Hypervalent Iodine Iodinative Decarboxylation of Cubyl and Homocubyl Carboxylic Acids

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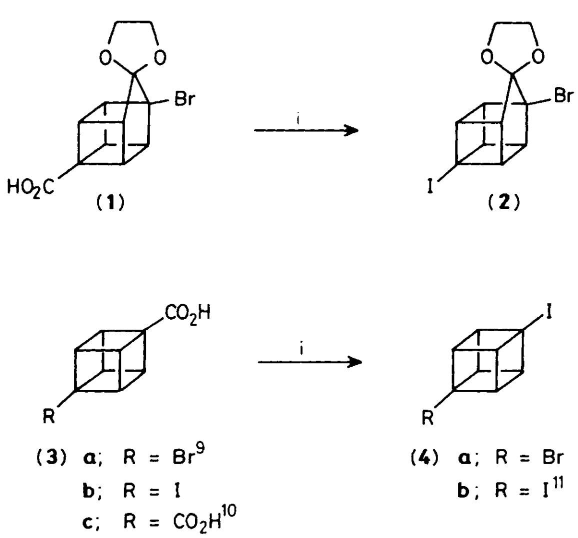
The hypervalent iodine oxidative decarboxylation of homocubyl and cubyl mono- and di-carboxylic acids is reported; the carboxylic acid is treated with $PhI(OAc)_2$–CCl_4–I_2 under irradiation conditions and 80–90% of the derived iodo compound is obtained.

Systematic functionalization of cubane is an important synthetic goal. The two main methods of cubane synthesis involve sequential Favorskii ring contractions to yield first a homocubyl carboxylic acid, and then, after a second Favorskii reaction, a 1,4[1,2] or 1,3[3] cubyl dicarboxylic acid. As a consequence of this synthetic procedure the carboxy group is a logical starting functionality for subsequent synthetic transformation in the cubyl ring system. The carboxy group has been converted into a nitro group in the synthesis of 1,4-dinitrocubane[4] and halogenodecarboxylation has been effected.[5,6] In a basically different approach Eaton *et al.* used *ortho*-lithiation of the derived carboxamide as a site for *ortho*-iodination.[7]

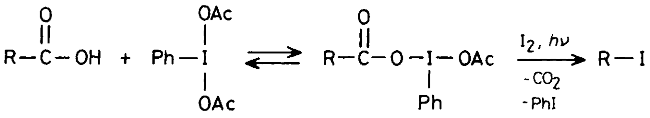
Introduction of an iodo group onto the cubyl system is especially desirable because hypervalent iodine synthetic methodology may be employed in order to effect displacement



Scheme 1. *Reagents:* i, CCl_4, $PhI(OAc)_2$, I_2, $h\nu$.†

reactions. This scheme has been successfully applied by Eaton *et al.*[8] in the cubyl system for $R–ICl_2 \rightarrow R–Cl$ and $R–I(OAc)_2 \rightarrow R–OAc$ where R = 1-iodo-2-*N*,*N*-di-isopropylcarboxamido-5-methylcubane.

Because of the position of substituted iodocubane as a point of departure for various synthetic objectives, we report now an extremely simple route to these compounds *via* hypervalent iodine oxidative decarboxylation. The reactions in Scheme 1 are illustrative.†


$$R-\overset{O}{\overset{\|}{C}}-OH + Ph-\underset{OAc}{\overset{OAc}{\underset{|}{\overset{|}{I}}}} \rightleftarrows R-\overset{O}{\overset{\|}{C}}-O-\underset{Ph}{\underset{|}{I}}-OAc \xrightarrow[-CO_2,\ -PhI]{I_2,\ h\nu} R-I$$

Scheme 2

The present oxidative decarboxylative iodination is an adaptation of the method of Suarez *et al.*[12] They showed that the method is effective for primary and secondary acyclic carboxylic acids but tertiary acids gave a mixture of tertiary alkenes.

On the basis of the results of the present work, it is probable that hypervalent iodine $[PhI(OAc)_2]$ exchanges one or two of its ligands with the carboxylic acid to generate the cubyl acyloxy hypervalent system which initiates the subsequent decomposition (Scheme 2). In fact the mixed acylate in which R is homocubyl as in (**1**) has been obtained and its structural characterization is in progress.

We thank the Office of Naval Research for support of this work.

Received, 30th December 1986; Com. 1842

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† In a typical reaction 4-iodo-1-bromopentacyclo[$4.3.0.0^{2,5}.0^{3,8}.0^{4,7}$]nonan-9-one ethylene acetal (**2**) was prepared *via* reaction of 1-bromo-9-oxopentacyclo[$4.3.0.0^{2,5}.0^{3,8}.0^{4,7}$]nonane-carboxylic acid (**1**) (10 mmol) in carbon tetrachloride (125 ml) with (diacetoxyiodo)benzene (10 mmol) and iodine, (10 mmol) and irradiation with 125 W tungsten-filament lamp for 4 h at reflux temperature. Then another portion of $PhI(OAc)_2$ (10 mmol) and iodine (10 mmol) was added and irradiation at reflux was continued overnight for 18 h. The reaction mixture was cooled, washed with aqueous sodium thiosulphate until the excess of iodine colour had disappeared, dried ($MgSO_4$), and evaporated to dryness to yield the crude iodo compound (**2**) which was crystallized by trituration with hexane, 85% yield: m.p. 138—139 °C; $\nu_{max.}$ 3010, 1310, and 1080 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 3.0—3.28 (m, 1H, 8-H), 3.65—3.85 (m, 5H), and 3.85—4.40 (sym. m, 4H, acetal); mass spectrum (70 eV), *m/z* 381 (M^+, 0.5%), 301 (M^+ – Br) (22.6%), 255 (M^+ – 127) (40%), 174 (M^+ – Br – I) (43%), 127 (81%), and 102 (100%); satisfactory elementary analyses. Compounds (**4a**) (80%), m.p. 190—196 °C, and (**4b**) (90%), m.p. 216—217 °C, were obtained similarly. The acid (**1**) was prepared in 6 steps from cyclopentanone in overall yield 50% according to the procedure in ref. 2.

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