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[Lab. of Pharm. Synthetic Chemistry]

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

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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.

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**α -Versus β -Elimination of (Z)-(β -Halovinyl)iodonium Salts: Generation
of (α -Alkylidene)carbenes and Their Facile Intramolecular 1,2-Migration**

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On a basic treatment (Z)-(2-Bromo-1-decenyl)(phenyl)iodonium bromide was found to generate (α -bromoalkylidene)carbene which undergo 1,2-migration of α -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-pentylcyclopentene. It was observed that the relative rates of 1,2-migration and 1,5-C-H insertion depend on the α -halogen atoms of alkylidene carbenes. That the generation of (α -alkylidene)carbenes involves not only α -elimination of phenyliodonio group but also anti β -elimination of hydrogen halides was demonstrated by the crossover experiments.

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

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

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