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Article

Synthesis of Organothioacrylonitriles and Organoselenoacrylonitriles by Reaction of 1-Halo-1-chalcogenoalkenes with CuCN

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Reação de 1-halo-1-organotio ou 1-halo-1-organoseleno alcenos com CuCN em NMP como solvente resulta em α-feniltio ou α-fenilseleno acrilonitrilas em bons rendimentos. A reação apresentou uma baixa estereosseletividade e os produtos foram obtidos como uma mistura de isômeros *E/Z*.

Reaction of 1-halo-1-organothio or 1-halo-1-organoseleno alkenes with CuCN in NMP as solvent provides α-phenylthio or α-phenylseleno acrylonitriles in good yields. The reaction showed a low stereoselectivity and the products were obtained as *E*/*Z* mixtures of isomers.

Keywords: organoselenoacrylonitriles, organothioacrylonitriles, vinylic substitution, cuprous cyanide, vinylic chalcogenides

Introduction

Functionalized alkenyl chalcogenides (S, Se and Te) have great potential in organic synthesis, since they are valuable intermediates for the selective preparation of several organic compounds.[1-7] The synthesis of vinylic chalcogenides has therefore attracted the attention of several research groups, and many novel methods for their preparation have been proposed in the last years.[1-7] We described practical methodologies for the preparation of vinylic chalcogenides based on Wittig and Wittig-Horner reactions.[8-10] Studies on the synthesis of α-phenylseleno and α-phenyltelluro acrylonitriles and the chemical reactivity of α-phenylseleno acrylonitriles in reactions with DIBAL-H, amines and in a Diels-Alder-type reaction were also described.[10] Among the functionalized vinylic chalcogenides, those containing electron withdrawing groups, like a cyano group at the sp^2 carbon (α-chalcogeno-α,β-unsaturated nitriles), are of great interest since they combine the chemical reactivity of the vinyl chalcogenide and the vinyl nitrile.[1]

Vinylic sulfides α-substituted by strong electron withdrawing groups have been synthetically used as potent Michael acceptors,[11,12] in a variety of cycloaddition reactions[13-18] and in studies as precursors of extended enolates.[19,20] The selenium analogs have been used as dienophiles in Diels-Alder reactions,[21,22] as Michael acceptors[23-26] and in the synthesis of 2,3-dihydroselenophenes and butadienes.[27] α-Cyano substituted vinylic sulfides have been prepared by a few different routes.[28,29] Methods for the preparation of α-phenylselenoacrylonitriles are also just a few[10,30] and the synthesis of the corresponding α-phenyltelluroacrylonitriles was recently described by us.[10] α-Phenylselenoacrylonitriles have been prepared by the addition of benzeneselanyl chloride or bromide to cyano olefins leading to α-seleno adducts, which are subjected to *in situ* dehydrohalogenation.[27,30,31] Recently, Chinese authors described the preparation of several α-phenylseleno-α,β-unsaturated nitriles in moderate to good yields *via* α-phenylselanyl cyanomethylene triphenyl-arsorane.[32,33] However, this method is restrict to aromatic aldehydes and no mention regarding the stereochemistry of the products was made. Besides these drawbacks, this method suffers from the high toxicity of arsenium compounds. More recently, Perin *et al.*[34] described the synthesis of α-phenylselenoacrylonitriles and α-phenylseleno-α,β-unsaturated esters by Knoevenagel reaction under solvent-free conditions.

Results and Discussion

Due to our continuous interest directed toward the development of new methods for the synthesis of functionalized vinylic chalcogenides, we would like to report herein a new, simple and efficient synthesis of α-organothioacrylonitriles and α-organoselenoacrylonitriles

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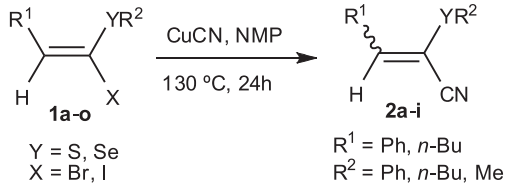
by the vinylic substitution of α-halo vinylic chalcogenides with CuCN in *N*-methylpyrrolidone, according to Scheme 1.



Scheme 1.

The α-halo vinylic chalcogenides **1a-o** were easily prepared stereoselectively by the addition of the hydrogen halide (generated *in situ* by reaction of trimethylsilyl halide with anhydrous methanol) to the acetylenic chalcogenides,[35] usually obtained as a single isomer. The 1-halo-1-selenium alkenes could also be prepared by addition of hydrogen halides to acetylenic selenides.[36]

Our initial studies were made toward to the determination of optimum conditions to perform the reaction. Thus, we chose the (*E*)-1-bromo-1-phenylselenohexene (**1c**) as starting material to establish the best conditions for the vinylic substitution reaction. The 1-bromo-1-phenylselenohexene (1.0 equiv.) was treated with CuCN (3.0 equiv.) as a source of cyanide anion in different solvents, such as DMSO, THF, NMP and mixtures of these solvents with HMPA under heating. The experiment carried out in NMP at 90 °C for 24 h was the only one to produce the desired α-phenylselenoacrylonitrile (40% yield after column chromatography). The use of HMPA as co-solvent with NMP did not increase the yield. The effect of the temperature in this reaction is noteworthy on the yield. We observed that satisfactory yield (60%) could only be obtained when the reaction was performed at 130 °C (oil bath temperature) for 24 h in NMP. The stoichiometry of CuCN was also studied, and the best results were achieved by using 3.0 equivalents of this reagent. Experiments carried out in presence of 1.0 and 2.0 equiv. of CuCN resulted in lower yields of desired products (10% and 43%, respectively) and a little amount of the starting material was recovered unchanged. At higher amounts of CuCN, no improvement on the yield was observed. Next step was a detailed study on the effect of the halogen atom on the α-halo vinylic chalcogenides and better yields were obtained using the iodo compared to the bromo derivatives, as can be observed in Table 1. The chloro derivatives showed to be inert under the conditions used by us. Thus, the optimum conditions for substitution reaction according to Scheme 1 were established to be the use of CuCN (3.0 mmol) in *N*-methylpyrrolidone (5 mL) and the 1-halo vinylic chalcogenide (1.0 mmol) at 130 °C for 24 h. A full study was performed with several different substrates, including sulfur and selenium derivatives substituted by alkyl and aryl groups. As can be seen on the Table 1, good yields of the products were obtained in most of the cases.

The method described here exhibits good generality to organoseleno- and organothioacrylonitriles and it is successful with aromatic and aliphatic derivatives. Although most experiments were performed on a 1.0 mmol scale, these reactions can also be performed successfully on higher scales with comparable yields.

Analysis of the ^{1}H NMR and ^{13}C NMR spectra showed that all α-organochalcogenoacrylonitrile compounds presented data in full agreement with their assigned structures. Concerning the stereochemistry of the obtained olefins, we usually observed the formation of *Z*/*E* mixture of isomers, even starting from pure (*E*)-1-halo vinylic chalcogenide. This is probably a result of the high temperature (130 °C) necessary to the reaction to occur. For most examples, a nearly 1:1 *E/Z* ratio was observed,

Table 1. Vinylic substitution of 1-halo vinylic chalcogenides according to Scheme 1

Entry	Substrate	R^1	R^2	Y	X	Product	Yield / (%)[a]	Z/E Ratio[b]
1	**1a**	*n*-C_4H_9	C_6H_5	S	Br	**2a**	64	1:1
2	**1b**	*n*-C_4H_9	C_6H_5	S	I	**2a**	73	1:1
3	**1c**	*n*-C_4H_9	C_6H_5	Se	Br	**2b**	60	1:1
4	**1d**	*n*-C_4H_9	C_6H_5	Se	I	**2b**	72	1:1
5	**1e**	C_6H_5	C_6H_5	S	Br	**2c**	56	1:2
6	**1f**	C_6H_5	C_6H_5	S	I	**2c**	61	1:2
7	**1g**	C_6H_5	C_6H_5	Se	Br	**2d**	70	3.6:1
8	**1h**	C_6H_5	C_6H_5	Se	I	**2d**	83	3.6:1
9	**1i**	C_6H_5	CH_3	S	Br	**2e**	64	1:1
10	**1j**	C_6H_5	CH_3	S	I	**2e**	67	1:1
11	**1k**	C_6H_5	CH_3	Se	Br	**2f**	43	1:20
12	**1l**	C_6H_5	CH_3	Se	I	**2f**	51	1:20
13	**1m**	C_6H_5	*n*-C_4H_9	Se	Br	**2g**	71	15:1
14	**1n**	C_6H_5	*n*-C_4H_9	Se	I	**2g**	76	15:1
15	**1o**	*n*-C_4H_9	*n*-C_4H_9	Se	I	**2h**	61	1:1

[a]Isolated yields of products after column chromatography. [b]diastereomeric ratio determined by ^{1}H NMR (200 MHz) from the crude reaction mixture.

usually with a very small preference for one isomer. In a few examples (entries 7, 8, 11-15, Table 1), a higher preference for one isomer could be observed, but we could not establish a general pattern for this preference. The relative stereochemistry and the diastereomeric ratio of the obtained compounds **2a**-**h** were assigned by comparing the chemical shifts with known aromatic acrylonitriles (**2c**-**g**).[10] The *E* and *Z* attributed stereochemistry was based on an X-ray structural analysis of one pure isomer and also from DIBAL-H reduction of the nitrile to the corresponding aldehyde, followed by a NOESY correlation study between the vinylic H and the aldehydic H. In the case of aliphatic acrylonitriles (**2a**, **2b** and **2h**), evidence for the determination of stereochemistry of the products was obtained by comparing ^{1}H and coupled and decoupled ^{13}C NMR spectra in an enriched mixture. The major isomer in aliphatic series can be easily determined by integration of the triplets (from the coupling of vinylic H with the vicinal CH_2) of the mixture. The determination of stereochemistry of the major isomer can be made, by analyzing of the nitrile carbon peaks in the ^{13}C NMR spectra. For example, for compound **2b**, in the decoupled spectra the carbon signals for the isomers are at 115.5 and 116.9 ppm. In the hydrogen-coupled ^{13}C NMR spectra, the singlets split into doublets, with $^{3}J_{C\text{-}H}$ couplings of 14.1 Hz and 7.1 Hz, typical of *E* (vinylic H and cyano *anti*) and *Z* (vinylic H and cyano *sin*) $^{3}J_{C\text{-}H}$ coupling constants,[37] respectively. Correlation of the most intense carbon in ^{13}C NMR with most intense triplet in ^{1}H NMR allows the determination of the upfield triplet as from the *E* isomer (for **2b** in 6.77 ppm) and the downfield triplet as from the *Z* isomer (for **2b** in 6.80 ppm). The mixture of isomers could not be separated by column chromatography, since they have nearly the same Rf values.

Conclusions

In summary, we have developed a new, simple and efficient methodology for the synthesis of α-organoseleno- and α-organothioacrylonitriles by the vinylic substitution of a halogen atom by a cyano group. The products were obtained as isomers mixtures in moderate to good yields.

Experimental

General

All ^{1}H and ^{13}C NMR spectra were recorded at 200 MHz and 50 MHz, respectively, on a Bruker DPX 200 instrument, using $CDCl_3$ as solvent. Chemical shifts (δ) are expressed in parts *per* million (ppm) downfield from tetramethylsilane or $CHCl_3$ as internal standard, and *J* values are given in Hz. Mass spectra (EI) were obtained at 70 eV with a Hewlett Packard EM/CG HP-5988A spectrometer. Infra-red spectra were acquired on a Perkin-Elmer 1310 Spectrometer and the elemental analyses were performed with a Vario EL Elementar Analysis System. Merck's silica gel (230-400 mesh) was used for flash chromatography. All reactions were performed in flame-dried glassware under a positive pressure of argon. Air and moisture sensitive reagents and solvents were transferred *via* syringe, and were introduced into reaction vessels through a rubber septum. NMP was distilled over argon before use.

*General procedure for the synthesis of α-phenylseleno and α-phenylthio acrylonitriles (**2a-h**)*

To a solution of the α-halo vinylic chalcogenide **1** (1.0 mmol) in NMP (5 mL) was added CuCN (0.26 g, 3.0 mmol) and the flask was immersed in an oil bath previously heated at 130 ºC. The reaction mixture was heated at this temperature for 24 h, cooled to room temperature, water was added and extracted with ethyl acetate (3 × 25 mL). The organic phase was washed with aqueous saturated solution of NH_4Cl (2 × 50 mL), dried over $MgSO_4$ and the solvent removed in vacuo. The residue was purified by column chromatography (SiO_2) using hexane/ethyl acetate (99:1) as eluent.

*(Z+E)-2-Phenylthio-hept-2-enenitrile (**2a**)*

IR (film) ν_{max}/cm^{-1}: 3060, 2958, 2860, 2216, 1630, 1440, 742. MS *m/z* (rel. int.) 217 (M^+, 97), 161 (95), 134 (47), 91 (100), 51 (81). ^{1}H NMR (200 MHz, $CDCl_3$) δ (*Z* + *E*) 7.37-7.30 (m, 5H); 6.77 and 6.75 (2t, 1H, *J* 7.8 Hz); 2.50-2.39 (m, 2H); 1.49-1.26 (m, 4H); 0.91 (t, 3H, *J* 7.8 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.8; 153.7; 131.8;. 131.2; 130.7; 129.2 (2C); 128.9; 128.2; 128.0; 116.4; 114.8; 109.1; 107.5; 32.2; 30.1; 30.0; 29.7; 22.1; 22.0; 13.5 (2C). Anal. calc. for $C_{13}H_{15}NS$: C, 71.84; H, 6.96; N, 6.44. Found: C, 71.26; H, 6.88; N, 6.28.

*(Z+E)-2-Phenylselanyl-hept-2-enenitrile (**2b**)*[33]

IR (film) ν_{max}/cm^{-1}: 3058, 2957, 2870, 2210, 1577, 1438, 738. MS *m/z* (rel. int.) 265 (M^+ + 1, 100), 209 (51), 157 (65), 115 (62), 77 (84). ^{1}H NMR (200 MHz, $CDCl_3$) δ (*Z* + *E*) 7.53-7.48 (m, 2H); 7.29-7.26 (m, 3H); 6.80 and 6.77 (2t, 1H, *J* 7.8 Hz); 2.43-2.30 (m, 2H); 1.47-1.21 (m, 4H); 0.97-0.84 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.4; 154.1; 133.5; 132.8; 129.1; 128.3 (2C); 128.1; 127.5; 126.9; 116.9; 115.5; 102.9; 99.3; 32.9; 31.5; 29.7; 29.6; 21.8; 21.6; 13.3 (2C).

*(Z+E)-3-Phenyl-2-phenylthio-acrylonitrile (**2c**)*[38]

IR (film) ν_{max}/cm^{-1}: 3074, 3058, 3019, 2213, 1588, 1438, 750. MS *m/z* (rel. int.) 237 (M^+, 95), 210 (36), 159 (42), 77 (97), 51 (100). ^{1}H NMR (200 MHz, $CDCl_3$) δ (*Z* + *E*) 7.75-7.65 (m, 2H); 7.50-7.34 (m, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.2; 144.4; 133.4; 132.8 (2C); 131.6; 131.5; 130.9; 130.6; 130.3 (2C); 130.2; 129.4 (2C); 129.2; 128.9; 128.6; 128.5; 116.8; 116.1; 109.2; 104.9. Anal. calc. for $C_{15}H_{11}NS$: C, 75.91; H, 4.67; N, 5.90. Found: C, 75.67; H, 4.84; N, 5.62.

*(Z+E)-3-Phenyl-2-phenylselanyl-acrylonitrile (**2d**)*[10]

IR (film) ν_{max}/cm^{-1}: 3055, 3018, 2201, 1589, 742. MS *m/z* (rel. int.) 285 (M^+ + 1, 53), 204 (55), 157 (29), 77 (100), 55 (83). ^{1}H NMR (200 MHz, $CDCl_3$) δ (*Z* + *E*) 7.77-7.74 (m, 2H); 7.66-7.64 (m, 2H); 7.52 (s, 1H); 7.60-7.35 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.1; 145.8; 135.5; 134.4; 134.1; 133.8; 130.9; 130.1; 129.7 (2C); 129.6 (2C); 129.0; 128.9; 128.8; 128.6; 127.8; 127.7; 117.5; 117.2; 109.2; 104.0.

*(Z+E)-3-Phenyl-2-methylthio-acrylonitrile (**2e**)*[39]

IR (film) ν_{max}/cm^{-1}: 3059**,** 2924, 2208, 1445, 754. MS *m/z* (rel. int.) 176 (M^+ + 1, 75), 159 (100), 133 (92), 89 (81), 51 (93). ^{1}H NMR (200 MHz, $CDCl_3$) δ (*Z* + *E*) 7.59-7.55 (m, 2H); 7.44-7.31 (m, 3.3H; includes 1H vinylic, minor isomer); 7.21 (s, 0.7H; major isomer); 2.53 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.4; 141.2; 133.7; 133.5; 130.0 (2C); 129.6; 129.4; 128.4 (2C); 115.8; 115.6; 110.3; 110.1; 17.2; 17.0.

*(Z+E)-3-Phenyl-2-methylselanyl-acrylonitrile (**2f**)*

IR (film) ν_{max}/cm^{-1}: 3059, 2924, 2211, 1585, 755. MS *m/z* (rel. int.) 223 (M^+ + 1, 47), 181 (100), 143 (54), 102 (27), 77 (21). ^{1}H NMR (200 MHz, $CDCl_3$) δ (*Z* + *E*) 7.55-7.37 (m, 6H); 2.43 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.6; 144.2; 134.6; 134.4; 130.4; 130.2; 129.8 (2C); 128.9 (2C); 116.7; 116.5; 102.7; 101.8; 9.2; 9.0. Anal. calc. for $C_{10}H_9NSe$: C, 54.07; H, 4.08; N, 6.31. Found: C, 53.93; H, 3.59; N, 5.97.

*(Z+E)-3-Phenyl-2-butylselanyl-acrylonitrile (**2g**)*

IR (film) ν_{max}/cm^{-1}: 3053, 3027, 2216, 1616, 746. MS *m/z* (rel. int.) 265 (M^+ + 1, 34), 181 (100), 180 (51), 102 (26), 41.0 (46). ^{1}H NMR (200 MHz, $CDCl_3$) δ (*Z* + *E*) 7.70-7.37 (m, 6H); 3.07 (t, 3H, *J* 7.4 Hz); 1.74 (quint, 2H, *J* 7.4 Hz); 1.44 (quint, 2H, *J* 7.4 Hz); 0.91 (t, 3H, *J* 7.4 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.8; 145.0; 134.5; 134.0; 130.4; 130.2; 128.8 (2C); 128.4 (2C); 116.9; 116.4; 101.9; 96.2; 32.2; 32.0; 29.1; 28.9; 22.6; 22.5; 13.4; 13.2.

*(Z+E)-2-Butylselanyl-hept-2-enenitrile (**2h**)*

IR (film) ν_{max}/cm^{-1}: 2961, 2943, 2887, 2201, 1476, 734. MS *m/z* (rel. int.) 245 (M^+ + 1, 21), 189 (18), 108 (39), 57 (66), 41 (100). ^{1}H NMR (200 MHz, $CDCl_3$) δ (*Z* + *E*) 6.78 and 6.71 (2t, 1H, *J* 7.8 Hz); 2.99-2.86 (m, 2H); 2.40 and 2.27 (2q, 2H, *J* 7.5 Hz); 1.73-1.62 (m, 2H); 1.48-1.25 (m, 6H); 0.93 (t, 6H, *J* 7.5 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.9; 152.4; 116.7; 115.6; 102.0; 98.1; 33.2; 32.3; 31.9; 31.7; 30.2; 29.8; 27.4 (2C); 22.5; 22.4; 22.1; 21.9; 13.5 (2C); 13.3 (2C).

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