



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

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A new chromium(VI) reagent, 3,4-dihydroisoquinolinium trichloroacetatochromate was prepared by reacting trichloroacetic acid with CrO_3 in water. This reagent is suitable to oxidize various primary and secondary alcohols to the corresponding carbonyl compounds and anthracene to anthraquinone in a good yields.

Keywords: 3,4-Dihydroisoquinolinium trichloroacetatochromate, Oxidation, Alcohols.

INTRODUCTION

The oxidation of organic substrates in aprotic solvents, under mild and neutral conditions, is important in modern organic synthesis. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists¹⁻⁷. The representative chromium-based reagents play a vital role in organic chemistry as oxidants for alcohols⁸. For instance, the Collins reagent⁹, pyridinium chlorochromate¹⁰, pyridinium bromochromate¹¹, cerium(III) bromate¹², quinolinium fluorochromate¹³ have been developed for this purpose. There are several examples using supported organic molecules on solid support as oxidizing agents such as silica gel, montmorillonite K10¹⁴.

Recently, we have introduced 3,4-dihydroisoquinolinium chlorochromate (DIQCC). As an efficient reagent for oxidation of alcohols to carbonyl compounds and arenes to their respective quinones¹⁵.

In continuation of our study, we wish to report 3,4-dihydroisoquinolinium trichloroacetatochromate, a facile oxidation reagent 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, anthracene, phenanthrene compounds.

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.

EXPERIMENTAL

Melting points were determined on Electrothermal 9100® apparatus. IR spectra were recorded on a Win First Satellite® model spectrophotometer. ¹H 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 reagent and solvents are of reagent grade. 3,4-Dihydroisoquinoline was prepared according to literature¹⁶.

Preparation of 3,4-dihydroisoquinolinium trichloroacetatochromate: A solution of CrO_3 (5 g, 0.05 mol) in water 10 mL cooled to °C was added trichloroacetic acid (8.15 g, 0.05 mol) in 50 mL glass beaker. The mixture was stirred to give a red-orange solution for 2-3 min. The solution was then cooled in an ice bath (0-5 °C) for 5 min and 3,4-dihydroisoquinoline (6.58 g, 0.05 mol) was added portion wise and the mixture was stirred at 0 °C 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 desiccator over P_2O_5 to give 3,4-dihydroisoquinolinium chlorochromate in 90 % yield. The reagent decomposes at 100 °C. IR (KBr pellet) cm^{-1} 3442, 3055, 1678, 1238, 962, 883. Anal. Calcd. For $\text{C}_{11}\text{H}_{10}\text{NO}_5\text{Cl}_3\text{Cr}$: C, 33.49; H, 2.55; N, 3.55. Found: C, 33.20; H, 2.50; N, 3.60. The acidity of 3,4-dihydroisoquinolinium chlorochromate is at pH. 2.4 in 0.01 M aqua solution.

Oxidation of alcohols to carbonyl compounds: A solution of the organic compounds (Table-1, 10 mmol) in 10 mL of dichloromethane was added to 3,4-dihydroisoquinolinium chlorochromate (Table-1, 1:1 ratio; 3.94 g, 10 mmol and 1:3 ratio; 11.83 g, 30 mmol). The mixture was stirred magnetically 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. Then 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 benzil, benzophenone, 3-oxocholesterol, 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 ^1H NMR.

TABLE-1
OXIDATION OF ORGANIC SUBSTRATES WITH
3,4-DIHYDROISOQUINOLINIUM CHLOROCHROMATE

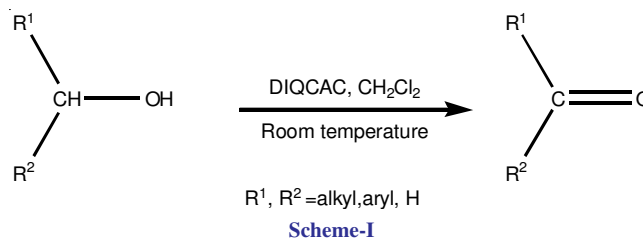
Entry	Substrate	Product ^d	Substrate /Oxidant	Time (h)	Yield (%)
1	<i>n</i> -Butanol	Butanal	1:1	0.5	98 ^b
2	Isoamylalcohol	3-Methylbutanal	1:1	0.5	90 ^b
3	1-Octanol	Octanal	1:1	0.5	85 ^b
4	Benzyl Alcohol	Benzaldehyde	1:1	0.5	90 ^b
5	2-Pentanol	2-Pentanone	1:1	0.5	93 ^b
6	Benzhydrol	Benzophenone	1:1	1	80 ^c
7	Cyclohexanol	Cyclohexanone	1:1	2	95 ^b
8	Cyclopentanol	Cyclopentanone	1:1	1	95 ^b
9	Cholesterol	3-Oxocholesterol	1:1	2	88 ^c
10	1-Menthol	1-Menthone	1:1	1	92 ^c
11	Indan	1-Indanone	1:3	2.5	85 ^c
12	Tetralin	Tetralone	1:3	2.5	75 ^c
13	Anthracene	9,10-Anthraquinone	1:3	1.5	85 ^c
14	Phenanthrene	Phenanthrene-9,10-quinone	1:3	2.0	85 ^c

Oxidations were carried out in dichloromethane at room temperature; Yields refer 2,4-DNP derivatives identified by melting points; ^bYields refer to isolated products melting points were taken directly and comparison with authentic samples (IR, TLC and NMR)

RESULTS AND DISCUSSION

This reagent was prepared by the addition of 3,4-tetrahydroisoquinoline¹⁶ to a solution of an equimolar amount of CrO_3 and trichloroacetic acid at 0 °C and obtained in 90 % yield as an orange solid. 3,4-Dihydroisoquinolinium trichloroacetatochromate was stable when kept at room temperature for a long period of time. The infrared absorption frequencies for the trichloroacetato group at 962, 883 and 722 cm^{-1} . 3,4-Dihydroisoquinolinium trichloroacetatochromate is soluble in polar solvent such as water, dimethyl formamide, dimethyl sulfoxide, acetone, ethylacetate, acetonitrile, but insoluble in dichloromethane, benzene, carbon tetrachloride and ether. The

compound is diamagnetic tested by means of magnetic susceptibility measurement. The compound decomposes at 100 °C. The molar conductance of 3,4-dihydroisoquinolinium chlorochromate in water at 25 °C is 140 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. The acidity of 3,4-dihydroisoquinolinium chlorochromate (pH of a 0.01 M, solution 2.4) is less than that of PCC, (pH of a 0.01 M solution 1.75)¹¹ and CPCC (pH of 0.01 M, solution 2.02)¹⁴.



This reagent can be stored as a solid for long periods without decomposition in dry medium. The structure of 3,4-dihydroisoquinolinium chlorochromate was determined by infrared spectra and elemental analysis. The amount of chromium(IV) was determined by colorimetric methods using diphenylcarbazide solution¹⁷. Anal. Calc. for $\text{C}_{11}\text{H}_{10}\text{NO}_5\text{Cl}_3\text{Cr}$: Cr: 15.03; Calc. 15.01.

As can be seen from Table-1, various substrates were tested with 3,4-dihydroisoquinolinium chlorochromate. 3,4-Dihydroisoquinolinium trichloroacetatochromate readily oxidizes primary (entries 1 to 4) and secondary alcohols (entries 5 to 10) to their corresponding carbonyl compounds in an excellent yield. 3,4-Dihydroisoquinolinium trichloroacetatochromate also oxidizes including benzylic carbon indan and tetralin¹⁸ (entries 11 to 12) those 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 phenanthrene¹⁹ (entries 13 to 14). Anthracene and phenanthrene are oxidized 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 ^1H NMR and IR spectroscopic data and their physical data compared with literature datas²⁰.

In conclusion, 3,4-dihydroisoquinolinium chlorochromate is suitable, an inexpensive and stable solids. We have developed a practical procedure for the oxidation of alcohols to corresponding carbonyl compounds, of benzylic carbon to those ketones and of arenes to their ketones. 3,4-Dihydroisoquinolinium trichloroacetatochromate can be easily prepared and serves as an excellent oxidizing agent for various types of alcohols, benzylic carbons and arenes under non-aqueous condition at ambient temperature. After the oxidation reaction by 3,4-dihydroisoquinolinium chlorochromate, working-up such as filtration and extraction is fairly easy due to granula reduces.

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