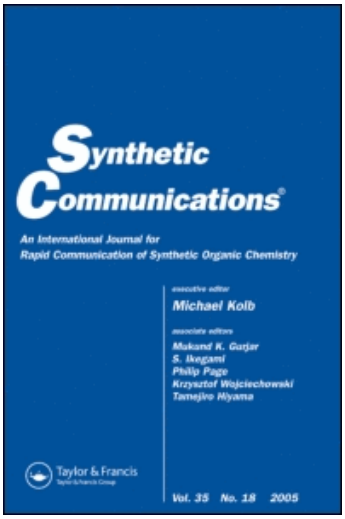

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A Convenient Method of Benzylic Oxidation with Pyridinium Chlorochromate

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A CONVENIENT METHOD OF BENZYLIC OXIDATION WITH PYRIDINIUM CHLOROCHROMATE

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Oxidation of indans and tetralin derivatives to their corresponding indanones and tetralones is of considerable value in organic synthesis and many methods have been reported for accomplishing this conversion.[1,2] Traditionally these oxidations are performed with chromic acid in acetic acid[3] and the yields in general are moderate. Recently Eisenbraun[4] has studied in detail the benzylic oxidation with the Jones reagent and compared the selectivity and yield of oxidation with other chromium(VI) reagents like bipyridinium chlorochromate, (BiPCC). It was found that there was no improvement in yield and in the case of BiPCC a molar ratio 16:1 (oxidant:substrate) was employed to get opt-

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imal yields. Pyridinium chlorochromate in dichloromethane was found to be unreactive.[4]

This prompts us to report our results on benzylic oxidation with pyridinium chlorochromate. In the course of our studies on oxidation with PCC, we find that by changing the solvent and the reactions conditions, benzylic oxidation can be brought about with ease. Treatment of a number of benzylic hydrocarbons with five molar equivalents of pyridinium chlorochromate in benzene under reflux for 8-15 h yield the benzylic oxidation products in very high yield (Table 1) and the oxidation of most of the substrates proceeded to completion. In all cases the yields were far superior to those obtained by chromic acid oxidation.[1,2,4]

1-Methyl tetralin was chosen as a model to test whether hydrocarbons of this type would be readily oxidised to ketones in good yield and whether attack at the methine hydrogen at a benzylic position would be preferred over that at a methylene position. Oxidation of 1-methyl tetralin with PCC in benzene under reflux for 20 h yielded 4-methyl-1-tetralone as the only product in 60% yield apart from some recovered starting material. Oxidation with Jones reagent of this substrate gave a mixture of products in low yield.[4]

Table 1

Entry	Substrate	Time (h)	Product[a]	Yield[b] %
1.	$Ph-CH_2CH_3$	15	$Ph-\overset{O}{\overset{\|}{C}}-CH_3$	71
2.	$Ph-CH_2-Ph$	10	$Ph-\overset{O}{\overset{\|}{C}}-Ph$	88
3.	$Ph-CH_2-\overset{O}{\overset{\|}{C}}-Ph$	12	$Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Ph$	86
4.	$CH_3CH_2-C_6H_4-NH-\overset{O}{\overset{\|}{C}}-Ph$	8	$CH_3-\overset{O}{\overset{\|}{C}}-C_6H_4-NH-\overset{O}{\overset{\|}{C}}-Ph$	82
5.	Tetralin	7	1-Tetralone	83
6.	Indane	8	Indanone	80
7.	6-Methoxy tetralin	13	6-Methoxy 1-tetralone	72
8.	Fluorene	10	Fluorenone	89
9.	Estrone methyl ether	25	3-Methoxy-1,3,5(10)-trien-17-one	54[c]
10.	1-Methyl tetralin	14	4-Methyl-1-tetralone	60

a. Products were characterized by comparison with authentic samples (spectra, TLC, m.p. and m.p. of 2,4-dinitrophenyl hydrazone.

b. All yields refer to isolated products.

c. Yield based on recovered starting material.

Chromic acid oxidation has been traditionally used for the conversion of estrones to their 6-oxo derivatives which are of potential value in the preparation steroid-protein conjugates useful for radioimmunoassay purposes.[5] However, low yields are reported for this reaction, due to a number of side products being formed by cleavage of the B and C ring.[1] tert-Butylhydroperoxide in the presence of chromium hexacarbonyl has been reported to give better yields in this case.[6] Oxidation of estrone 3-methyl ether with PCC in benzene under reflux for 25 h gave 3-methoxyestra-1,3,5(10)-trien-17-one in 54% yield.

We hope this simple methodology would prove to be a convenient and useful procedure for benzylic oxidation. A general procedure for benzylic oxidation with PCC is given below:

To a solution of the hydrocarbon (2 mmol) in benzene (20 ml), a finely powdered and homogenized mixture of pyridinium chlorochromate (10 mmol) and celite (5 g) was added. The reaction mixture was stirred and refluxed for 8-15 h and then diluted with ether (60 ml) and filtered through a short pad of Celite and anhydrous magnesium sulphate. The filter cake was washed with two 10 ml portions of ether and the combined fil-

trate was concentrated to reveal the crude product. Flash chromatography yielded the pure compounds.

References

1. R.C. Cambie and T.D.R., Manning, J. Chem. Soc. C, 2603 (1968); R.C. Cambie, V.F. Carlisle and R.D.R., Manning, J. Chem. Soc. C, 1240 (1969); A.C. Ghosh, B.G. Hazra and W.L. Duax, J. Org. Chem., 42, 3091 (1977); H. Hofmeister, H. Laurent and R. Wiechert, Chem. Ber., 106, 723 (1973); R.C. Cambie, L.N. Mander, A.K. Bose, M.S. Manhas, Tetrahedron, 20, 409 (1964); E.P. Burrows, S.L. Jones and H.E. Smith, J. Org. Chem., 38, 3977 (1973); G. Cainelli and G. Cardillo in "Chromium Oxidations in Organic Chemistry," p. 23-29, Springer Verlag, New York, 1984.

2. P. Garble and C. Casas-Campillo, J. Org. Chem., 29, 2731 (1964); A.J. Birch and G.S.R. Subba Rao, Tetrahedron Lett., 2917 (1968); J. Blum, H. Rosenman and E.D. Bergmann, Tetrahedron Lett., 3665 (1967); D.H.R. Barton, R.A.H.F. Hui, D.J. Lester and S.V. Ley, Tetrahedron Lett., 3331 (1979); M.V. Bhat and P.T. Perumanl, Tetrahedron Lett., 22, 2605 (1981).

3. K.B. Wilberg, "Oxidation in Organic Chemistry," Academic Press, New York (1965).

4. R. Rangarajan and E.J. Eisenbraun, J. Org. Chem., 50, 2435 (1985).

5. P.N. Rao, Steriods, 23, 173 (1974); N. Kundu, Steriods, 22, 327 (1973); P.D.G. Dean, D. Exley and M.W. Johnson, Steriods, 18, 593 (1971).

6. A.J. Pearson and G.R. Han, J. Org. Chem., 50, 2791 (1985).