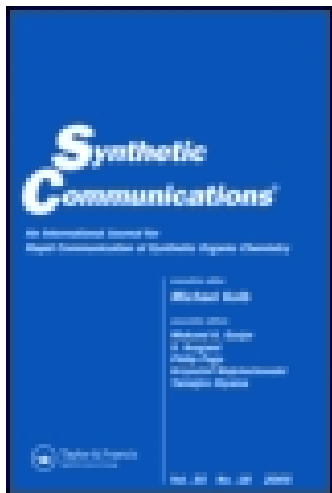


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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lcyc20>

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Published online: 22 Aug 2006.

To cite this article: R. Srinivasan, Preethi Stanley & K. Balasubramanian (1997) Isoquinolinium Fluorochromate: A New and Efficient Oxidant for Organic Substrates, *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*, 27:12, 2057-2064, DOI: [10.1080/00397919708006810](https://doi.org/10.1080/00397919708006810)

To link to this article: <http://dx.doi.org/10.1080/00397919708006810>

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ISOQUINOLINIUM FLUOROCHROMATE: A NEW AND EFFICIENT
OXIDANT FOR ORGANIC SUBSTRATES

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Abstract: Isoquinolinium fluorochromate is a versatile reagent for the effective and selective oxidation of organic substrates, in particular for alcohols, under mild conditions.

There is continued interest in the development of new chromium (VI) reagents¹⁻⁶ for the effective oxidation of organic substrates. Most of the oxidizing agents prove impractical when attempts are made to scale up the reaction process. In the past twenty years, significant improvements were achieved by the use of new oxidizing agents such as pyridinium chlorochromate^{2,3}, pyridinium fluoro-chromate⁴, quinolinium dichromate⁵, 2,2'-bipyridinium chlorochromate⁶, and quinolinium chlorochromate⁷. However, we have successfully used pyridinium chlorochromate for the selective oxidation of collagen^{8,9}.

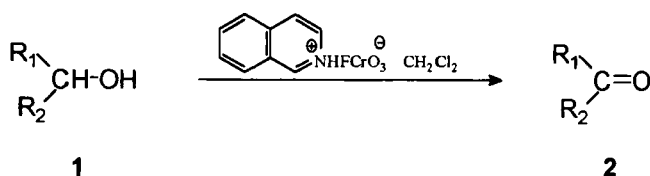
We have now investigated the synthetic potential of Isoquinolinium fluorochromate, $C_9H_7NHCrO_3F$, and we have found that this reagent has certain

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advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, easier working up and high yields.

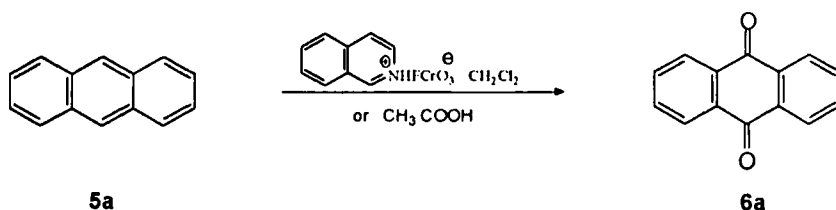
Further, isoquinolinium fluorochromate does not react with acetonitrile which is a suitable medium for studying kinetics and mechanism. The acidity of isoquinolinium fluorochromate (pH of a 0.01 molar solution : 3.43) is less pronounced than that of pyridinium fluorochromate (pH of a 0.01 molar solution : 2.45). The results obtained with isoquinolinium fluorochromate are very satisfactory and shows the new reagent as a valuable addition to the existing oxidizing agents.

Isoquinolinium fluorochromate in dichloromethane oxidizes primary (**1a-d**) and secondary alcohols (**3**) to the corresponding aldehydes or ketones (**2a-d and 4**) in high yields; this reagent is also efficiently applied to the oxidation of 3,4,5-trimethoxybenzyl alcohol (**1e**) and benzoin (**3**) to 3,4,5-trimethoxy benzaldehyde (**2e**) and benzil (**4**), respectively.



Isoquinolinium fluorochromate in dichloromethane also oxidizes anthracene (**5a**) and phenanthrene (**5b**) to anthraquinone (**6a**) and phenanthraquinone (**6b**) in 72% and 51% yields respectively and the yields are

increased to 98% and 72% by using acetic acid as the reaction medium. These yields are higher than those obtained by other oxidizing agents under mild conditions and we used only equimolar ratio of the reagent. This reagent works as efficiently as activated manganese dioxide¹⁰ or Collins reagent¹¹.

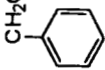
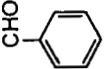
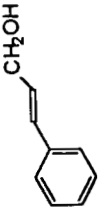
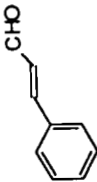
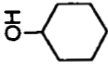
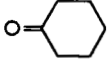


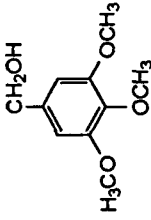
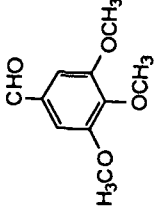
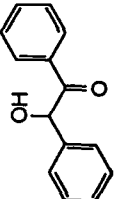
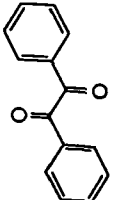
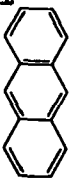
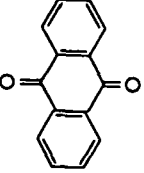
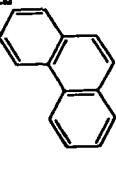
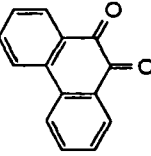
Isoquinolinium fluorochromate is easily prepared in 96% yield from isoquinoline, aqueous 40% hydrofluoric acid and chromium (VI) oxide in a molar ratio of 1:1.5:1. The bright orange crystalline reagent can be stored in polythene containers for long periods without decomposition. The chromium (VI) content may be easily determined iodometrically. The IR spectrum is similar to that of potassium fluorochromate^{12,13}. Isoquinolinium fluorochromate is soluble in water, dimethylformamide, dimethylsulfoxide and acetone, it is less soluble in dichloromethane and only sparingly soluble in benzene, carbontetrachloride, chloroform and hexane.

Isoquinolinium fluorochromate (VI), $\text{C}_9\text{H}_7\text{NHCrO}_3\text{F}$:

Chromium (VI) oxide (15.0 g, 0.15 mol) is dissolved in water (25 ml) in a polythene beaker and 40% hydrofluoric acid (11.25 ml, 0.225 mol) is added with

Table: Oxidation of Alcohols (1,3) and Polycyclic Arenes (5) with Isoquinolinium Fluorochromate.

Substrate ^a	Reaction time (h)	Product	yield (%)	M.p. (°C)	B.p. (°C)
1a n-C ₈ H ₁₇ OH	5	2a n-C ₇ H ₁₅ CHO	80		170(171)
1b 	1	2b 	91		176-179 (178-179)
1c 	5	2c 	70		248(248)
1d 	4	2d 	90		154(155)

1e 	4	2e 	86	73-74 (73-75)	
3 	3	4 	98	95(94-95)	
5a 	5 2	6a 	72 98 ^c	283-285 (284-286)	
5b 	6 2.5	6b 	51 78 ^c	208-211 (209-211)	

^a: Oxidations were carried out in Methylene Chloride with a substrate to oxidant ratio 1:1. ^b: The substrate to oxidant ratio used was 1:2. ^c: Acetic acid was used as the solvent.

stirring at room temperature. To the resultant clear orange solution, isoquinoline (17.75 ml, 0.15 mol) is added dropwise with stirring. The mixture is heated on a water bath for about 15 minutes then cooled to room temperature, and allowed to stand for 40-45 minutes. The bright orange, crystalline isoquinolinium fluorochromate is isolated by filtration in buchner funnel. It is recrystallized using hot water and dried in vacuo for about one hour. Yield : 35.80 g (96%); m.pt. 171-172°C.

$C_9H_8CrFNO_3$: Calc. C, 43.39; H, 3.24; N, 5.62.

(249.160) found. C, 43.36; H, 3.23; N, 5.59.

I.R.(KBr) : 952, 910, 640, 493 cm^{-1} .

The above procedure can be performed on a 250g. scale without any difficulty.

General procedure for Oxidation of Organic Substrates with Isoquinolinium Fluorochromate:

To a stirred suspension of isoquinolinium fluorochromate (2.65g) in dichloromethane (generally 5 ml), a solution of the substrate in the minimum amount of dichloromethane is added dropwise, the molar ratio of substrate to the oxidant being 1:1 in the case of alcohols (1,3) and 1:2 in the case of arenes (5) (See Table). The mixture is refluxed for the time indicated in the table. [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 vol/vol) 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.

References

1. Collins, J. C. and Hess, W. W. *Org. Synthesis*. **1972**, 52, 5.
2. Corey, E. J. and Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.
3. Corey, E. J. and Boger, D. L. *Tetrahedron Lett.* **1978**, 2461.
4. Bhattacharjee, M. N., Chauduri, M. K. and Dasgupta, H. S. *Synthesis*. **1982**, 588.
5. Balasubramanian, K. and Prathiba, V. *Indian J. Chem. Sec. B.* **1986**, 25B, 326.
6. Guziec, F. S. and Luzzio, F. A. *Synthesis*. **1980**, 691.
7. Srinivasan, R., Ramesh, C. V., Madhulatha, W. and Balasubramanian, K. *Indian J. Chem. Sec. B.* **1996**, 35B, 480.
8. Sehgal, P. K., Balasubramanian, K. and Joseph, K. T. *Indian J. Biochem. Biophys.* **1980**, 17, 98.
9. Sehgal, P. K., Balasubramanian, K. and Joseph, K. T. *Leather Science*.

1984, 38.

10. Fatiadi, A. J. *Synthesis*. **1976**, 65, 133.
11. Collins, J. C., Hess, W. W. and Frank, F. J. *Tetrahedron Lett.* **1968**, 3363.
12. Colton, R. and Canterford, J. H. "Halides of the First Row Transition Metals", John Wiley & Sons, New York, **1969**, 190.
13. Chauduri, M. K., Dasgupta, H. S. and Roy, N. *Indian J. Chem. Sec. A.* **1981**, 20A, 1227.

(Received in The Netherlands 23 January 1997)