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[Lab. of Pharm. Synthetic Chemistry]

**Inversion of Configuration in Nucleophilic Vinylic Substitutions of (*E*)- $\beta$ -Alkylvinylidonium Tetrafluoroborates with Halides.**

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Exclusive inversion in nucleophilic substitutions at vinylic carbons has not been observed. Nucleophilic vinylic substitution of simple (*E*)- $\beta$ -alkylvinylidonium salts with *n*-Bu<sub>4</sub>NX (X=Cl, Br, and I), which competes with an alkyne-forming elimination, proceeded with exclusive inversion of configuration at room temperature. In contrast complete retention of stereochemistry was found in substitutions of these vinylidonium salts using a combination of cuprous halides and potassium halides. The hyperleaving ability of the phenylidonium group would be the origin of this unusual inversion of configuration in the nucleophilic vinylic substitution. A mechanism involving the formation of vinylidonium halides as reactive intermediates was proposed.

[Tetrahedron Lett., **32**, 1327-1328 (1991)]

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**Synthesis and Structure of 1-(Diacetoxyiodo)-2,4,6-tri-*tert*-butylbenzen and Its Analogues.**

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Synthesis of the title hypervalent organoiodine (III) compound, which has sterically demanding *tert*-butyl groups at the both ortho sites, is described. Oxidation of 1-iodo-2,4,6-tri-*tert*-butylbenzene with sodium perborate in acetic acid at 40°C afforded quantitatively the desired diacetate. The iodine is a stable crystal and the decomposition was not observed even on standing at room temperature for more than six months. In order to investigate the steric effect of the bulky *t*-butyl groups at ortho sites toward the hypervalent structure around iodine (III) and to establish the exact molecular structure the X-ray structure analysis was carried out, which revealed some degree of deformation from the normal geometries.

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**Michael Type Addition of Halides to Alkynyl (phenyl) iodonium Tetrafluoroborates. Stereoselective Synthesis of (*Z*)- $\beta$ -Halovinyl (phenyl)iodonium Halides.**

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Michael type addition of halide ions (Cl<sup>-</sup> and Br<sup>-</sup>) to alkynyl (phenyl) iodonium salts under acidic conditions proceeds in a completely stereoselective manner and affords (*Z*)- $\beta$ -halovinyl-(phenyl) iodonium halides, potential progenitors for generating  $\alpha$ -haloalkylidenecarbenes, in high yields. The attempted addition of fluoride ion gave poor results because of the low nucleophilicity. The (*Z*)-stereochemistry of these iodonium halides (X=Cl and Br) was established by observation of a nuclear Overhauser effect enhancement between the vinylic and allylic protons.