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

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-pentylcyclopenten. 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)] [Lab. of Pharm. Synthetic Chemistry]

Nucleohilic 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.