, 40.36; H, 3.73; N, 5.20. The acidity of DIQCC is at pH. 2.2 in 0.01 M aquo solution.

Oxidation of alcohols to carbonyl compounds: A solution of the organic compounds (Table-1), (10 mmol) in 10 mL of dichlorometane was added to DIQCC (Table-1, 1:1 ratio; 0.267 g, 10 mmol and 1:3 ratio; 0.801g, 30 mmol). The mixture was stirred on magnetic stirrer at room temperature until the complete consumption of the substrate. The progress of the reaction was monitored by TLC analysis. After completion of the reaction, 50 mL of water was added to the reaction mixture and extracted with ether (3 × 20 mL). The combined organic layer was dried over $MgSO_4$ and evaporated on a rotary evaporator under reduced pressure. The product was chromatographed over silica gel using ethyl acetate-hexane (1:4) as the eluent to separate the product. After evaporation of the solvent, the fairly pure solid were crystallized out the liquid carbonyl compounds were derivatized with 2,4-dinitrophenylhydrazine. The melting points of solid compounds such as benzophenone, 3-oxocholestorol, 1-menthone, 1-indanone, tetralone, 10-anthraquinone and phenanthrene-9,10-quinone were checked and these compounds were identified by spectral data like IR and ^{1}H NMR.

RESULTS AND DISCUSSION

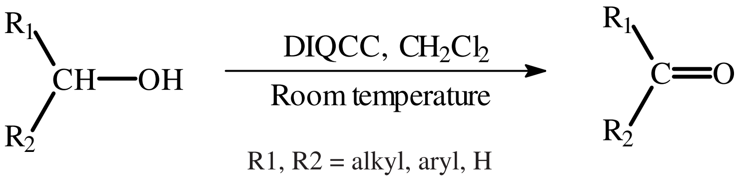
This reagent was prepared by the addition of 3,4-tetrahydroisoquinoline[10] to a solution of an equimolar amount of CrO_3 in 6 N hydrochloric acid at 0ºC and obtained in 90 % yield as an red-orange solid. DIQCC was stable when kept at room temperature for a long period of time. DIQCC is soluble in polar solvent such as water, dimethylformamide, dimethylsulfoxide, acetone, ethylacetate, acetonitrile, but insoluble in dichloromethane,

TABLE-1
OXIDATION OF ORGANIC SUBSTRATES WITH DIQCC

Entry	Substrate	Product	Substrate/ oxidant	Time (h)	Yield (%)
1	*n*-Butanol	Butanal	1:1	1	95[b]
2	*Iso*amylalcohol	3-methylbutanal	1:1	1	87[b]
3	1-octanol	Octanal	1:1	2	80[b]
4	Benzyl Alcohol	Benzaldehyde	1:1	1	90[b]
5	2-Pentanol	2-Pentanone	1:1	1	900[b]
6	Benzhydrol	Benzophenone	1:1	2	85[c]
7	Cyclohexanol	Cyclohexanone	1:1	2	85[b]
8	Cyclopentanol	Cyclopentanone	1:1	1	90[b]
9	Cholesterol	3-Oxocholesterol	1:1	2	75[c]
10	1-Menthol	1-Menthone	1:1	1.5	82[c]
11	Indan	1-Indanone	1:3	2.5	85[c]
12	Tetralin	Tetralone	1:3	4.5	73[c]
13	Anthracene	9,10-Anthraquinone	1:3	1.5	80[c]
14	Phenanthrene	Phenanthrene-9,10-quinone	1:3	3.0	75[c]

[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 isolated products melting points were taken directly and comparison with authetic samples (IR, TLC and NMR).

benzene, carbon tetrachloride and ether. The molar conductance of DIQCC in water at 25°C is 140 Ω^{-1} cm^{2} mol^{-1}. The acidity of DIQCC (pH of a 0.01 M, solution 2.02) is less than that of PCC, (pH of a 0.01 M solution 1.75)[5] and is the same acidity as CPCC (pH of 0.01 M, solution 2.02)[8].



R1, R2 = alkyl, aryl, H

Scheme-I

DIQCC readily oxidizes primary (entires 1 to 4) and secondary alcohols (entires 5 to 10) to their corresponding carbonyl compounds in an excellent yield. DIQCC also oxidizes benzylic carbon indan and tetralin[11] (entires 11 to 12) converted to ketones in a good yields. In order to ascertain the efficacy of the reagent as an oxidant, it was treated with fused ring hydrocarbon anthracene and phenanthrene[12] (entires 13 to 14). Anthracene and phenanthrene are oxidised to 9,10-anthraquinone and phenanthrene-9,10-quinone, respectively in good to excellent yields using substrate/oxidant ratio 1:3.

All products were characterized by NMR and IR spectroscopic data and their physical data compared with literature datas[13].

In conclusion, DIQCC is suitable, an inexpensive and stable solid for the oxidation of alcohols to corresponding carbonyl compounds, of benzylic carbon to those ketones and of arenes to their ketones.

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