Functionalized Homocubanes: Oxidative Deiodination of Homocubyl Iodide. Synthesis of 4-Mesyloxy-, 4-Tosyloxy-, and 4-Chloro-1-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one Ethylene Acetal from the Corresponding 4-Iodo-1-bromohomocubyl with Hypervalent Iodine

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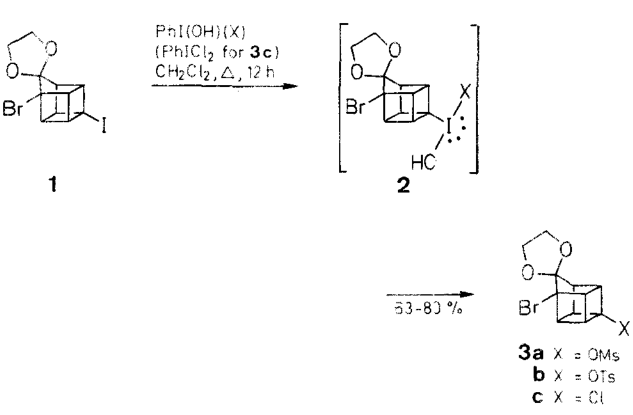
4-Iodo-1-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one ethylene acetal (**1**) undergoes substitution via a ligand exchange process.

The three-coordinated hypervalent aliphatic iodine compounds are unstable (with few exceptions) and react rapidly after formation *in situ.*[1] Oxidation of alkyl iodides with hydroxy(aryl/alkylsulfonyloxy)iodobenzene, (dichloroiodo)benzene, [bis(trifluoroacetoxy)iodo]benzene, etc. generates a hypervalent iodine substituent, which is a strong nucleofuge; substitutions, eliminations, or rearangements occur.[2] Oxidative elimination of iodine has been carried out in the case of a norbornyl iodide with peracid to yield the corresponding norbornene; the double bond formed in the product is a result of a *syn* [2,3]-sigmatropic elimination.[3] Substitution occurs in the case of three-coordinated hydroxy(3-chlorobenzyloxy)cubyl iodide formed from the reaction of a cubyl iodide with 3-chloroperoxybenzoic acid.[4] 4-Tricycloiodonium bis(3-chlorobenzoate) was isolated as a stable aliphatic trivalent iodine compound.[5] The nucleofugacity of iodine increases enormously upon oxidation to the three-coordinated state;[6] this fact is illustrated by facile solvolysis of bicyclo iodides such as 1- and 7-iodonorbornane with bromine to the corresponding 1- and 7-bromonorbornanes.[7] The reaction involves the formation of three-coordinated $RIBr_2$ as an intermediate.



1 **2**

3a X = OMs
b X = OTs
c X = Cl

The formation of electron-deficient intermediates is generally difficult at bridgehead carbon atoms, and is in an extreme form in cubane carbocation.[8] The results presented above suggest that these reactions proceed via carbocation-like intermediates. We found that homocubyl iodide **1** reacts with oxidizing reagents such as hydroxy (mesyloxy)iodobenzene,[9] hydroxy(tosyloxy)iodobenzene,[9] (dichloroiodo)benzene to produce the corresponding substituted homocubyl compounds **3a–c**.

Iodohomocubanes like **1** are now readily available as a result of the discovery in our laboratory that [bis(acetoxy)iodo]benzene/iodine effectively decarboxylates homocubyl carboxylic acids upon irradiation in carbon tetrachloride.[10] With hydroxy(tosyloxy)iodobenzene in a mole ratio of ca. 1 : 2 in anhydrous dichloromethane at reflux temperature compound **1** was consumed completely within 12 hours (^{1}H-NMR monitoring) and product **3b** was isolated upon work-up in ca. 67 % yield.

Similarly good conversion of **1** to the homocubyl mesylate **3a**, was achieved by reacting the former with hydroxy(tosyloxy)iodobenzene. Homocubyl iodide **1** reacts with (dichloroiodo)benzene and gives good yield of the corresponding homocubyl chloride **3c.**[11]

All melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded with an Unicam SP 1000 spectrophotometer. ^{1}H-NMR spectra were obtained with a IBM WP-400-SY Bruker NMR spectrometer. Chemical shifts are reported in parts per million relative to internal TMS in $CDCl_3$.

4-Mesyloxy-1-bromopentacyclo[4.3.0.0.^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one Ethylene Acetal (3a); Typical Procedure:

To a solution of **1**[10] (381 mg, 1 mmol) in anhydrous CH_2Cl_2 (60 mL) is added PhI(OH)(OMs) (632 mg, 2 mmol). The reaction is kept at reflux for 12 h. Within 20 min after the start of the reaction a purple color develops in the solution, and the color intensifies as the reaction progresses. Then the mixture is cooled and washed with 25 % aq. $Na_2S_2O_3$ until the purple color disappears. The organic layer is washed with 5 % $NaHCO_3$, dried ($MgSO_4$) and evaporated to dryness. The crude product is triturated with hexane (25 mL) to give **3a** as white crystals; yield: 278 mg (80 %); mp 97–98 °C.

$C_{12}H_{13}BrO_5S$	calc.	C 41.14	H 3.72	Br 22.88	S 9.16
(349.2)	found	41.18	3.74	23.11	9.15

IR (Nujol): $\nu = 3010, 1310, 1080\ cm^{-1}$.

^{1}H-NMR ($CDCl_3$/TMS): $\delta = 3.04$ (s, 3H, CH_3); 3.06–3.10 (m, 1H, H-8); 3.55–3.58 (m, 2H); 3.96–3.99 (m, 3H); 3.95–4.25 (sym m, 4H, OCH_2CH_2).

^{13}C-NMR ($CDCl_3$): $\delta = 39.62$, 41.55, 45.06, 50.27, 50.46, 63.56, 66.12, 83.84, 125.01.

MS: $m/z = 349$ (M^+); 269 ($M^+ - Br$).

3b; is obtained by oxidative deiodination of **1** with PhI(OH)(OTs) using the typical procedure for **3a**; yield: 284 mg (67%); white crystals; mp 90–91 °C.

$C_{18}H_{17}BrO_5S$	calc.	C 50.83	H 4.02	Br 18.78	S 7.53
(425.3)	found	50.76	3.89	18.88	7.67

IR (Nujol): $\nu = 3010, 1310, 1080\ cm^{-1}$.

^{1}H-NMR ($CDCl_3$/TMS): $\delta = 2.46$ (s, 3H, CH_3); 2.95–2.97 (m, 1H, H-8); 3.42–3.45 (m, 2H); 3.76–3.78 (m, 3H); 3.95–4.23 (sym m, 4H, OCH_2CH_2); 7.35–7.80 (AB quartet, 4H_{arom}).

^{13}H-NMR ($CDCl_3$/TMS): $\delta = 21.73$, 41.51, 45.01, 49.95, 50.18, 63.63, 66.08, 83.82, 125.02, 127.77, 129.99, 134.32, 145.29.

3c; is obtained by the oxidative deiodination of **1** with $PhICl_2$ using the typical procedure for **3a**; the crude product after evaporation of the solvent is recrystallized from EtOH; yield: 182 mg (63%); white crystals; mp 120–122 °C (Lit.[11] mp 118–120 °C). Spectral data (^{1}H-NMR, IR, MS) are identical with those of Ref. 11.

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