

## Oxidative Displacement of Iodine from Vicinal Iodocarboxylates and Alkyl Iodides

By RICHARD C. CAMBIE, BARRY G. LINDSAY, PETER S. RUTLEDGE, and PAUL D. WOODGATE\*

(Department of Chemistry, University of Auckland, Auckland, New Zealand)

**Summary** *trans*-Vicinal iodotrifluoroacetates and iodoacetates are readily converted into *cis*-hydroxy-esters by oxidative displacement with *m*-chloroperbenzoic acid; simple alkyl iodides are converted into alcohols.

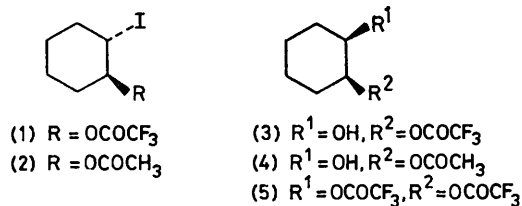
In the Prévost and related reactions an alkene is converted into a *trans*-vic-iodocarboxylate which is then solvolysed to an ester of a vic-diol.<sup>1</sup> Recently we described methods for the preparation of the intermediate vic-iodocarboxylates in high yield.<sup>2</sup> From the premise that iodine in a higher oxidation state would provide a better leaving group than univalent iodine, we have found that high yields of *cis*-hydroxy-esters can be formed from *trans*-iodotrifluoroacetates and *trans*-iodoacetates by oxidative displacement with *m*-chloroperbenzoic acid.† Thus, for example, treatment of the *trans*-iodotrifluoroacetate (1) with *m*-chloroperbenzoic acid in dichloromethane at room temperature under nitrogen for 3 h gave a quantitative yield of the *cis*-hydroxytrifluoroacetate (3) while similar oxidation of the *trans*-iodoacetate (2) gave an 89% yield of the corresponding *cis*-hydroxyacetate (4). Reaction of (1) with trifluoroacetic acid (2.4 mol. equiv.) in trifluoroacetic anhydride-

dichloromethane resulted in its complete conversion into a mixture of the bis(trifluoroacetate) (5) and the mono-hydroxy analogue (3). Lithium aluminium hydride reduction of the crude product (>95% of one compound by g.l.c.) afforded *cis*-cyclohexane-1,2-diol in an overall yield of 90%.

With simple alkyl iodides the oxidative displacement with *m*-chloroperbenzoic acid also proceeded smoothly. Thus, brief (1 min) treatment of 1-iodo-octane with the peracid (2.2 mol. equiv.) in dichloromethane gave a high yield (>95%) of octan-1-ol. Repetition of this reaction in methanol as solvent afforded octyl methyl ether (91%) while reaction in glacial acetic acid gave a mixture of octanyl acetate (72%), octan-1-ol (24%), and starting material (4%).

Oxidation of the secondary halide 2-iodo-octane with *m*-chloroperbenzoic acid in dichloromethane at room temperature for 10 min afforded octan-2-ol (60%) together with its *m*-chlorobenzoate ester (30%) and octan-2-one (10%). Similar reaction in glacial acetic acid gave 1-methylheptyl acetate (84%) and octan-2-one (15%).

Oxidation of the vic-iodocarboxylates with *m*-chloroperbenzoic acid gives the same products, *viz.* *cis*-hydroxy-carboxylates, as the Woodward-Prévost reaction. However, it allows their preparation at room temperature without the use of a silver salt. The conversion of an alkyl iodide into an alcohol with a peracid<sup>3</sup> contrasts with their transformation to vic-iodo-alkyl trifluoroacetates with iodine tris(trifluoroacetate) in ether.<sup>4</sup>



(Received, 4th July 1978; Com. 715.)

† Mangoni *et al.* (M. Parrilli, G. Barone, M. Adinolfi, and L. Mangoni, *Gazzetta*, 1974, **104**, 835; L. Mangoni, M. Adinolfi, G. Barone, and M. Parrilli, *ibid.*, 1975, **105**, 377) have shown that alkenes can be converted into *cis*-diols with iodine and potassium iodate in acetic acid followed by treatment with potassium acetate in refluxing acetic acid, while Buddrus (J. Buddrus, *Angew. Chem. Internat. Edn.*, 1973, **12**, 163) has shown that alkenes can be oxidised at room temperature to *cis*-vic-trifluoroacetates with iodine tris(trifluoroacetate) in pentane.

<sup>1</sup> C. V. Wilson, *Org. Reactions*, 1957, **9**, 332; F. D. Gunstone, in 'Advances in Organic Chemistry: Methods and Results,' eds. R. A. Raphael, E. C. Taylor, and H. Wynberg, Interscience, New York, 1960, vol. 1, p. 103.

<sup>2</sup> R. C. Cambie, R. C. Hayward, J. L. Roberts, and P. S. Rutledge, *J.C.S. Perkin I*, 1974, 1858; R. C. Cambie, W. I. Noall, G. J. Potter, P. S. Rutledge, and P. D. Woodgate, *ibid.*, 1977, 226; R. C. Cambie, D. Chambers, P. S. Rutledge, and P. D. Woodgate, *ibid.*, p. 2231.

<sup>3</sup> Cf. Y. Ogata and K. Aoki, *J. Org. Chem.*, 1969, **34**, 3979.

<sup>4</sup> M. Linskeseder and E. Zbiral, *Annalen*, 1977, 1039.