

[Tetrahedron Lett., **32**, 4945-4948 (1991)]

[Lab. of Pharm. Synthetic Chemistry]

**On the Mechanism of Stereoisomerization of Methyl Groups of 1,3-Diaxial [*cis*-3-(Benzyloxy)cyclohexyl]chlorodimethylstannane.**

MASAHITO OCHIAI\*, SHIGERU IWAKI, YOSHIMITSU NAGAO,  
SUSUMU KITAGAWA, MEGUMU MUNAKATA

The  $^{13}\text{C}$  NMR chemical shifts for (*cis*-3-(benzyloxy) cyclohexyl) chlorodimethylstannane, which adopts a 1,3-diaxial conformation not only in the solid state but also in solution by intramolecular hypervalent Sn-O interaction, are found to be temperature-dependent. The degenerate stereoisomerization of methyl groups of the 1,3-diaxial (*cis*-3-(benzyloxy) cyclohexyl) chlorodimethylstannane is interpreted in terms of a dissociation-inversion mechanism which involves an intervention of the corresponding 1,3-diequatorial conformer, followed by stereoisomerization by pseudorotation.

[Tetrahedron Lett., **32**, 7711-7714 (1991)]

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**Nucleophilic Vinylic Substitutions of (*Z*)-( $\beta$ -(Phenylsulfonyl) alkenyl)-iodonium Tetrafluoroborates with Tetrabutylammonium Halides: Retention of Configuration.**

MASAHITO OCHIAI\*, KUNIO OSHIMA, YUKIO MASAKI

In contrast to the  $\text{S}_{\text{N}}2$  type reaction of (*E*)-( $\beta$ -alkyl) vinyliodonium salts with  $n\text{-Bu}_4\text{NX}$ , which proceeds with complete inversion of configuration, nucleophilic vinylic substitutions of (*Z*)-( $\beta$ (phenylsulfonyl) alkenyl) iodonium salts with  $n\text{-Bu}_4\text{NX}$  proceed with exclusive retention of configuration, which is compatible with an addition-elimination mechanism. The  $\beta$ -phenylsulfonyl group makes it possible the perpendicular attack of halide ions to the  $\pi^*$  orbital, which produces an  $\alpha$ -sulfonyl-stabilized carbanion. The internal  $60^\circ\text{C}$  rotation followed by reductive elimination of the hypernucleofuge would reasonably explain the retention of configuration.

[J. Chem. Soc., Chem. Commun., **1991**, 869-870]

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**Stereoselective Synthesis of Highly Labile (*Z*)- $\beta$ -Alkylvinyl (phenyl) iodonium Perchlorates.**

MASAHITO OCHIAI\*, KUNIO OSHIMA, YUKIO MASAKI

Labile (*Z*)-vinyl (phenyl) iodonium perchlorates were synthesized from (*Z*)-vinylsilanes by the reaction with (diacetoxyiodo) benzene in the presence of  $\text{BF}_3\text{-Et}_2\text{O}$  in dichloromethane, followed by quenching with an aqueous potassium perchlorate solution. These synthetic operations should be carried out quickly at  $0^\circ\text{C}$  to avoid extensive decomposition of the product. The (*Z*)-vinyl (phenyl) iodonium perchlorates are highly labile both in the solid state and in solution. The rate of decomposition of (*Z*)-decenyl (phenyl) iodonium perchlorate in  $\text{CDCl}_3$  at room temperature, which yields 1-decyne quantitatively through the reductive *anti*  $\beta$ -elimination, is large and the half-life period is about 20 min.