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Chalcogenide-$TiCl_4$-mediated Reactions of *S*-Ethyl Thioacrylate with Aldehydes.

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The reaction of *p*-nitrobenzaldehyde (**1a**) with *S*-ethyl thioacrylate (**2**) catalyzed by chalcogenide-$TiCl_4$ gave a mixture of Baylis-Hillman adduct **3a** and *syn*- and *anti*-2-(chloromethyl)-3-hydroxy-3-(*p*-nitrophenyl)propanethioates **4a** in the ratio of **3**:*syn*-**4**:*anti*-**4**=5:65:30. The crude product obtained from the reaction of *p*-trifluoromethyl derivative **1b** with **2** was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene to give **3** (71% overall yield), while treatment of the crude product with $Ti(O\text{-}i\text{-}Pr)_4$ afforded isopropyl 2-(α-hydroxy-*p*-trifluoromethylbenzyl)acrylate **5** (49%), *S*-ethyl 2-(ethylthiomethyl)-3- hydroxy-3-(*p*-trifluoromethylphenyl)thiopropyonate **6** (2%) and *S*-ethyl 2-(chloromethyl)-3-(*p*-trifluoromethylphenyl)thioacrylate **7** (15%). Reactions of **2** with other various aldehydes followed by the treatment with DBU or $Ti(O\text{-}i\text{-}Pr)_4$ gave the thioacrylates **3** and isopropyl acrylates **5**, respectively in fair to good yields. The formation mechanism for 2-(chloromethyl)propanethioate **4** is discussed.

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A Novel Synthesis of 1,2-Dialkylthio- and 2-Alkoxy-1-alkylthioethenes from β-Arylthioalkenylselenonium Salts and Its Application to the Synthesis of Medium-Membered Heterocycles Containing S and O Atoms.

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The treatment of alkynylselenonium salts and thiophenol derivatives with a catalytic amount of triethylamine afforded β-arylthiovinylselenonium salts in good yields The reactions of the vinylselenonim salts with nucleophiles produced (*Z*)-β-arylthio-α-functionalized ethenes in high yields. In addition, the vinylselenonium salts bearing a hydroxy group underwent intramolecular cyclization upon treatment with sodium hydride to produce medium-membered heterocyclic compounds containing S and O atoms.

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The First Aryne Evolution from the Reactions of Selenonium Salts with Aryllithiums.

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The first example of the benzyne generation was found in the reactions of diphenyl(phenylethynyl)selenonium triflate with 1.0 equivalent of phenyllithium in THF at room temperature for 3 h. The formation of the aryne intermediate was confirmed in the reactions of ditolyl(phenylethynyl)selenonium triflate and tri-*p*-tolylselenonium triflate with tolyllithium, which gave a mixture of 2-(phenylethynyl)-5,4'-dimethyl-1,1'-biphenyl **18** and 2-(phenylethynyl)-4,4'-dimethyl-1,1'-biphenyl **19** in 19% yield (**18**:**19** = 11:8) and a mixture of 4,4'-dimethyl-biphenyl **28** and 3,4'-dimethyl-biphenyl **29** in 63% yield (**28**:**29** = 2:1), respectively. The reaction mechanisms of these reactions are discussed.

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Reexamination of Products and the Reaction Mechanism of the Chalcogeno-Baylis-Hillman Reaction: Chalcogenide-$TiCl_4$-mediated Reactions of Electron-deficient Alkenes with Aldehydes.

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Reactions of *p*-nitrobenzaldehyde (**4**) with methyl vinyl ketone (**5**) were conducted in the presence of $TiCl_4$ and dimethyl sulfide (**3**) or selenopyranone **6**. When the raw product was purified by column chromatography on silica gel, α-chloromethyl aldol **8** was obtained as a mixture of diastereoisomers **8a** and **8b**. In contrast, purification of the raw product by preparative TLC on silica gel gave α-methylene aldol **7**. The mechanism for the formation of α-chloromethyl aldol **8** and diasteroselection for the *syn*-isomer **8a** and *anti*-isomer **8b** are discussed.