4-Tricyclyliodonium Bis(*m*-chlorobenzoate): a Stable Aliphatic Trivalent Iodine Diester

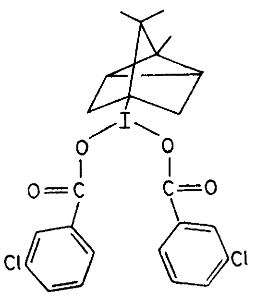
By DAVID G. MORRIS* and ALISTAIR G. SHEPHERD
(*Department of Chemistry, University of Glasgow, Glasgow* G12 8QQ)

Summary The first saturated aliphatic trivalent iodine diester and the rationale on which the synthesis is based are described.

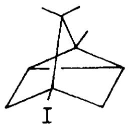
POLYVALENT aliphatic iodine compounds are unstable and react rapidly after formation *in situ*. Thus a *syn*-elimination has been carried out from an iodosyl-alkane formed from reaction of a peracid with an alkyl iodide carrying hydrogen on a carbon β to iodine.[1] Cambie *et al.*[2] treated a number of alkyl iodides with *m*-chloroperbenzoic acid and found *inter alia* that (*S*)-2-iodo-octane gave almost completely inverted (*R*)-octan-2-ol. By way of contrast 1-iodoadamantane gave rise to adamantan-1-ol; the purported mechanism of adamantanol formation involved homolytic cleavage of the carbon–iodine bond as the key step.[3]

Although formation of electron deficient intermediates, in particular carbocations, is generally difficult at bridgehead carbon atoms, the situation represented by 1-iodoadamantane is by no means limiting. Previously the solvolysis of 4-tricyclyl trifluoromethanesulphonate has been found to involve the slowest rate of formation of a bridgehead carbocation yet recorded,[4] and although formation of a bridgehead radical is less disfavoured than that of the corresponding carbocation[5] we sought to prepare the first polyvalent iodine ester using 4-iodotricyclene as a substrate.

Reaction of 4-iodotricyclene (**2**), m.p. 90—90·5 °C, prepared from iodocamphene in the conventional manner,[6] with *m*-chloroperbenzoic acid in a molar ratio *ca.* 1:3 in dichloromethane at room temperature gave a precipitate of (**1**), m.p. 180—182 °C (from toluene), in *ca.* 65% yield.



(1)



(2)

Compound (**1**) appears to be indefinitely stable at room temperature and stability was further indicated by its recovery unchanged after fusion. The nature of the iodine in (**1**) is confirmed by the ^{13}C chemical shift of the iodine-bearing carbon atom C(4), 80·29 p.p.m. (from internal $SiMe_4$ in $CDCl_3$) as compared with a shift for C(4) in 4-iodotricyclene of 43·90 p.p.m. The observed deshielding is similar to, but greater than, that of the corresponding carbon atom in phenyliodonium diacetate as compared with iodobenzene.[7] The absence of the heavy atom effect in the ^{13}C chemical shift of (**1**) may have three contributions; thus a deshielding effect of the two electronegative ester groups, a change in the hybridisation of iodine in the higher valency state, and a mixing in of the less well separated excited states of iodine will serve to produce the observed chemical shift for the iodine bonded to C(4) in (**1**).

Treatment of (**1**) with base gave 4-iodotricyclene (**2**) in *ca.* 50% yield; we were consistently unable to isolate the sought for iodosyltricyclene or one of its products of disproportionation, 4-iodyltricyclene. Our inability to execute this reaction successfully mirrors that of Roberts' group[8] with the unstable 1-dichloroiodoapocamphane.

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[1] N. R. A. Beeley and J. K. Sutherland, *J. Chem. Soc., Chem. Commun.*, 1977, 321.

[2] R. C. Cambie, D. Chambers, B. G. Lindsay, P. S. Rutledge, and P. D. Woodgate, *J. Chem. Soc., Perkin Trans.* 1, 1980, 822.

[3] M. J. Perkins and E. S. Turner, *J. Chem. Soc., Chem. Commun.*, 1981, 139.

[4] S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, *J. Am. Chem. Soc.*, 1972, **94**, 4615.

[5] R. C. Bingham and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1971, **93**, 3189.

[6] D. G. Morris and A. M. Murray, *J. Chem. Soc., Perkin Trans.* 2, 1975, 734.

[7] T. M. Balthazor, D. E. Godar, and B. S. Stults, *J. Org. Chem.*, 1979, **44**, 1447.

[8] J. B. Dence and J. D. Roberts, *J. Org. Chem.*, 1968, **33**, 1251.