
Chalcogenide-TiCl₄-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-TiCl₄ gave a mixture of Baylis-Hillman adduct 3a and syn- and anti-2-(chloromethyl)-3-hydroxy-3-(p-nitrophenyl)propenethioates 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]jundec-7-ene (DBU) in toluene to give 3 (71% overall yield), while treatment of the crude product with Ti(O-i-Pr)₄ afforded isopropyl 2-(α-hydroxy-p-trifluoromethylbenzyl)acrylate 5 (49%), S-ethyl 2-(ethylthiomethyl)-3-hydroxy-3-(p-
trifluoromethylphenyl)thiopropionate 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-i-Pr)₄ gave the thioacrylates 3 and isopropyl acrylates 5, respectively in fair to good yields. The formation mechanism for 2-(chloromethyl)propenethioate 4 is discussed.

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A Novel Synthesis of 1,2-Dialkythio- and 2-Alkoxy-1-alkylthioethenes from
β-Aryltioalkenylselenonium 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-
aryltiovinylselenium salts in good yields. The reactions of the vinylselenonium salts with nucleophiles produced (Z)-β-aryltio-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.

[Tetrahedron, 56, 855-863 (2000)]

The First Aryne Evolution from the Reactions of Selenonium Salts with Aryllithiums.
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The first example of the benzylene 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-
(pheny lethynyl)-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.

[Tetrahedron, 56, 4725-4731 (2000)]

Reexamination of Products and the Reaction Mechanism of the Chalcogeno-Baylis-Hillman Reaction:
Chalcogenide-TiCl₄-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 TiCl₄ 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 diastereoselection for the syn-isomer 8a and anti-isomer 8b are discussed.