

[Chem. Lett., 1993, 17-20]

[Lab. of Pharm. Synthetic Chemistry]

**Substrate-Specific Rearrangement and Acetonidation of Epoxy-Ethers  
Catalyzed by Tetracyanoethylene**

YUKIO MASAKI\*, TSUYOSHI MIURA, MASAHIITO OCHIAI

Rearrangement of epoxy-ethers providing carbonyl compounds was catalyzed by tetracyanoethylene (TCNE) in acetonitrile under the preferential anchimeric assistance of intramolecular etheric oxygen function in the 5-exo mode for the 1,2-disubstituted epoxide unit and in the quaternary 5-exo, 5-endo, and 6-endo mode for the trisubstituted type. In acetone, epoxy-ethers favored by neighboring group participation were led to carbonyl compounds and the other epoxides furnished acetonides.

[J. Am. Chem. Soc., 115, 2528-2529 (1993)]

[Lab. of Pharm. Synthetic Chemistry]

**$\alpha$ -Versus  $\beta$ -Elimination of (Z)-( $\beta$ -Halovinyl)iodonium Salts: Generation  
of ( $\alpha$ -Alkylidene)carbenes and Their Facile Intramolecular 1,2-Migration**

MASAHITO OCHIAI\*, KOJI UEMURA, YUKIO MASAKI

On a basic treatment (Z)-(2-Bromo-1-decenyl)(phenyl)iodonium bromide was found to generate ( $\alpha$ -bromoalkylidene)carbene which undergo 1,2-migration of  $\alpha$ -bromine to terminal carbon to produce 1-bromo-1-decyne more rapidly than the intramolecular 1,5-carbon-hydrogen insertion yielding 1-bromo-3-n-pentylcyclopenten. It was observed that the relative rates of 1,2-migration and 1,5-C-H insertion depend on the  $\alpha$ -halogen atoms of alkylidene carbenes. That the generation of ( $\alpha$ -alkylidene)carbenes involves not only  $\alpha$ -elimination of phenyliodonio group but also anti  $\beta$ -elimination of hydrogen halides was demonstrated by the crossover experiments.

[Tetrahedron Lett., 34, 4829-4830 (1993)]

[Lab. of Pharm. Synthetic Chemistry]

**Nucleophilic Vinylic Substitutions of (Z)-( $\beta$ -(Phenylsulfonyl)alkenyl) iodonium  
Tetrafluoroborates with Sodium Benzenesulfinate: Stereoselective Synthesis of  
(Z)-1,2-Bis(Phenylsulfonyl)alkenes**

MASAHITO OCHIAI\*, KUNIO OSHIMA, YUKIO MASAKI,

MUNEKATA KUNISHIMA, SHOHEI TANI

Nucleophilic vinylic substitutions of (Z)-( $\beta$ -(Phenylsulfonyl)alkenyl)iodonium tetrafluoroborates with sodium benzenesulfinate afford (Z)-1,2-bis(Phenylsulfonyl)alkenes with retention of stereochemistry in good yields.