

**Functionalized Cubanes. Oxidative Displacement Upon Methyl 4-Iodocubane
Carboxylate Using Hypervalent Iodine Reagents**

Robert M. Moriarty, Jaffar S. Khosrowshahi and Raju Penmasta

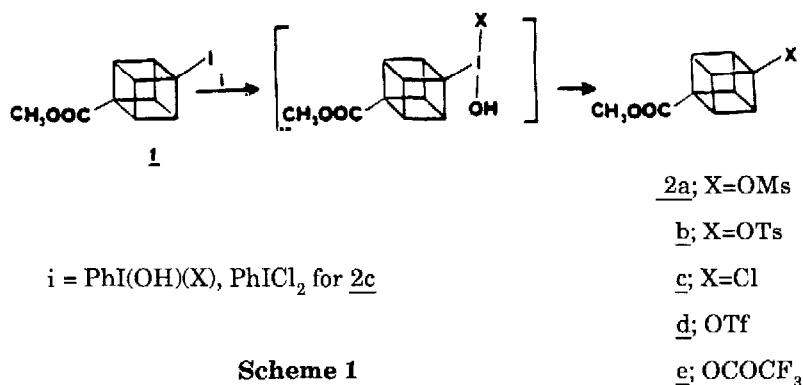
Department of Chemistry, University of Illinois at Chicago

P. O. Box 4348, Chicago, Illinois 60607

Summary: Methyl 4-iodocubane carboxylate undergoes substitution via ligand exchange with the hypervalent reagents $C_6H_5I(OH)OTs$, $C_6H_5I(OH)OMs$ and $C_6H_5ICl_2$.

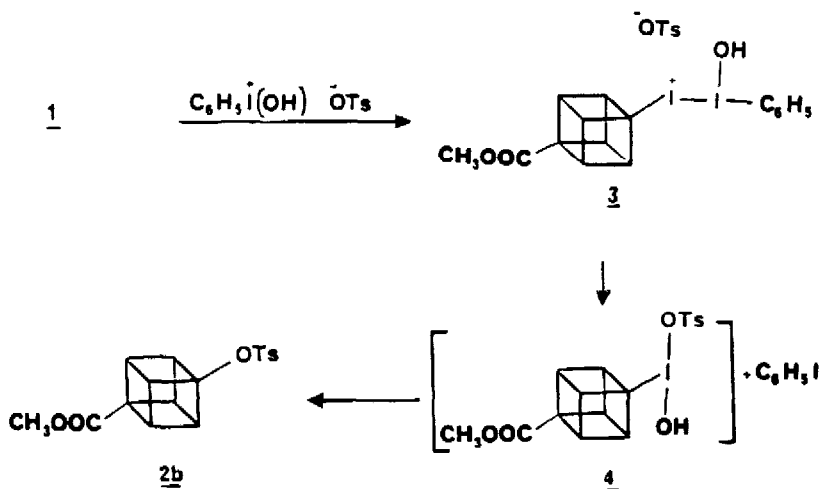
Displacement reactions upon the cubyl system represent a synthetic challenge because cubane embodies bridgehead unreactivity in its most extreme form.¹ An approach towards effecting displacement reactions is conversion of the iodine atom in a precursor cubyl iodide to a super nucleofuge² by means of hypervalent iodine ligand exchange from $C_6H_5IX_2$. The monocoordinate RI(I) system undergoes oxidative addition to the tricoordinate RI(III) intermediate.³ Frontside 1,2 shift from iodine to carbon of the nucleophile followed by reductive elimination I(III) \rightarrow I(I) yields the substitution product. Oxidative deiodination of iodocubanes has been used by Eaton and Cunkle for introduction of Cl and *m*-Cl- $C_6H_4CO_2$.⁴

We have applied ligand exchange in the case of methyl 4-iodocubane carboxylate (1)⁵ using $C_6H_5I(OH)OTs$,⁶ $C_6H_5I(OH)OMs$ ⁷ and $C_6H_5ICl_2$ ⁸ as transfer reagents. The reaction procedure is straightforward; the reactants are dissolved in CH_2Cl_2 and refluxed overnight. The iodine color (purple, disproportionation of IOH) which develops is dispelled with aqueous sodium thiosulfate and the products are obtained directly from CH_2Cl_2 solution (C_6H_5I is the only other product).^{*} The yields of 2a-e are 80%, 75%, 65%, 85% and 55% respectively.



Scheme 1

In all cases we visualize the reactions occurring by ligand transfer from the aryl iodonium reagent to cubyl iodide in a bimolecular process. The pathway for the overall process in the case of 2b (Scheme 2) may involve associative iodine-iodine bonding 1 → 3 followed by 1,2 iodine to iodine group transfer with concomitant reductive elimination of C₆H₅I to yield intermediate 4. 1,2 Shift of OTs 4 → 2b yields I-OH which is the source of the iodine color.⁹



Scheme 2

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*In a typical reaction methyl-4-mesyloxycubane carboxylate (2a) was prepared upon treatment of methyl-4-iodocubane carboxylate (1) (288 mg, 1 mmol) in CH_2Cl_2 (60 ml) with hydroxy(mesyloxy)iodobenzene (632mg, 2 mmol) at the reflux temperature for 3 days. The reaction solution was poured into ice water and the CH_2Cl_2 layer was washed with sodium thiosulfate solution until the purple color was disappeared. The dichloromethane layer was washed, NaHCO_3 , H_2O , dried (MgSO_4), concentrated under reduced pressure to give the crude methyl 4-mesyloxycubane carboxylate (2a) which was washed with hexane to remove the side product iodobenzene. Chromatography gave (200 mg, 80%) of white crystalline solid, m.p. 109-110°C. IR: ν_{max} 1730(C=O) cm^{-1} ; ^1H n.m.r. (CDCl_3 , 200 MHz) δ 4.47-4.16 (sym m, 6H, cubyl), 3.71 (s, 3H, $-\text{CO}_2\text{CH}_3$) and 3.08 (s, 3H, $-\text{SO}_2\text{CH}_3$); mass spectrum (70 eV), m/e 225 ($\text{M}^+\text{-OMe}$) (1.36%), 161 ($\text{M}^+\text{-OMs}$) (1.31%), 145 ($\text{M}^+\text{-OMs-Me}$) (22.17%), 129 ($\text{M}^+\text{-OMs-OMe}$) (3.15%), 118 (22.91%), 102 (7.09%) and 89 (100%). Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_5\text{S}$; S, 12.50 found S, 12.35; compounds (2b) (75%), m.p. 86-87°C; (2c) (65%), m.p. 104-105°C; (2d) (85%), oil and (2e) (55%) oil were obtained in similar fashion.

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