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[2+2] Cycloaddition reactions of imines with alkynyl selenides catalyzed by scandium triflate

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Abstract

It was found that a new reaction of imines with alkynyl selenides proceeded smoothly in the presence of a catalytic amount of $Sc(OTf)_3$ affording α,β-unsaturated selenylimidates. These reactions are assumed to proceed by a [2+2] cycloaddition of the imines to the alkynyl selenides to form azetine intermediates, which are unstable and immediately fragment to the corresponding α,β-unsaturated selenylimidates. © 2000 Elsevier Science Ltd. All rights reserved.

Following the wide application of organic sulfides in organic synthesis, organic selenides have attracted much attention in recent years.[1] Compared with organic sulfides, the σ-bonding of selenium is weaker than that of sulfur, therefore, C–Se, O–Se and N–Se bonds are more easily cleaved.[2] Acetylenic selenides are useful intermediates for synthesis and much attention has been devoted to their preparation and synthetic utilization.[3] Acetylenic selenides have been submitted to hydroamination,[4] hydrohalogenation,[5] hydrosulfonation,[6] hydrostannylation,[7] hydrozirconation[8] and hydroboration.[9] DIBAL-H has recently been employed to reduce acetylenic selenides[10] furnishing the corresponding vinylic selenides in good yields. The addition of nucleophiles such as lithium butyl cyanocuprate[11] to acetylenic selenides provides an important synthesis of vinyl selenides.

On the other hand, the rare earth metal triflates are excellent water-tolerant and reusable catalysts and have shown unique properties compared to traditional Lewis acids in several important carbon–carbon bond forming reactions,[12] such as aldol condensations,[13] Friedel–Crafts acylations[14] and aza Diels–Alder reactions.[15] We have reported that glyoxylates react smoothly with alkenes in the presence of ytterbium triflate[16] and a one-pot synthesis of amino phosphonates from aldehydes using ytterbium triflate as the catalyst.[17] However, [2+2] cycloadditions of imines to alkynyl chalcogenides have rarely been reported.[18] Herein, we describe a convenient preparation of α,β-unsaturated selenylimidates by [2+2] cycloaddition of imines to alkynyl selenides in the presence of $Sc(OTf)_3$.

The reaction of *N*-benzylidene-*p*-toluenesulfonamide (**1**) with alkynyl selenides (**2**) in acetonitrile, in the presence of 20 mol% of $Sc(OTf)_3$ gives new adducts that were detected by TLC after 15 h at room

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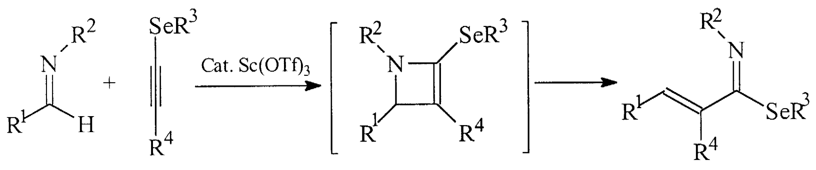
temperature. The adducts were found to be stable under the usual aqueous work-up conditions and could be purified by silica gel column chromatography to afford α,β-unsaturated selenylimidates,[19] identifiable by their IR, ^{1}H NMR, ^{13}C NMR and mass spectra. The *trans*-configuration of product **4b** was finally confirmed by means of a nuclear Overhauser effect (NOE) investigation.

Several imines and alkynyl selenides were examined and the results are listed in Table 1. In the presence of $Sc(OTf)_3$, the [2+2] cycloaddition of imines, except for *n*-butylbenzylamine and benzylideneaniline, proceeded smoothly to give the corresponding products (Scheme 1) in moderate yield.

Table 1
Synthesis of α,β-unsaturated selenylimidates by Lewis acid catalyzed [2+2] cycloaddition of imines to alkynyl selenides

entry	R^1	R^2	R^3	R^4	Catalyst	Selenylimidate	Yield(%)[a]
1	Ph	Ts	CH_3	CH_3OCH_2	$Sc(OTf)_3$	**4a**	71
2	Ph	Ts	CH_3	CH_3OCH_2	$Yb(OTf)_3$	**4a**	58
3	Ph	Ts	CH_3	CH_3OCH_2	$BF_3 \cdot OEt_2$	**4a**	trace
4	Ph	Ts	CH_3	CH_3OCH_2	$ZnCl_2$	**4a**	0
5	Ph	Ts	CH_3	CH_3OCH_2	$MgBr_2$	**4a**	0
6	Ph	Ts	CH_3	CH_3OCH_2	$ScCl_3$	**4a**	0
7	Ph	Ts	Ph	*n*-Bu	$Sc(OTf)_3$	**4b**	54
8	*p*-ClC_6H_4	Ts	CH_3	CH_3OCH_2	$Sc(OTf)_3$	**4c**	59
9	Ph	Ts	Ph	Ph	$Sc(OTf)_3$	**4d**	48
10	*p*-ClC_6H_4	Ts	CH_3	*n*-Bu	$Sc(OTf)_3$	**4e**	60
11	Ph	n-Bu	CH_3	CH_3OCH_2	$Sc(OTf)_3$	**4f**	0
12	Ph	Ph	CH_3	CH_3OCH_2	$Sc(OTf)_3$	**4g**	0

a. Isolated yield.



1 **2** **3** **4**

Scheme 1.

Arenes and Bos[20] reported that the reaction of aldehydes or ketones with alkynyl ethers or alkynyl sulfides afforded α,β-unsaturated esters or α,β-unsaturated thioesters in the presence of a stoichiometric amount of a Lewis acid such as $BF_3 \cdot OEt_2$. We attempted to employ $BF_3 \cdot OEt_2$, $ZnCl_2$, $MgBr_2$, $ScCl_3$ as the catalyst to catalyze our reaction, but failed. In contrast, *n*-butylbenzylamine and benzylideneaniline did not react with alkynyl selenides in the presence of $Sc(OTf)_3$.

The reactions are assumed to proceed via a [2+2] cycloaddition and successive fragmentation[21] similar to the reaction of imines with alkynylsulfides.[18] Several attempts to isolate the azetine intermediates or to detect them by NMR failed. Dihydroisoquinoline react with ynamines to afford the intermediate azetidine, which in this case can be detected by competitive hydrolysis.[22] The α,β-unsaturated selenylimidates are trifunctional reagents which can be expected to serve as precursors for the synthesis of other complex organic compounds.

In summary, we have found that $Sc(OTf)_3$ is an efficient catalyst for the reaction of imines with alkynyl selenides to provide α,β-unsaturated selenylimidates. These reactions are assumed to proceed by [2+2] cycloaddition of imines to alkynyl selenides to form azetine intermediates which are unstable and immediately fragment to the α,β-unsaturated selenylimidates. A distinct advantage of this procedure is the simplicity and robustness of the reaction: the catalyst is stable in water, recoverable and reusable with no loss of yield.

Acknowledgements

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19. A typical experimental procedure is described: To a suspension of $Sc(OTf)_3$ (0.10 mmol, 20 mol%) in acetonitrile (3 ml) were added *N*-benzylidene-*p*-toluenesulfonamide (0.50 mmol) and the alkynyl selenide (0.75 mmol) at room temperature and the mixture was stirred for 15 h. Water was added and the product was extracted with ethyl acetate. Then the organic layer was dried (Na_2SO_4) and evaporated. The residue was chromatographed on silica gel to afford the products. For compound **4a**: ^1H NMR: 7.87 (2H, d, J=8.3 Hz), 7.41–7.25 (7H, m), 6.95 (1H, s), 4.35 (2H, s), 3.33 (3H, s), 2.62 (3H, s), 2.31 (3H, s). IR: 1598, 1549, 1156, 1089, 815; ^{13}C NMR: 143.76, 138.01, 136.35, 134.38, 129.82, 129.52, 128.90, 128.61, 127.45, 126.58, 69.94, 58.84, 29.79, 21.68, 10.45. Calcd: C, 54.03; H, 4.98; N, 3.32. Found: C, 53.97; H, 5.10; N, 3.21.
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