

[J. Org. Chem., 59, 3262-3264 (1994)]

[Lab. of Pharm. Synthetic Chemistry]

Optically Pure Haloselenuranes. First Synthesis and Nucleophilic Substitutions.TAMIKO TAKAHASHI, NORIYUKI KUROSE, SABURO KAWANAMI,
YOSHITSUGU ARAI,* TORU KOIZUMI, MOTOO SHIRO

The first synthesis of optically active pure haloselenuranes was accomplished by utilizing the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand. Complete retention of the configuration was observed in interconversion reactions between haloselenuranes and selenoxide and in nucleophilic substitution reactions.

[Yakugaku Zasshi, 114, 201-218 (1994)]

[Lab. of Pharm. Synthetic Chemistry]

Asymmetric Diels-Alder Reactions Using Chiral α, β -Unsaturated Sulfoxides and Its Application to Natural Product Synthesis.

YOSHITSUGU ARAI

The use of chiral auxiliary (*i.e.* (2-*exo*-hydroxy-10-bornyl)sulfinyl) realized not only a facile preparation of chiral α, β -unsaturated sulfoxides but also the synthesis of chiral α -sulfinylmaleate and α -sulfinylmaleimide derivatives which effected Diels-Alder cycloadditions with high diastereoselectivity. Especially the α -sulfinylmaleimides readily reacted with the Diels-Alder dienes with rather low reactivity such as furan, to afford the corresponding Diels-Alder adducts under conventional conditions. The chirally functionalized adducts derived from the Diels-Alder reactions were transformed into some, biologically important natural products.

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[Lab. of Pharm. Physical Chemistry]

Molecular Orbital Study on Photoreaction of Peroxy Radicals of Polytetrafluoroethylene.

AKIHIRO NOGUCHI, SHIN-ICHI KONDO, MASAYUKI KUZUYA*

The photoreaction of peroxy radicals of polytetrafluoroethylene (PTFE) was investigated by means of the molecular orbital (intermediate neglect of differential overlap/spectroscopy-configuration interaction (INDO/S-CI)) calculations of the excited states of model compounds for two types of radicals, *i.e.* the endchain peroxy and midchain peroxy radicals. Calculations showed that the midchain radicals are excited to the second lowest excited doublet (D_2) state, which is responsible for the photoreaction, with much higher efficiency than the endchain peroxy radicals. The bond order perturbations accompanied by the transition from the ground doublet (D_0) state to the D_2 state in the midchain radicals seem to well explain the experimental results.