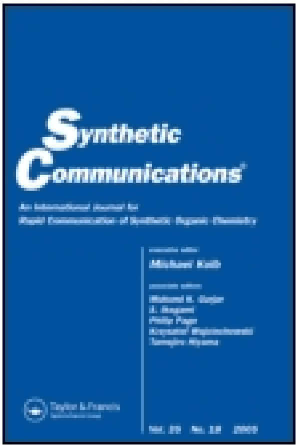

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Isoquinolinium Dichromate: A New and Selective Oxidant for Primary and Secondary Alcohols

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Isoquinolinium Dichromate: A New and Selective Oxidant for Primary and Secondary Alcohols

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Abstract: Isoquinolinium dichromate is a new versatile reagent for selective oxidation of primary and secondary alcohols under mild conditions. It also oxidises vicinal and nonvicinal diols to the corresponding α-hydroxy carbonyl compounds.

Primary and secondary alcohols have been oxidised by a variety of Cr(VI) reagents[1, 2] such as pyridine-chromium trioxide complexes[3], pyridinium chlorochromate[4], pyridinium fluorochromate[5], pyridinium dichromate[6], 2,2′-bipyridinium chlorochromate[7], quinolinium dichromate[8], quinolinium chlorochromate[9], quinolinium fluorochromate[10], isoquinolinium fluorochromate[11] etc. We have been interested in the selective oxidation of primary and secondary alcoholic groups present in the amino acid residues of collagen. Due to poor solubility of Cr(VI) reagents reported prior to pyridinium chlorochromate in water, these reagents were not useful for oxidation of collagen. However we have

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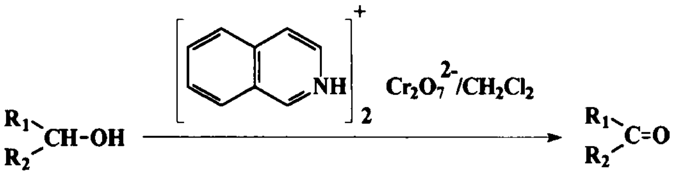
successfully used pyridinium chlorochromate for the selective oxidation of collagen[12, 13].

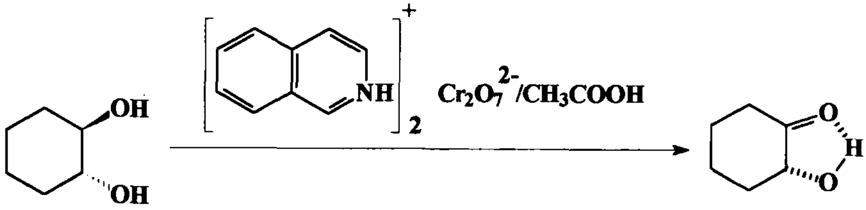
This letter reports the preparation and synthetic potential of isoquinolinium dichromate, $(C_9H_7NH^+)_2\ Cr_2O_7^{2-}$, and we have found that this reagent has certain advantages over similar oxidising agents in terms of amounts of oxidant and solvent required, selectivity in oxidation and improvement of yields.

The results obtained with isoquinolinium dichromate are very satisfactory and shows the new reagent as a valuable addition to the existing oxidising agents. Isoquinolinium dichromate in dichloromethane oxidises primary and secondary alcohols to the corresponding aldehydes or ketones in high yields (as shown in the table 1).



Isoquinolinium dichromate in methylene chloride and traces of free acid also oxidises both trans-cyclohexane diol and 1,5-pentane diol to 2-hydroxy cyclohexanone and 5-hydroxy pentanal respectively in 60% and the yields are increased to 90% by using acetic acid as the reaction medium. These oxidations are selective and yields are higher than those obtained by other oxidising agents and we used only equimolar ratio of the reagent.

Isoquinolinium dichromate, a stable orange solid, mp. 169°-170°C was prepared by dissolving CrO_3 in water, adding isoquinoline and collecting the product. The



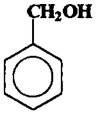
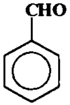
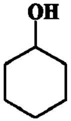
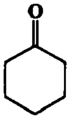
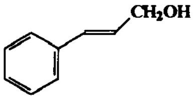
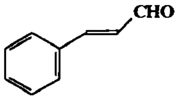
crystalline reagent can be stored in polythene containers for long periods without decomposition. The structure of the product was confirmed by elemental analysis and the infrared spectrum exhibits peaks characteristic of the dichromate ion[14]. Isoquinolinium dichromate is soluble in water, dimethylformamide and dimethylsulfoxide, sparingly soluble in methylene chloride, chloroform and insoluble in ether, ethylacetate, toluene and heptane.

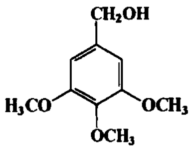
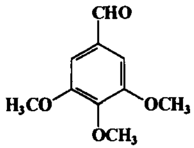
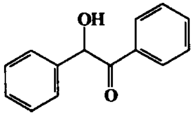
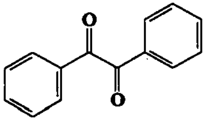
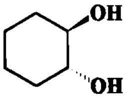
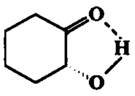
Isoquinolinium dichromate (1 molar equivalent) oxidises primary alcohols to the corresponding aldehydes in refluxing methylene chloride (6 h) and reasonably oxidises secondary alcohols to ketones. Solutions of isoquinolinium dichromate (1.5 molar equivalent) in DMF oxidises both saturated and allylic alcohols to the corresponding aldehydes. The results are tabulated in Table 1.

Isoquinolinium dichromate, $[C_9H_7NH^+]_2\ Cr_2O_7^{2-}$

Chromium (VI) oxide (30.0 g, 0.30 mol) is dissolved in water (30 ml) in a beaker cooled in ice. Isoquinoline (30 ml, 0.25 mol) is added in small portions with stirring over 30 min. The solution was diluted with 100 ml of acetone and cooled to -10°C. The orange crystalline isoquinolinium dichromate is filtered, washed with acetone, recrystallised from hot water and dried in vacuo for about 2 h. Yield : 63.5 g. (89%); m.p. 169-170°C.

Table 1: Oxidation of alcohols with Isoquinolinium Dichromate

Substrate	Product	bp (°C)	Isolated Yield (%) CH$_2$Cl$_2$	Isolated Yield (%) DMF
n-$C_7H_{15}OH$	n-$C_6H_{13}CHO$	177-179	64	60
n-$C_8H_{17}OH$	n-$C_7H_{15}CHO$	153	74	70
		171	81	77
		154	72	66
		bp$_{200}$ 198	78	71

		73-74^{m}	83	79
		95^{m}	91	90
$HOH_2C\text{-}(CH_2)_3\text{-}CH_2OH$	$HOH_2C\text{-}(CH_2)_3\text{-}CHO$	80*		90^{a}
		130^{m}		90^{a}

m : Melting point of the product. * : Melting poing of 2,4-dinitrophenylhydrazone derivative.
a : Reaction is carried out in the presence of acetic acid as a solvent.

$[C_9H_7NH^+]_2\,Cr_2O_7^{2-}$: Calc. C, 45.39; H, 3.39; N, 5.88

(476.33) found. C, 45.23; H, 3.37; N, 5.84

I.R. (KBr) : 930.03, 875.27, 765.40, 730 cm^{-1}.

The above procedure can be performed on a 200 g scale without any difficulty.

General procedure for oxidation of alcohols by isoquinolinium dichromate

(i) In methylene chloride : To a stirred suspension of isoquinolinium dichromate (4.76 g) in dichloromethane (generally 10 ml), a solution of the substrate in the minimum amount of dichloromethane is added dropwise, the molar ratio of the substrate to the oxidant being 1:1. The mixture is refluxed for about 6 h. The completion of the reaction is followed by TLC using ether/petroleum ether (60/40) as eluant. The mixture is diluted with ether (1:1 v/v) and filtered through a short column of silica gel to give a clear solution. The solution is evaporated and the residual product purified by distillation / recrystallization or column chromatography.

(ii) In DMF/Acetic acid : In the case of DMF/acetic acid as solvent, similar conditions are adopted except after stirring for 4 h. the mixture is poured into excess water, extracted with ether, dried (Na_2SO_4) and concentrated in vacuum to furnish the product.

References and Notes

1. Fieser, M.; Fieser, L. F. *Reagents for organic synthesis*, Vol. 6. Wiley-Interscience, New York, **1977**, 123.
2. House, H. O. *Modern Synthetic Reactions*, 2nd Ed. W. A. Benjamin, New York, **1972**, 257.
3. Collins, J. C.; Hess, W. W.; Frank, F. J. *Tetrahedron Lett.* **1968**, 3363.
4. Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.
5. Bhattacharjee, M. N.; Chauduri, M. K.; Dasgupta, H. S. *Synthesis* **1982**, 588.
6. Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.
7. Guziec, Jr. F. S.; Luzzio, F. A. *Synthesis* **1980**, 691.

8. Balasubramanian, K.; Prathiba, V. *Indian J. Chem. Sec. B.* **1986,** *25B*, 326.

9. Srinivasan, R.; Ramesh, C. V.; Madhulatha, W.; Balasubramanian, K. *Indian J. Chem. Sec. B.* **1996,** *35B*, 480.

10. (a) Chandrasekhar, S.; Mohanty, P. K.; Takhi, M. *J. Org. Chem.* **1997**, *62*, 2628. (b) Murugesan, V.; Pandurangan, A. *Indian J. Chem. Sec. B.* **1992,** *31(B)*, 337.

11. Srinivasan, R.; Preethi, S.; Balasubramanian, K. *Synth. Commun.* **1997**, *27*, 2051.

12. Sehgal, P. K.; Balasubramanian, K.; Joseph, K. T. *Indian J. Biochem. Biophy.* **1980,** *17*, 98.

13. Sehgal, P. K.; Balasubramanian, K.; Joseph, K. T. *Leather Science* **1984,** 38.

14. Miller, F. A.; Wilkins, C. H. *Anal. Chem.* **1952,** *24*, 1253.

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