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Short Report

Clean and Atom-Economic Synthesis of α-Phenylselenoacrylonitriles and α-Phenylseleno-α,β-Unsaturated Esters by Knoevenagel Reaction under Solvent-Free Conditions

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Um método simples e eficiente foi desenvolvido para a síntese de α-fenilselenoacrilonitrilas e ésteres α-fenilseleno-α,β-insaturados através, respectivamente, da reação *one-pot* de aldeídos com fenilselenoacetonitrila ou acetato de (fenilseleno)etila na presença de um catalisador em suporte sólido (KF/Al_2O_3), sem o uso de solvente.

A simple, clean and efficient method has been developed for the synthesis of α-phenylselenoacrylonitriles and α-phenylseleno-α,β-unsaturated esters by a one-pot reaction of aldehydes with phenylselenoacetonitrile or ethyl(phenylseleno)acetate respectively, in the presence of a solid supported catalyst (KF/Al_2O_3), without any solvent.

Keywords: solvent-free reaction, Knoevenagel condensation, phenylselenoacrylonitriles

Introduction

Organoselenium compounds have been used as key intermediates in several modern organic synthesis.[1] Among the different classes of organoselenium compounds, vinyl selenides constitute a very useful intermediate, because the versatile reactivities of the selanyl group and the carbon-carbon double bond.[2] Special attention has been devoted to the synthesis of vinyl selenides substituted by electron-withdrawing groups, like nitriles **3** and esters **4**. These highly functionalized compounds can be submitted to several transformations, including their use in [2+2] cycloaddition reactions,[3] Diels-Alder reactions,[4-6] and like Michael acceptors.[4,7]

The α-phenylseleno-α,β-unsaturated esters **4** have been prepared by different routes,[2] including selenilation of ester enolates,[8] oxidative elimination of α,α-bis(phenylselanyl)esters,[8] dehydrochlorination of α-phenylseleno-β-chloro esters[8] and of α-phenylseleno-α-chloro esters,[9] and Wittig-type reactions.[6,10] On the other hand, the preparation of α-phenylselenoacrylonitriles **3** was studied in a minor extent.[2,3,4,11,12] Between the described methods for preparation of **3**, those involving Wittig-type reactions are the most efficient.[4,12] Recently, Chinese authors have been described the preparation of several α-phenylseleno-α,β-unsaturated nitriles in moderate to good yields via α-phenylselenenyl cyanomethylene triphenylarsorane.[12] However, this method is restrict to aromatic aldehydes and no mention regarding the stereochemistry of the products was made. Besides these drawbacks, these protocols make use of environmentally harmful, volatile organic solvents, inert atmosphere, low temperatures (-78 °C)[4] or heating,[12] expensive and stoichiometric reagents and strong bases. More recently, an improvement was achieved with the use of MW under solvent-free conditions in the selective preparation of **4**, in reasonable yields, by a Wittig-type reaction of selenophosphorane with aldehydes.[6] In contrast to Wittig type reactions, Knoevenagel condensation is an atom-economic and cleaner tool for constructing the α,β-unsaturated structure unit from a carbonyl and an active methylene components.[13] Knoevenagel reactions can be promoted by solid supported reagents,[14] fluoride anion,[15] and KF/Al_2O_3[16] and the generation of large amounts of salts at the end of the synthesis as well as the use of stoichiometric strong bases can be avoided.

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Looking for cleaner approaches to classical syntheses, we have developed several protocols involving solid supported catalyst under solvent-free conditions and MW irradiation.[17,18] As a continuation of our studies directed toward the development of new methods for the synthesis of vinyl selenides and their great potential in organic synthesis,[2] we report herein the synthesis of α-phenylselenoacrylonitriles **3** and α-phenylseleno-α,β-unsaturated esters **4** by means of Knoevenagel reactions between phenylselenoacetonitrile **1a** or ethyl-phenylselenoacetate **1b** and aldehydes **2**, using KF/Al_2O_3 without any solvent (Scheme 1, Table 1).

Experimental

General remarks

^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded with a 200 MHz or a 400 MHz spectrometer as noted. Chemical shifts are expressed as parts per million (ppm) downfield from tetramethylsilane as an internal standard. Mass spectra (EI) were obtained at 70 eV with a Hewlett Packard EM/CG HP-5988A spectrometer, infrared spectra were acquired on a Perkin-Elmer 1310 spectrometer and elemental analyses were performed with a Vario EL Elemental Analysis System. The microwave reactions were performed on a domestic apparatus, Brastemp model VIP-38 Sensor Crisp operating at 2.45 GHz. Merck's silica gel (230-400 mesh) was used for flash chromatography.

Preparation of alumina supported potassium fluoride[19]

To a 100 mL beaker was added alumina (6.0g of Al_2O_3 90, 0.063-0.200 mm, Merck), KF.2H_2O (4.0 g) and water (8 mL). The suspension was stirred for 1 h at 65 °C, dried at 80 °C for 1 h and for additional 4 h at 300 °C in an oven and then cooled in a desiccator. The content of KF is about 30 % (m/m).

*General procedure for the synthesis of α-phenylseleno-acrylonitriles (**3a-e**)*

A mixture of aldehyde **2** (1.2 mmol) and phenylseleno-acetonitrile **1a**[20] (0.197g; 1 mmol) was added to KF/Al_2O_3 (0.1g, obtained as described above). The whole mixture was stirred at room temperature until completion of the reaction (4-5 h, Table 1), as monitored by thin layer chromatography (TLC). The catalyst was filtered off, washed with ethyl acetate (10 mL) and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography over silica gel (SiO_2) eluting with hexanes/ethyl acetate (99:1), yielding **3** as mixture of *Z* and *E* isomers.

*3-(2-Furyl)-2-phenylselanylacrylonitrile (**3a**)*

The aforementioned procedure was used, employing 2-furfuraldehyde **2a**. Yield: 0.220g (80%); *Z:E* ratio = 85:15. *Z isomer:* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48-6.50 (m, 1H), 6.97 (d, *J* 3.6 Hz, 1H), 7.29 (s, 1H), 7.32-7.44 (m, 3H), 7.52-7.53 (m, 1H), 7.61-7.64 (m, 2H); *E isomer:* δ 6.54-6.56 (m, 1H), 6.86 (d, *J* 3.6 Hz, 1H), 7.32-7.44 (m, 4H), 7.68-7.71 (m, 3H); *Z + E isomers:* ^{13}C NMR (100 MHz, $CDCl_3$) δ 93.5, 100.2, 112.4, 112.6, 115.4, 116.3, 117.0, 117.1, 126.7, 127.8, 128.7, 129.4, 129.5, 130.3, 133.5, 133.6, 135.7, 136.4, 144.9, 145.0, 149.5, 150.3; IR (film) ν_{max}/cm^{-1}: 2203 (CN). MS *m/z* (rel. int.) 275 (M^+, 52.7), 157 (59.9), 77 (89.0), 51 (100.0). Anal. Calc. for $C_{13}H_9NOSe$: C, 56.95; H, 3.31; N, 5.11. Found: C, 56.40; H, 3.48, N, 4.68.

*3-Phenyl-2-phenylselanylacrylonitrile (**3b**)*[4]

The aforementioned procedure was used, employing benzaldehyde **2b**. Yield: 0.202g (71%); *Z:E* ratio = 71:29. *Z + E isomers:* ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35-7.42 (m, 6H), 7.51 (s, 1H), 7.61-7.66 (m, 2H), 7.72-7.77 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 97.9, 104.0, 117.2, 117.5, 127.7, 127.8, 128.6, 128.8, 128.9, 129.0, 129.6 (2C), 129.7 (2C), 130.1, 130.9, 133.8, 134.1, 134.4, 135.5, 145.8, 150.1.

*3-(2-Chlorophenyl)-2-phenylselanylacrylonitrile (**3c**)*

The aforementioned procedure was used, employing 2-chlorobenzaldehyde **2c**. Yield: 0.163g (51%); *Z:E* ratio = 79:21. *Z isomer:* ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.15-7.60 (m, 8H), 7.66 (s, 1H), 7.82-7.92 (m, 1H); *E isomer:* δ 7.15-7.60 (m, 8H), 7.72 (s, 1H), 7.82-7.92 (m, 1H); *Z + E isomers:* ^{13}C NMR (50 MHz, $CDCl_3$) δ 101.9, 107.1, 116.2, 116.8, 126.5, 126.9, 127.1, 128.6, 129.3, 129.5, 129.6, 129.7, 129.8, 129.9, 131.0, 131.4, 132.0, 133.9, 134.7, 135.4, 142.5, 142.6, 144.8; IR (film) ν_{max}/cm^{-1}: 2206 (CN). MS *m/z* (rel. int.) 320 (M^+ + 1, 10.0), 318 (24.0), 286 (19.0), 284 (94.0), 207 (12.0), 162 (5.0), 157 (28.0), 127 (30.0), 77 (100.0), 51 (64.0). Anal. Calc. for $C_{15}H_{10}ClNSe$: C, 56.54; H, 3.16; N, 4.40. Found: C, 56.59; H, 3.49; N, 3.96.

*5,9-Dimethyl-2-phenylselanyl-2,8-decadienenitrile (**3d**)*

The aforementioned procedure was used, employing citronellal **2d**. Yield 0.140g (42%); *Z:E* ratio = 60:40. *Z isomer:* ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (d, *J* 6.4 Hz, 3H), 1.05-1.42 (m, 2H), 1.59 (s, 3H), 1.68 (s, 3H), 1.88-2.08

(m, 2H), 2.20-2.53 (m, 1H), 4.98-5.17 (m, 1H), 6.81 (t, *J* 7.8Hz, 1H), 7.20-7.42 (m, 3H), 7.48-7.63 (m, 2H); *E isomer:* δ 0.94 (d, *J* 6.2 Hz, 3H), 1.05-1.42 (m, 2H), 1.59 (s, 3H), 1.68 (s, 3H), 1.88-2.08 (m, 2H), 2.20-2.53 (m, 1H), 4.98-5.17 (m, 1H), 6.87 (t, *J* 7.4Hz, 1H), 7.20-7.42 (m, 3H), 7.48-7.63 (m, 2H); *Z + E isomers:* ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.5, 17.6, 19.3, 19.5, 25.2, 25.3, 25.6, 32.3, 36.4, 36.5, 39.2, 40.6, 100.6, 104.3, 115.9, 117.2, 123.9, 127.2, 127.9, 128.5, 128.7, 129.4, 131.5, 133.4, 134.1, 153.0, 156.4; IR (film) ν_{max}/cm^{-1}: 2211 (CN). MS *m/z* (rel. int.) 333 (M^+, 5.0), 207 (4.0), 176 (74.0), 156 (33.0), 149 (14.0), 77 (53.0), 69 (100.0), 55 (75.0). Anal. Calc. for $C_{18}H_{23}NSe$: C, 65.05; H, 6.98; N, 4.21. Found: C, 65.07; H, 7.03; N, 3.96.

*5,9-Dimethyl-2-phenylselanyl-2,4,8-decatrienenitrile (**3e**)*

The aforementioned procedure was used, employing citral **2e**. Yield 0.132g (40%); *Z:E* ratio = 57:43. *Z isomer:* ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 3H), 1.70 (s, 3H), 1.93 (s, 3H), 2.12-2.37 (m, 4H), 5.05-5.14 (m, 1H), 6.33 (d, *J* 10.8Hz, 1H), 7.29-7.38 (m, 3H), 7.43 (d, *J* 10.8Hz, 1H), 7.50-7.62 (m, 2H); *E isomer:* δ 1.61 (s, 3H), 1.70 (s, 3H), 1.93 (s, 3H), 2.12-2.37 (m, 4H), 5.05-5.14 (m, 1H), 6.44 (d, *J* 11.2Hz, 1H), 7.29-7.38 (m, 3H), 7.35 (d, *J* 11.2Hz, 1H), 7.50-7.62 (m, 2H); *Z + E isomers:* ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.7, 17.8, 24.5, 25.6, 26.3, 26.7, 29.6, 33.2, 40.3, 95.7, 96.2, 122.2, 122.3, 127.9, 128.4, 128.5, 128.6, 128.7, 133.9, 135.0, 135.1, 138.1, 138.5, 138.7, 138.8, 139.0, 139.1, 154.0, 154.1, 157.7, 157.8; IR (film) ν_{max}/cm^{-1}: 2201 (CN). MS *m/z* (rel. int.) 331 (M^+, 4.0), 207 (9.0), 183 (54.0), 157 (32.0), 77 (24.0), 69 (100.0), 51 (13.0). Anal. Calc. for $C_{18}H_{21}NSe$: C, 65.45; H, 6.41; N, 4.24. Found: C, 65.58; H, 6.48; N, 4.25.

*General procedure for the synthesis of α-phenylseleno-α,β-unsaturated esters (**4a** and **4b**)*

A mixture of aldehyde **2** (1.2 mmol) and ethyl phenylselenoacetate **1b**[21] (0.244g; 1 mmol) was added to KF/Al_2O_3 (0.1g, obtained as described above). The whole mixture was stirred at room temperature for 5 hours. The catalyst was filtered off, washed with ethyl acetate (10 mL) and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography over silica gel (SiO_2) eluting with hexanes/ethyl acetate (99:1), yielding **4** as mixture of *Z* and *E* isomers.

*Ethyl 3-(2-furyl)-2-phenylselanylpropenoate (**4a**)*[6,10,22]

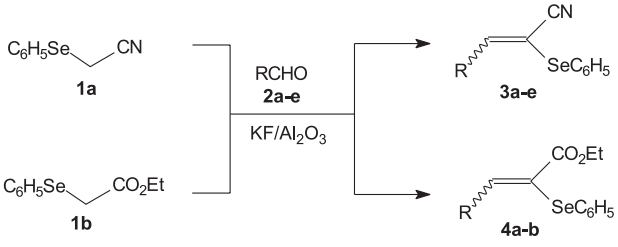
The aforementioned procedure was used, employing 2-furfuraldehyde **2a**. Yield: 0.129g (40%); *Z:E* ratio = 63:37. *Z + E isomers:* ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 and 1.18 (2t, *J* 7.2 Hz, 3H), 4.05 and 4.10 (2q, *J* 7.2 Hz, 2H), 6.37 (dd, *J* 3.6 and 2.0 Hz, 1H), 6.48 (dd, *J* 3.6 and 2.0 Hz, 1H), 6.69 (d, J 3.4 Hz, 1H), 6.77 (s, *E* isomer), 8.03 (s, *Z* isomer, *E* + *Z* = 1H), 7.14-7.60 (m, 5H).

*Ethyl 3-phenyl-2-phenylselanylpropenoate (**4b**)*[6,10]

The aforementioned procedure was used, employing benzaldehyde **2b**. Yield: 0.129g (39%); *Z:E* ratio = 55:45. *Z + E isomers:* ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 and 1.10 (2t, *J* 7.2 Hz, 3H), 3.98 and 4.05 (2q, *J* 7.2 Hz, 2H), 7.04 (s, *E* isomer), 8.15 (s, *Z* isomer; *E* + *Z* = 1H), 7.16-7.72 (m, 10H).

Results and Discussion

In order to find the best experimental conditions to access **3**, a detailed study was performed using furfural **2a** as the standard aldehyde. When the reaction was performed using KOH, *t*-BuOK or KF/Al_2O_3 (stoichiometric amounts) without any solvent or in THF, the desired product was obtained in good yields (78-80%) after 1-4 hours at room temperature. However, when the same protocol was applied to other aldehydes (**2b-e**), the use of KOH or *t*-BuOK allowed incomplete consumption of starting material **1a** and decomposition of product in all conditions tested.



Scheme 1.

For example, when phenylselenoacetonitrile **1a** was submitted to reaction with benzaldehyde **2b**, the α-phenylseleno cinnamonitrile **3b** was obtained in unsatisfactory yields (20-25%, after 3-4 hours at rt), together with diphenyl diselenide (40-44%). However, using KF/Al_2O_3 (30%), **3b** was obtained in 71% isolated yield, along with a small amount of unreacted **1a** (4%). When the same protocol was performed in THF, the product was obtained in poor yield (10%), with incomplete consumption of the starting materials and formation of diphenyl diselenide. The use of higher temperature or a larger amount of solid supported catalysts or aldehyde was not effective to complete consumption of the starting materials and there has been no increase in the yields.

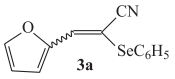
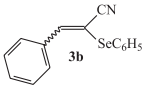
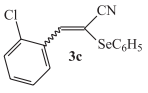
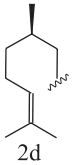
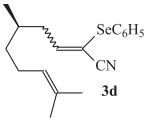
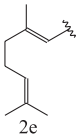
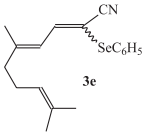
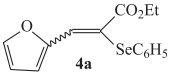
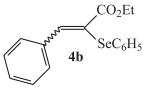
Aiming to reduce the reaction time, we tested the reaction using MW irradiation. The use of "MORE Chemistry" (microwave oven-induced reaction enhancement) under solvent-free conditions is well stablished.[23] In general increases in rates, yields and purities of products have been associated with this technique. In fact, when a mixture of furfural **2a** and phenylselenoacetonitrile **1a** was irradiated with MW (427W) in the presence of KF/Al_2O_3 (30%), **3a** was obtained after 8 min (55% yield). Starting from benzaldehyde **2b**, phenylseleno cinnamonitrile **3b** was obtained after 20 min under MW in 37% yield. Attempts to increase the yields of **3a,b** were unsuccessful. Even increasing the power and time of irradiation no significant change in yields and products distribution was observed.

Thus, the optimum condition for Knoevenagel condensation of **1a** and **2** (Scheme 1) consists of stirring for 4-5 h at room temperature a mixture of **1a** and **2** in the presence of 0.1g of KF/Al_2O_3 (30%) as base, without any solvent. The products were obtained in moderate to good yields (40-80%, entries 1-5, Table 1). The presence of an electron-withdrawing group in the aromatic ring of the aldehyde (**2c**, entry 3) caused a reduction in the yield. Similarly, aliphatic aldehydes citronellal and citral (**2d** and **2e**, entries 4 and 5) gave moderated yields of **3d** and **3e**.

Other bases, such as K_2CO_3, Na_2CO_3, Et_3N or piperidine, and the use of solvents (CH_3CN, EtOH, DMF) proved to be less effective. By using only Al_2O_3, no reaction took place in all conditions tested and **1a** was recovered unchanged.

Attempts to directly reuse the solid supported catalysts in a new condensation reaction were unsuccessful, with a complete loss of the catalytic activity. However, the solid supports were regenerated

Table 1. Synthesis of α-phenylselenoacrylonitriles **3** and α-phenylseleno-α,β-unsaturated esters **4** under solvent-free conditions

Entry	1	2	Product	Reaction time (h)	Yield[a] (%)	Ratio (*Z*/*E*)
1	**1a**	2-furyl **2a**	 **3a**	4	80	85 : 15
2	**1a**	C_6H_5 **2b**	 **3b**	4	71	71 : 29
3	**1a**	2-ClC_6H_4 **2c**	 **3c**	4	51	79 : 21
4	**1a**	 2d	 **3d**	5	42	60 : 40
5	**1a**	 2e	 **3e**	5	40	57 : 43
6	**1b**	2-furyl **2a**	 **4a**	5	40	63 : 37
7	**1b**	C_6H_5 **2b**	 **4b**	5	39	55 : 45

[a] Yields in pure products isolated by chromatography (AcOEt/hexanes) and identified by mass spectra, ^1H, ^{13}C NMR.[4,6,10,22]

by new treatment with KF. The KF/Al_2O_3 (30%) prepared from used Al_2O_3 showed the same catalytic activity, affording **3** in almost identical yields.

The same protocol was performed using ethyl phenylselenoacetate **1b**, affording the products **4a,b** in moderate yields after purification (entries 6 and 7, Table 1). The Knoevenagel reaction have been already employed to synthesize this class of compounds.[22] However, the procedure early described makes use of strong Lewis acid ($TiCl_4$), volatile organic solvents (CCl_4 and THF), low temperature and is limited to aromatic aldehydes.

Although the yields of the method described in Scheme 1 are moderate (39 – 80%, Table 1), the simplicity of this clean, solvent-free and atom-economic method makes it suitable for the preparation of products derived from aromatic and aliphatic aldehydes.

For all the substrates, the formation of *Z* and *E* isomers mixture was observed. The stereochemistry of the obtained olefins **3** and **4** was assigned by ^{1}H NMR.[4,6,10,22] However, for **3b** this ratio could not be determined directly by ^{1}H NMR, because the vinylic hydrogen signals overlaped with the aromatic hydrogens. The *Z* : *E* ratio of **3b** was determined according to described by Silveira and co-workers.[4]

Conclusions

Several α-phenylselenoacrylonitriles **3** and α-phenylseleno-α,β-unsaturated esters **4** could be prepared by Knoevenagel condensation under solid supported catalysis (KF/Al_2O_3) and solvent-free conditions at room temperature. This atom-economic protocol consists in low consumption of solvent, short reaction time, mild reaction conditions, good yields and simplicity, with non-aqueous work-up. Finally, the elimination of the large amount of salts and other solid residues generated in the conventional methods to the title compounds was achieved.

Acknowledgments

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