[J. Org. Chem., **60**, 2624-2626 (1995)] [Lab. of Pharm. Synthetic Chemistry]

Nature of Alkylidenecarbenes Generated from Alkenyl(phenyl)iodium Tetrafluoroborates via Base-Induced α -Elimination.

MASAHIKO OCHIAI, TAKUYA SUEDA, KOJI UEMURA, YUKIO MASAKI*

Nature of alkylidenecarbene generated from alkenyl(phenyl)iodonium tetrafluoroborate was investigated in the addition reaction with olefins. 2-Methyl-1-propenylidene generated from 2-methyl-1-propenyl(phenyl)iodonium tetrafluoroborate with triethylamine was found to react with *cis*- and *trans*-4-methyl-2-pentene in CH_2Cl_2 at 3° C with complete stereoselectivity. Hammet study for the cycloaddition of the carbene, generated with Et_3N and *t*-BuOK, with ring-substituted styrenes (*p*-MeO, *p*-Me, *p*-Cl) in CH_2Cl_2 at 3° C revealed small ρ values of -0.56 (Et_3N) and -0.55 (*t*-BuOK). These evidences indicated the alkenyliodonium salt-derived alkylidenecarbenes to be mildly electrophilic and the free carbene rather than the carbenoid.

[Chem. Pharm. Bull., **43**, 686-688 (1995)] [Lab. of Pharm. Synthetic Chemistry]

Tetracyanoethylene-Hydrogen Peroxide, a Mild Epoxidation System of Olefins.

YUKIO MASAKI*, TSUYOSHI MIURA, ISAO MUKAI, IKUHIRO IWATA, HIROHISA ODA, AKICHIKA ITOH

A reagent combination system, tetracyanoethylene-30% hydrogen peroxide, was found to epoxidize olefins efficiently in acetonitrile at room temperature in a stereospecific manner with retention of the configuration of the double bond.

[Chem. Pharm. Bull., **43**, 523-525 (1995)] [Lab. of Pharm. Synthetic Chemistry]

Catalytic Activities of Dicyanoketene Acetals in Alcoholysis of Epoxides.

TSUYOSHI MIURA, YUKIO MASAKI*

The catalytic activity of various types of capto-dative ethylenes has been investigated on alcoholysis of epoxides, and dicyanoketene dimethyl acetal (DCKDMA) and dicyanoketene ethylene acetal (DCKEA) are found to be efficient and mild catalysts.