
Chalcogénide-TiCl₄-mediated Reactions of S-Ethyl Thioacrylate with Aldehydes.
Tadashi KATAOKA,* Tetsuo IWAMA, Hironori KINOSHITA, Yasuo TSURUKAMI, Shin-iccho TSUJIYAMAMA,
Masaru FUJITA, Eiji HONDA, Tatsunori IWAMURA and Shin-ichi WATANABE

The reaction of p-nitrobenzaldehyde (1a) with S-ethyl thioacrylate (2) catalyzed by chalcogénide-TiCl₄, gave a mixture of Baylis-Hillman adduct 3a and syn- and anti-2-(chloromethyl)-3-hydroxy-3-(p-nitrophenyl)propaniothioate 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]junctic-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)propiothioate 4 is discussed.

[Synlett, 49-52 (2000)]

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.
Shin-ichi WATANABE, Eiji MORI, Hirotada NAGAI and Tadashi KATAOKA*

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 (2)-β-arylthio-β-functionalized ethenes in high yields. In addition, the vinylselenonim 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.
Shin-ichi WATANABE, Keiichiro YAMAMOTO, Yukiko ITAGAKI, Tatsunori IWAMURA,
Tetsuo IWAMA and Tadashi KATAOKA*

The first example of the benzylene generation was found in the reactions of diphenyldiphenylselenonium 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(diphenylselenonium triflate and tri-p-tolylselenonium triflate with tolyllithium, which gave a mixture of 2-(phenylethyl)-5,4′-dimethyl-1,1′-biphenyl 18 and 2-(phenylethyl)-4,4′-dimethyl-1,1′-biphenyl 19 (19%) yield (18:19 = 11.8) and a mixture of 4,4′-dimethyl-biphenyl 28 and 3,3′-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 Chalcogénom-Baylis-Hillman Reaction:

Chalcogénide-TiCl₄-mediated Reactions of Electron-deficient Alkenes with Aldehydes.
Tadashi KATAOKA,* Hironori KINOSHITA, Tetsuo IWAMA, Shin-ichiro TSUJIYAMAMA, Tastunori IWAMURA,
Shin-ichi WATANABE, Osamu MURAOKA and Genzoh TANABE

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 is discussed.