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

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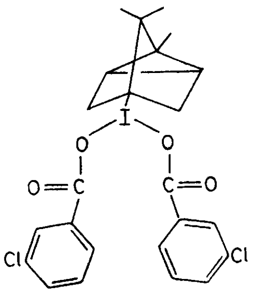
Summary The first saturated aliphatic trivalent iodine diester and the rationale on which the synthesis is based are described.

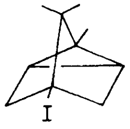
Polyvalent aliphatic iodine compounds are unstable and react rapidly after formation *in situ*. Thus a *syn*-elimination has been carried out from an iodosyl-alkane formed from reaction of a peracid with an alkyl iodide carrying hydrogen on a carbon β to iodine.[1] Cambie *et al.*[2] treated a number 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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