Chromate Ion as a Synthetically Useful Nucleophile: a Novel Synthesis of Aldehydes from Alkyl Halides

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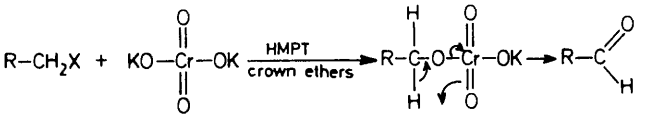
Summary The reaction between alkyl halides and K_2CrO_4 in HMPT in the presence of crown ethers provides an attractive synthetic route to aldehydes in good yields.

ALTHOUGH the oxidation of alkyl halides to aldehydes may be considered a synthetically useful step, very few methods are available in the literature for this purpose.[1] On the other hand it is well known that chromic acid is one of the most important reagents in the oxidation of alcohols, the reaction very probably proceeding *via* the decomposition of the corresponding chromate ester.[2] If it were possible to effect an S_N2 displacement of the halogen atom in the halide by means of a chromate ion, the chromate ester so obtained should decompose to the corresponding carbonyl compound (Scheme).



SCHEME

To our knowledge, no examples of this kind of reaction have been reported in the literature; we have therefore studied the possibility of using the chromate ion as a nucleophilic agent. The greatest difficulty we have encountered lies in the very poor solubility of chromate salts in organic solvents. We have found that these salts have an appreciable solubility in hexamethylphosphoramide (HMPT) and react in this solvent with primary allylic bromides and benzyl chloride to give the corresponding aldehydes in low yield; *e.g.* geranyl bromide (1·5 mmol) was treated with K_2CrO_4 (2·5 mmol) in 10 ml HMPT at 100 °C for 6 h to give geranial (20%) and geraniol (5%), the remainder being starting material. Much better results were obtained when 1 mol. equiv. of dicyclohexyl-18-crown-6 (or dibenzo-18-crown-6) per mol. equiv. of allylic halide is added to the reaction mixture. From this reaction 80% geranial and 20% geraniol were isolated. Geraniol, treated under the same conditions, does not give the corresponding aldehyde. The Table summarizes the results obtained using this method.

TABLE

Alkyl halide	Time/h	Aldehyde yield/%[a]
γ,γ-Dimethylallyl bromide ..	2	78
Geranyl bromide	2	82
Farnesyl bromide	2	80
Benzyl chloride	6	80
Octyl bromide	6	20

[a] Determined by g.l.c. analysis.

In a typical reaction dicyclohexyl-18-crown-6 (0·5 ml, 2 mmol) and geranyl bromide (0·42 g, 2 mmol) were added to a mixture of potassium chromate (0·5 g, 2·5 mmol) in 8 ml of anhydrous HMPT. The mixture was heated under stirring at 100 °C for 2 h and then worked up. Products were identified by direct comparison with authentic material and by n.m.r. spectroscopy.

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[1] N. Kornblum, W. J. Jones, and G. J. Andersen, *J. Amer. Chem. Soc.*, 1959, **81**, 4113; B. Ganem and R. K. Boeckman Jr., *Tetrahedron Letters*, 1974, 917.

[2] W. Carruthers, 'Modern Methods of Organic Synthesis,' Cambridge University Press, New York, 1971, 246.