

[J. Org. Chem., **60**, 2624-2626 (1995)]

[Lab. of Pharm. Synthetic Chemistry]

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

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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 CH₂Cl₂ at 3 °C with complete stereoselectivity. Hammett study for the cycloaddition of the carbene, generated with Et₃N and *t*-BuOK, with ring-substituted styrenes (*p*-MeO, *p*-Me, *p*-Cl) in CH₂Cl₂ at 3 °C revealed small ρ values of -0.56 (Et₃N) 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.

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[Lab. of Pharm. Synthetic Chemistry]

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

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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.

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Catalytic Activities of Dicyanoketene Acetals in Alcoholysis of Epoxides.

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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.