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Effect of Silica Gel on the Benzenesulfinic Acid Catalyzed Isomerization of Vinylsilanes. Formation of Silyl Benzenesulfinate.

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In contrast to the facile protodesilylation of vinylsilanes with arenesulfinic acids, use of silica gel as an additive in the reaction of vinylsilanes with benzenesulfinic acid makes possible the selective isomerization of the double bond geometry. Based on the finding that the isomerization proceeds on the surface of the silica gel activated with benzenesulfinic acid and benzenesulfinic esters such as trimethylsilyl benzenesulfinate are effective as catalysts for the isomerization, the selective isomerization was interpreted in terms of the formation of silyl benzenesulfinate bound to a silanol group of the surface of silica gel in situ as active species.

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Conjugate Addition of Acyloxy Groups to Alkynylphenyliodonium Tetrafluoroborates under Both Basic and Acidic Conditions. Synthesis of α -Acyloxy Ketones.

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Reaction of alkynyl(phenyl)iodonium tetrafluoroborates with sodium salts of carboxylic acids in the presence of water affords α -acyloxy ketones. The reaction also proceeds under acidic conditions. The fact that the reaction of 4-hydroxy-1-butynyl(phenyl)iodonium tetrafluoroborate with 2 equiv of sodium acetate in THF-water (3:1) gives 1,4-diacetoxy-2-butanone suggests a reaction mechanism involving an intervention of 2-acyloxy-1-alkenyl(phenyl)iodonium tetrafluoroborates, produced by Michael-type addition of acyloxy groups to alkynyl(phenyl)iodonium tetrafluoroborates.

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Oxidative Grob Fragmentation of γ -Tributylstannyl Alcohols with a Combination of Iodosylbenzene, Dicyclohexylcarbodiimide, and Boron Trifluoride.

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Exposure of cyclic γ -stannyl alcohols to a combination of iodosylbenzene, dicyclohexylcarbodiimide, and BF_3 in dichloromethane undergoes an oxidative Grob fragmentation to give unsaturated carbonyl compounds. The dicyclohexylcarbodiimide apparently activates iodosylbenzene as well as decreases Lewis acidity of BF_3 . The fact that the iodine(III)-mediated Grob fragmentation proceeds stereospecifically suggests the fragmentation is concerted. The fragmentation, combined with conjugate addition of tributylstannyl lithium and reduction or alkylation, offers an efficient procedure for the reductive and alkylative ring opening of cyclic vinyl ketones.