Novel Oxidative Elimination in a Norbornyl Iodide

By Nigel R. A. Beeley and James K. Sutherland,*
(*Chemistry Department, The University, Manchester* M13 9PL)

Summary A norbornyl iodide is shown to undergo oxidative elimination to yield a norbornene, the double bond of which is sufficiently hindered not to react with oxidizing species present in the reaction mixture.

In the course of some synthetic work[1] we had cause to treat the iodide (**1**) with peracetic acid. After methylation (CH_2N_2) the esters (**4**) [τ 6·3 (3H,s), 4·4 (1H,m), and 3·9 (2H,m); ν_{max} (CCl_4) 1780 and 1740 cm^{-1}] and (**7**) [τ 6·35 (3H,s), 4·65 (1H,brs), 3·70 (1H,m), and 3·50 (1H,m); ν_{max} (CCl_4) 1740—1750 cm^{-1}] were isolated. Similar oxidation of the methyl ester (**2**), followed by treatment of the reaction mixture with toluene-*p*-sulphonic acid–benzene gave (**4**) in 81% yield. An authentic sample of (**7**) was prepared from (**9**)[2] by methylation (CH_2N_2) followed by Baeyer–Villiger oxidation† (*m*-chloroperbenzoic acid); acid-catalysed

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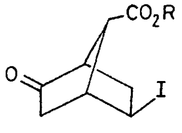
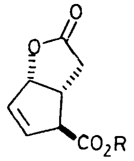
† Rather surprisingly a small amount of *endo*-epoxide was formed whereas the compounds with -CH_2OCH_2Ph (ref. 2) and -CH($OMe)_2$ (E. D. Brown, personal communication) at C-7 are inert.

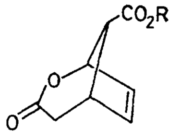
isomerisation of (**7**) gave (**4**). Reaction of the ethylene acetal of (**2**) with peracid gave (after hydrolysis with aqueous oxalic acid) the ketone (**10**) accompanied by small amounts of the acetal (**11**) and the lactone[1]‡ (**12**). The most reasonable explanation for the original observation is that the iodide (**1**) is oxidized to an iodoso-intermediate which then eliminates 'HOI' to yield (**9**). Rapid Baeyer–Villiger oxidation then yields the bridged lactone which, in turn, is partially isomerised by the acidic conditions to (**5**).§ To our knowledge the only previous study of the reaction of peracids with alkyl iodides is by Ogata[3] who showed that cyclohexyl iodide yielded products derivable from the interaction of cyclohexene, iodonium ion, and solvent. In our case the addition does not occur because of hindrance to both *exo* and *endo* faces of (**7**) and (**10**). It is attractive to consider the elimination as a *syn*-[2,3]-sigmatropic process (*cf.* selenoxide[4] and sulphoxide eliminations). In support, no nortricyclone elimination products were observed though these are sole products in base-catalysed elimination[1] and, in addition, the iodo-lactone (**13**) can be recovered quantitatively after long exposure to peracid. Against the concerted mechanism is the small amount of substitution product (**11**) isolated by us in one case and the substantial amounts obtained by Ogata. However, their genesis by an I → O rearrangement process cannot be excluded.¶



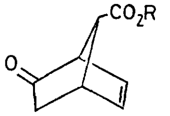
(1), R = H
(2), R = Me
(3), R = CH$_2$CCl$_3$



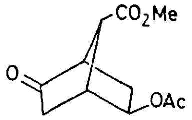
(4), R = Me
(5), R = H
(6), R = CH$_2$CCl$_3$



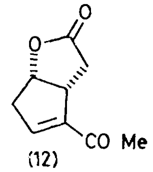
(7), R = Me
(8), R = CH$_2$CCl$_3$



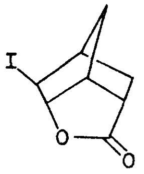
(9), R = H
(10), R = Me



(11)



(12)



(13)

As a general method of elimination this reaction is clearly limited but might prove useful in (a) the formation of hindered olefins, (b) the formation of weakly nucleophilic olefins in the presence of a nucleophilic trap, and (c) the conversion of vinyl iodides into acetylenes or allenes.

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‡ This could arise by a radical induced fragmentation of the acetal to give an *ortho*-ester derivative which on work-up yields the lactone.

§ Oxidation of the ester (**3**) with peracetic acid gave the lactone (**8**) uncontaminated with γ-lactone (**6**); however, the acidity of the medium required for reductive removal of the protecting group caused partial isomerisation to γ-lactone.

¶ We thank Professor K. B. Sharpless for this suggestion.

[1] R. Peel and J. K. Sutherland, *J.C.S. Chem. Comm.*, 1974, 151.
[2] J. S. Bindra, A. Grodski, T. K. Schaaf, and E. J. Corey, *J. Amer. Chem. Soc.*, 1973, **95**, 7522.
[3] Y. Ogata and K. Aoki, *J. Org. Chem.*, 1969, **34**, 3978.
[4] K. B. Sharpless and M. W. Young, *J. Org. Chem.*, 1975, **40**, 947.