A Reaction of γ-Chalcogen-substituted Prop-2-ynyl Cations with Mild Nucleophiles

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 γ -Chalcogen-substituted prop-2-ynyl cations are generated by the reactions of diethyl acetals **1** and **2** with BF₃-Et₂O and react with various mild nucleophiles without isomerisation to allenyl cations to afford the prop-2-ynylated products **3a–e** and **5a–c** in good yields.

Isomerisation of the prop-2-ynyl group to allenyl group is well recognised and widely employed in the synthesis of allenic compounds.1 Therefore, prop-2-ynylation is an important functionalisation to be solved. α -Prop-2-ynyl ketones are versatile intermediates and are converted into chromanols,² other heterocycles,3 cyclohexenones,4 and 1,4-diketones.5 Direct coupling of ketone enolate with prop-2-ynyl halides or tosylates has rarely been reported because of the isomerisation to allenes. Nicholas et al. explored an elegant method using (prop-2-ynyl)Co₂(CO)₆+ complexes⁶ which react not only with trimethylsilyl enol ethers,7 but also with allylsilanes,8 and alkyland alkynyl-aluminium reagents.9 Dicobalt octacarbonyl is highly toxic and air sensitive, and all operations with this reagent should be carried out in an inert atmosphere. If prop-2-ynyl cations can be generated by a method without dicobalt octacarbonyl, this novel method will be useful and convenient for prop-2-ynylation. Since the Lewis acid mediated reaction of



Table 1 Reactions of γ -chalcogen-substituted prop-2-ynyl cations with nucleophiles



prop-2-ynyl aldehyde acetals with nucleophiles has not been reported, we examined reactions of prop-2-ynyl cations generated from γ -chalcogen-substituted propynal diethyl acetals and report here the reactions of prop-2-ynyl cations with the mild nucleophiles. γ -Chalcogen-substituted propynal diethyl acetals 1 and 2 were prepared by the reaction of propynal diethyl acetal with ethylmagnesium bromide followed by treatment with benzenesulfenyl or benzeneselenenyl chloride (Scheme 1).

 γ -Selenopropynal diethyl acetal **1** reacted with trimethylsilyl enol ethers in the presence of BF₃-Et₂O to give α -alkoxyprop-2-ynyl ketones 3a and 3b accompanied by the alkynyl ether 4a, which would be formed by the hydride abstraction (entry 1). The addition reactions of 1 with various nucleophiles were performed and their results are shown in Table 1. The reaction of 1 with allyltrimethylsilane afforded the allylated selenoalkyne 3d in good yield, while the reaction of 1 with trimethylsilylnitrile gave a complex mixture. Although the (prop-2-ynyl)-Co₂(CO)₆⁺ complex reacted with trialkylaluminium reagents, the yields of the alkylated products were low.9 The chalcogen-substituted propynal diethyl acetal 1 reacted with triethylaluminium or diethylzinc to give the ethylated product 3d in high yield (entries 4 and 5). Alkynylation using diethyl octynyl aluminium provided the octynylated product 3e (20%) and the ethylated product 3d (25%) (entry 6), and reaction with trioctynylaluminium produced the product 3e in low yield.

 γ -Phenylthiopropynal diethyl acetal **2** reacted similarly with the soft nucleophiles in the presence of BF₃-Et₂O (entries 8–10). The prop-2-ynylated products **5a**, **5b** and **5c** were obtained in good yields. Reactions of other prop-2-ynyl aldehyde diethyl acetals bearing an alkyl, a phenyl, a silyl and a stannyl groups at the terminal acetylenic carbon were fruitless and gave the complex mixtures. This indicates that γ -substituted chalcogen atoms stabilised the prop-2-ynyl cations and have an effect on the α -selective prop-2-ynylations.

Table 2 Synthesis of γ -chalcogen-substituted propynal mono- and diheteroacetals at room temp.

_ Entry	Acetal	Conditions	Products (% yields)
1	1	2 equiv. Bu ⁱ ₂ AlSePh	PhSe 6 (41) OEt SePh
2	1	4 equiv. Bu ⁱ ₂ AlSePh	
3	1	2 equiv Bu ⁱ ₂ AlSPh	PhSe
4	1	4 equiv. Bu ⁱ ₂ AlSPh	PhSe SPh 8 (48)
5	1	4 equiv. Bu ⁱ ₂ AlSPh/ CF ₃ CO ₂ H	8 (56) 7 (39) PhS
6	2	4 equiv. Bu ⁱ ₂ AlSePh	`SePh 9 (46)
7	2	4 equiv. Bu ⁱ ₂ AlSPh	PhS SPh PhS SPh

We also examined the nucleophilic addition reactions with other soft nucleophiles such as B(SePh)₃,¹⁰ TMSSePh,¹¹ and Bui₂AlSePh.¹² Reaction of acetal 1 with 2 equiv. of Bui₂AlSePh gave O,Se-heteroacetal 6 (Table 2, entry 1) and reaction with Buⁱ₂AlSPh afforded O,S-heteroacetal 7 in good yield (entry 3). The structures of these compounds could be satisfied by the analytical and spectral data. When 4 equiv. of Bui₂AlSPh was used, no O,S-heteroacetal but dithioacetals 8 and 10 were obtained from γ -phenylseleno- 1 and γ -phenylthiopropynal 2, respectively. The diselenoacetal 9 was similarly obtained from 2 and 4 equiv. of Buⁱ₂AlSePh in 46% yield. We made attempts to prepare y-phenylselenopropynal diselenoacetal, but could not obtain it in a pure form. These heteroacetals would be utilised as a source of prop-2-ynyl cations stabilized by a chalcogen atom.¹³ Since the alkynyl chalcogenmoieties can be easily transformed to other functional groups,14 y-chalcogen-substituted prop-2-ynyl compounds will become useful intermediates for organic synthesis.

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