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[Lab. of Pharm. Synthetic Chemistry]

Ethyl Cyanofornate/Hydrogen Peroxide and Related Combination Systems, Novel Epoxidizing Systems of Olefins.YUKIO MASAKI*, TSUYOSHI MIURA, ISAO MUKAI,
AKICHIKA ITO, HIROHISA ODA

A combination system of ethyl cyanofornate and hydrogen peroxide was found to epoxidize olefins in a stereospecific manner at room temperature. Asymmetric epoxidation was observed with menthyl cyanofornate/hydrogen peroxide system.

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Generation of Allenyliodines and Their Reductive Iodonio-Claisen Rearrangement.

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Reported for the first time are the generation of allenyliodines and their reductive idonio-Claisen rearrangement. Reaction of propargylsilanes with arylidines in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ undergoes a reductive idonio-Claisen rearrangement under mild conditions, yielding ortho-propargyl iodoarenes. The reductive ortho-propargylation probably involves the intermediate formation of allenyl (aryl) idines, which undergo [3,3]-sigmatropic rearrangement. The lack of the crossover products argues for the intramolecularity of the rearrangement. The lower activation energy associated with the idonio-Claisen rearrangement of allenyl (aryl) idines can be interpreted in terms of the small bond energy of the breaking apical carbon-iodine (III) bond.

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Generation of $[\beta$ -(Phenylsulfonyl)alkylidene]carbenes from Hypervalent Alkenyl- and Alkynyliodonium Tetrafluoroborates and Synthesis of 1-(Phenylsulfonyl)cyclopentenes.

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Michael-type addition of benzenesulfinic acid to alkynyliodonium salts in methanol gives stereoselectively (*Z*)- β -(phenylsulfonyl) alkenyl) idonium salts. β -(Phenylsulfonyl) alkylidenecarbenes derived from the (*Z*)- β -(sulfonylalkenyl) idonium salts by base treatment predominantly undergo intramolecular 1,5 C-H insertions to give 1-(phenylsulfonyl) cyclopentenes, which is in a marked contrast with the facile 1,2-migration of β -phenylsulfonyl and β -phenylsulfinyl groups of alkylidenecarbenes. Reaction of alkynyliodonium salts with benzenesulfonates directly affords 1-(phenylsulfonyl) cyclopentenes *via* tandem Michael-carbene insertion reactions.