Efficient and Selective Oxidation of Alcohols by Potassium Dichromate Solutions

Enzo Santaniello*, Patrizia Ferraboschi[1]

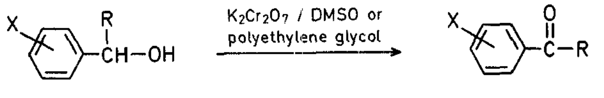
Istituto di Chimica, Facoltà di Medicina, Università di Milano, Via Saldini 50, I-20133 Milano, Italy

Piero Sozzani

Cattedra di Chimica Macromolecolare, Università di Milano, Via Saldini 50, I-20133 Milano, Italy

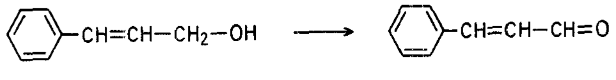
Aqueous sodium dichromate oxidizes in moderate yields almost exclusively benzylic and allylic alcohols[2]. It was also reported that this oxidation can be carried out by dichromate, solid-liquid phase-transferred into organic solvents[3].

More recently, we have shown that bis-tetrabutylammonium dichromate, $[(n\text{-}C_4H_9)_4N]_2Cr_2O_7$, is able to oxidize benzylic and allylic alcohols in aprotic solvents[4]. Thus, a solution of any dichromate in a suitable solvent would be expected to convert activated alcohols selectively to the corresponding carbonyl compounds. Potassium dichromate is a readily available, inexpensive reagent, its use as an oxidant in neutral conditions, however, is limited by its very low solubility in most organic solvents [i.e., acetone, ethyl acetate, *t*-butanol, hexamethylphosphoric triamide (potassium dichromate is soluble in hexamethylphosphoric triamide to an extent of 1% and, although these solutions apparently oxidized benzylic alcohols, they were not further investigated because of the large volumes of solvent necessary)]. The salt has a good solubility in dimethyl sulfoxide (10 g/100 ml, ~0.3 molar solutions) and in polyethylene glycols[5] (4 g in 100 g of solvent, ~0.13 molar solutions). Therefore, we have developed a simple and efficient method for selective oxidation of benzylic and allylic alcohols by means of potassium dichromate/dimethyl sulfoxide or polyethylene glycol 400 solutions to the corresponding carbonyl compounds. When the reaction is carried out at 90–100 °C for 1–3 h, yields of isolated carbonyl compounds are in the range of 80–90%, irrespective of the system used. Saturated alcohols are unreactive under the same conditions. With allylic alcohols some isomerization is observed in the isolated carbonyl compound (~30% as shown by G.L.C. and ^{1}H-N.M.R. analysis).

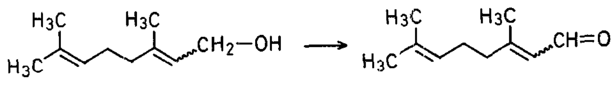


1a X = H , R = H
b X = 4-H$_3$CO , R = H
c X = 4-Cl , R = H
d X = 4-O$_2$N , R = H
e X = H , R = CH$_3$
f X = H , R = C$_6$H$_5$

2a-f



3 **4**



5a (*Z*)
b (*E*)

6a,b

0039-7881/80/0832-0646 $ 03.00

Table. Oxidation of Alcohols by Potassium Dichromate/Dimethyl Sulfoxide (A) and Potassium Dichromate/Polyethyleneglycol (B)

Substrate[a]	Product[b]	Reaction time (h)		Yield [%][c]		m.p. [°C] or b.p. [°C]/torr		I.R. $\nu_{C=O}$ [cm^{-1}]
		A	B	A	B	found	reported	
1a	**2a**	3	4	82	86	176°/760	178°/760[7]	1695
1b	**2b**	3	0.5	85	88[d]	80–82°/2	83°/2[7]	1680
1c	**2c**	3	3	80	82[d]	72–74°	72°[7]	1695
1d	**2d**	3	3	86	86	104–106°	106°[7]	1700
1e	**2e**	2	2	82	80	77–79°/16	79°/10[7]	1690
1f	**2f**	2	2	86	86	46–48°	48°[7]	1660
3	**4**	3	2	88	82[d]	125–127°/16	127°/16[7]	1680
5a	**6a**	3	1	78	70[d]	172°/14	172–174°/14[8]	1695
5b	**6b**	3	1	78	70	117°/20	118°/20[8]	1695

[a] Molar ratio substrate:oxidizing agent = 1:1.

[b] Products identical with authentic sample as determined by ^{1}H-N.M.R. as well as T.L.C. (silica gel plates, benzene/ethyl acetate, 9:1 or 8:2 V:V eluent) and G.L.C. (1% OV 17 on 100–120 mesh Gas Chrom Q column, N_2 carrier, 70–150 °C).

[c] Yields of isolated products.

[d] Molar ratio substrate:oxidizing agent = 1:1.5.

One feature of the above oxidations is the fact that they do not occur under acidic catalysis as is the case for most chromium(VI) oxidations[6]. A simple explanation of the selective oxidation of benzylic and allylic alcohols by the above systems and by tetra-*n*-butylammonium dichromate is lacking at present. However, it can be reasonably assumed that also in the above oxidations a chromate ester is formed as intermediate and that the formation of this unstable ester may be the critical step. In this respect, the easy cleavage of the C—O bonds of benzylic and allylic alcohols and the formation of the relatively separated anion from the loose ion pair resulting from the solvent effect, can concur to explain the selectivity of the above systems.

Potassium Dichromate/Dimethyl Sulfoxide (System A) and Potassium Dichromate/Polyethyleneglycol (System B):

System A: A solution of potassium dichromate (10 g) in dimethyl sulfoxide (reagent grade, not purified, 100 ml) is obtained at 50 °C. The solutions (0.3 molar) are stable at ambient temperature and darken without losing their oxidizing power for the time of the reactions described.

System B: A solution of potassium dichromate (4 g) in polyethylene glycol 400 (100 g) is obtained analogously at 50 °C and stored at room temperature, without appreciable changes with the time.

Oxidation of 4-Methoxybenzyl Alcohol (1b) by System B:

To a solution of System B (75 ml, 0.01 mol of oxidant) alcohol **1b** (1.38 g, 0.01 mol) is added and the solution is heated at 95 °C for 3 h. After cooling to room temperature, a solution of 1 normal hydrochloric acid (50 ml) is added to the above viscous solution to acidic pH and water (75 ml) is added to give a volume of 200 ml. Extraction with diethyl ether (3 × 50 ml), drying with sodium sulfate, and evaporation of the solvent affords a crude product (1.8 g) from which **2b** is distilled; yield: 1.2 g (88%).

Oxidation of 4-Chlorobenzyl Alcohol (1c) by System A:

To a solution of System A (33 ml, 0.01 mol of oxidant) alcohol **1c** (1.42 g, 0.01 mol) is added and the solution is heated at 100 °C for 3 h. After cooling to ambient temperature, water (100 ml) is added and the product is extracted with diethyl ether (3 × 30 ml) and the ethereal solution repeatedly washed with water (3 × 50 ml). After drying with sodium sulfate and evaporation of solvent, the crude product is crystallized; yield: 1.12 g (80%).

T.L.C., G.L.C., I.R., and ^{1}H-N.M.R. analyses of the products thus obtained (see Table) indicated a purity of 98% (G.L.C. conditions: 1% OV 17 on 100–120 Gas Chrom Q, 70–230 °C).

The work of P. F. at the Istituto di Chimica was supported by a grant from C.N.R. (Rome).

Received: December 27, 1979
(Revised form: February 4, 1980)

---

[1] Post-doctoral fellow from Istituto di Endocrinologia, Facoltà di Farmacia, Università di Milano.

[2] D. G. Lee, U. A. Spitzer, *J. Org. Chem.* **35**, 3589 (1970).

[3] R. O. Hutchins, N. R. Natale, W. J. Cook, J. Ohrr, *Tetrahedron Lett.* **1977**, 4167.

[4] E. Santaniello, P. Ferraboschi, *Synth. Commun.*, in press.

[5] Use of polyethyleneglycols as solvents (mainly PEG 400) has been recently proposed; E. Santaniello, A. Manzocchi, P. Sozzani, *Tetrahedron Lett.* **1979**, 4581.

[6] H. O. House, *Modern Synthetic Reactions*, 2nd Edn., W. A. Benjamin, Ed., Menlo Park, California, 1972, p. 270.

[7] *Handbook of Chemistry and Physics*, 52nd Edn., The Chemical Rubber Co., Cleveland, Ohio, 1971–1972.

[8] *Beilstein Handbuch der Organischen Chemie*, Vol. 1, p. 393, 1928.