Tetrahedron Vol. 48, No. 13, pp. 2613-2626, 1992
Printed in Great Britain

0040-4020/92 $3.00+.00

The Invention of Radical Reactions. Part XXIII[1] New Reactions: Nitrile and Thiocyanate Transfer to Carbon Radicals from Sulfonyl Cyanides and Sulfonyl Isothiocyanates.

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(*Received in USA* 6 *February* 1992)

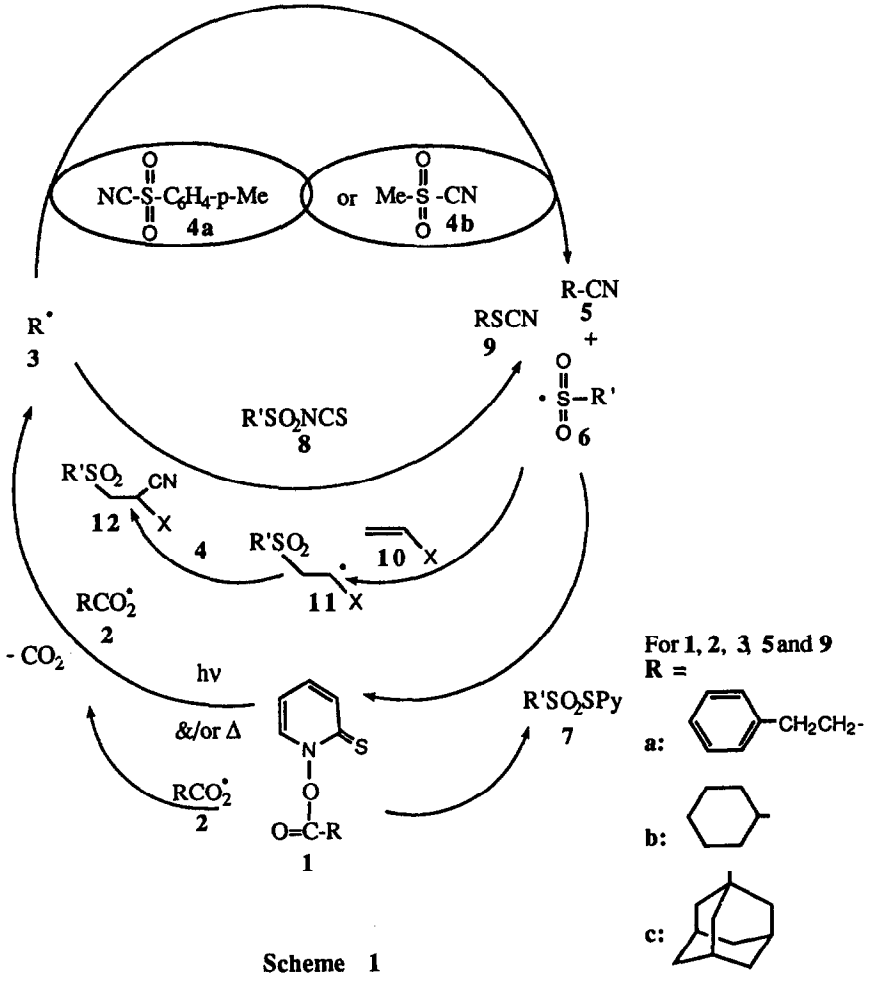
Key Words: Sulfonyl cyanides, sulfonyl isothiocyanates, O-acyl-N-hydroxy-2-thiopyridone, free radical, hv.

Abstract: *Reaction of p-toluenesulphonyl cyanide or methanesulfonyl cyanide with carbon radicals, generated from the corresponding O-acyl-N-hydroxy-2-thiopyridone derivatives by visible light photolysis gives nitriles in good yield. The homolysis products of these sulfonyl nitriles can also be trapped by electron rich olefins. We have also found that carbon radicals react easily with mesyl or tosyl isothiocyanate producing thiocyanates.*

Because of its mildness and selectivity, radical chemistry is becoming more and more important in organic synthesis[2]. This is due also to the fact that functional group transformations as well as synthesis of complex structures can easily be accomplished based upon this methodology[3]. The compatibility of radical reactions with various sensitive functional groups and/or structural elements is further enhanced when the generation of carbon radicals can be achieved by mild methods at or below room temperature. Acyl derivatives of N-hydroxy-2-thiopyridone (Barton esters)[4] proved almost ideal for this purpose, since they can be photolysed by visible (tungsten) light without temperature restrictions. This is reflected in the number of successful applications[5] that have appeared since the publication of the original paper[6]. In addition to carbon-centered radicals, nitrogen-[7] and oxygen-centered[8] radicals have also been generated by this method.

Nitrile transfer to carbon radicals.

We have shown recently that sulfonyl cyanides are good precursors of sulfinates[9, 10] and also that they can be used for nitrile transfer to carbon radicals[11]. The latter is interesting from that point of view that the transformation of a given acid to the corresponding nitrile is not always an easy procedure[12]. Chlorosulfonyl isocyanate,[13] thionyl chloride and sulfamide[14] or ethyl polyphosphate[15] have been employed. In a recent publication the dehydration of amides to nitriles was accomplished in a mild way by using methyl (carboxysulfamoyl) triethylammonium hydroxide (Burgess reagent).[16]



Scheme 1

We have employed the visible light induced photolysis of Barton esters **1** to generate the corresponding carbon radicals **3** via the primarily formed acyloxy radicals **2** (Scheme 1). Photolysis of these acyl derivatives of the thiohydroxamic acid *N*-hydroxy-2-thiopyridone in the presence of **4a** or **4b** resulted in the formation of the corresponding nitriles **5** (Scheme 1).

The W-light induced photolysis of the acyl derivatives **1** takes place very quickly (5-30 minutes at 0°C), no side-product formation is observed and the excess **4a** or **4b** can be separated and used again. The experiments concerning this radical nitrile transfer are in Table 1.

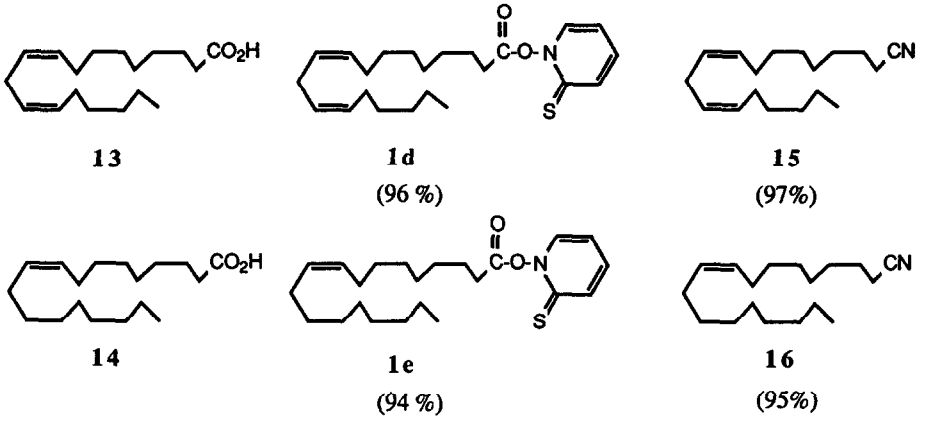
Table 1 Radical nitrile transfer to the carbon radicals generated from **1a-e.**

Radical source	Sulfonyl nitrile equivalents	Yield of the nitriles [a] with TsCN (**4b**) %	with MsCN (**4b**)
1a	1	78	65
	3	93	82
	5	-	91
1b	1	73	60
	3	88	86
	5	-	90
1c	1	65	55
	3	82	77
	5	-	84
1d	1	80	60
	3	93	78
	5	> 95 (97)[b]	83
1e	1	77	62
	3	89	75
	5	95[b]	87

[a] by ^{1}H NMR.
[b] isolated yield, with 6 equivalents of **4b**

In order to decrease the excess of **4a** or **4b** used in this reaction the Barton esters **1** can be dissolved in methylene dichloride and added in small portions into the flask containing the tosyl cyanide **1**, irradiated with a tungsten lamp. The disappearance of the yellow color of the mixed anhydrides indicates that the photolysis of a given portion is complete. In this radical chain process ideally the sulfonyl radical **6** carries the chain and not the carbon radical **3**, furnishing the thiosulfonate **7** and acyloxy radical **2** as depicted in Scheme 1.

The use of this new reaction has been demonstrated in the high yielding transformations of linoleic acid **13** and oleic acid **14** to the corresponding nitriles **15** and **16**, respectively, *via* their mixed anhydrides **1d** and **1e**. Nitriles **15** and **16** were readily hydrolysed under mild alkaline conditions to give back acids **13** and **14** respectively.



Scheme 2

Although this conversion of a carboxylic acid into a nitrile may not be useful for robust acids, it could be applicable for sensitive natural products. Also it could avoid functional group protection, if the Barton esters are made by the carbodiimide route[30,31]. It should be a simple way to replace a carboxyl group with ^{13}C or ^{14}C or to make a ^{15}N nitrile. The overall yield of **13** from the **13** ⟶ **1d** ⟶ **15** ⟶ **13** sequence was 74%, while **14** was obtained from **14** *via* **1e** and **16** in a 70% (not optimized) yield. There was no rearrangement (the reaction between **1** and **3**) or any reaction of the double bond(s) of **13**, **14**, **15** or **16**.

Thiocyanate transfer to carbon radicals.

The efficiency of sulfonyl radicals as chain carriers in the case of the radical nitrile transfer lead us to examine the possibility of thiocyanate transfer from isothiocyanates. We have prepared thiocyanogen **17**[17] and p-toluenesulfonyl thiocyanate **18**[18], but both of these compounds proved to be too reactive towards the Barton esters resulting in ionic reactions instead of the desired homolytic cleavage and radical reactions.

However, the radical thiocyanate transfer was easily accomplished with p-toluenesulfonyl isothiocyanate[19] **8a** or methanesulfonyl isothiocyanate[19] **8b** (Scheme 1). The thiocyanates were obtained this way in moderate to good yields (Table 2). Similarly to the nitrile transfer reactions, the use of the methanesulfonyl reagent resulted in higher yields. The only other products isolated were the corresponding thiosulfonates **7a** (R' = p-tolyl) and **7b** (R' = Me), respectively. The presence of these compounds indicate a chain mechanism depicted in Scheme 1. This transformation of an acid to the corresponding thiocyanate allows the easy introduction of a sulfur atom into the radical generated from the acid providing entry to a series of sulfur compounds (e. g. thiols, disulfides, sulfonic acids).[17]

Table 2 Thiocyanate transfer to carbon radicals from sulfonyl isothiocyanates.

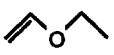
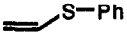
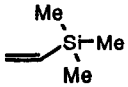
Radical source	Sulfonyl isothiocyanate equivalents	Yield of thiocyanates (%) with **8a**	with **8b**
	1.2	55[20]	71
1a	3.0	72	81
	5.0	80	89
	1.2	45[21]	66
1b	3.0	64	77
	5.0	75	83
	1.2	38[22]	62
1c	3.0	45	73
	5.0	51	78

Addition of sulfonyl cyanides to electron rich olefins.

There are many ways to generate sulfonyl radicals,[23] the use of sulfonyl halides being the most commonly employed. Recently methanesulfonyl bromide has been shown to add to olefins (alkenes, cycloalkenes, alkenylsilanes)in a UV-light initiated radical chain reaction.[24] The aim of the study was to

determine the relative rates of addition of the methanesulfonyl radical. The generation of sulfonyl radicals from sulfonates[25] and the addition of p-toluenesulfonyl cyanide[26] or the p-toluenesulfonyl radical[27] to alkenes have also been described. These reactions, however, require UV-light irradiation, AIBN or dibenzoyl peroxide initiated thermolytic cleavage. We have attempted to apply acyl derivatives of N-hydroxy-2-thiopyridone as initiators of the homolytic cleavage of sulfonyl nitriles **4a** and **4b**. This has easily been accomplished by visible light irradiation at 0-5°C. When a controlled amount of initiator **1a** was added during visible light photolysis, the reaction furnished the desired β-cyanosulfones (**12**, Scheme 1) in good to excellent yield.

Table 3 Addition of sulfonyl cyanides to electron rich olefins

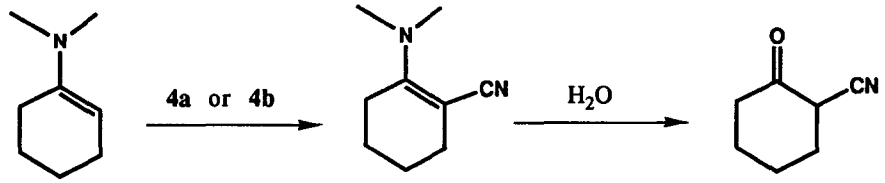
Olefin (10 equivalents)	Initiator (equivalents)	Yield of the adducts [a] % with **4a**	with **4b**
	0.05	-	60[c]
	0.05	55	91
	0.1	74[b]	-
	0.2	83[b]	-
	0.05	0	51
	0.1	25[b]	87[b]
	0.2	42	89[b]
 (5 equivalents)	0.05	57[b]	68[b]
	0.1	72[b]	84[b]
	0.2	81	91
	0.05	0[b]	33
	0.1	18[b]	51[b]
	0.2	25	55[b]
	0.05	8	12
	0.1	21[b]	25[b]
	0.2	30	41
	0.05	19[b]	29[b]
	0.1	38[b]	45[b]
	0.2	45	59

[a] Isolated yields, unless otherwise stated. [b]Yields determined by ^{1}H NMR. [c]Only 1 equivalent of the olefin was used.

There was no indication of oligomer or polymer formation.[26] The highest yielding reactions were those of electron rich olefins, probably due to a favorable polar effect in the transition state which increases the rate of the addition (Table 3).

The photolysis was done in all cases at 0-5°C (ice bath). The corresponding sulfonyl cyanide (3 mmol) was dissolved in methylene chloride (5.0 ml) and 10 equivalents of the trap was then added. A methylene chloride solution of the initiator **1a** was used. It was added portionwise to the reaction mixture. The disappearance of the yellow color of **1a** indicated that it was completely consumed.

The enamine[28] **19** was also tested as an electron rich olefin in this radical chain reaction. However, an ionic dark reaction was observed in this case with **4a** or **4b**, resulting in the formation of nitrile[29] **20**, which, in turn, furnished the ketone **21** upon aqueous work-up in a quantitative yield (Scheme 3).



19 **20** (100%) **21** (100%)

Scheme 3

Experimental Section

General Procedures and Starting Materials.

Melting points were determined with a Kofler hot-stage melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 881 spectrophotometer. UV spectra were recorded on a Beckman DU-7 spectrometer. ^{1}H and ^{13}C NMR spectra were determined for solutions in deuteriochloroform (unless specified otherwise) with TMS internal reference on Varian Gemini 200, Varian XL 200E or Varian XL 400 instruments. Gas chromatography (glc) measurements were performed on a Chrompack Packard Model 439 gas chromatograph on 30 m capillary columns. GC-MS data were obtained on a Hewlett-Packard 5890 GC-MS system. Mass spectra were obtained on a VG Analytical 70S high resolution double focusing magnetic sector mass spectrometer with attached VG 11/250J data system

in the EI or FAB mode. FAB spectra were obtained neat or in glycerol matrix. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, Georgia. Solvents were used either as purchased or dried and purified by standard methods, under dry, pure nitrogen or argon. N-hydroxy-2-thiopyridone was isolated from its sodium salt (Omadine®). A 40% solution of the sodium salt of N-hydroxy-2-thiopyridone was a kind gift of the Olin Corporation, Cheshire, CT. Other reference compounds and starting materials were purchased from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin.

Preparation of the mixed anhydrides of N-hydroxy-2-thiopyridone **1a-e** were carried out according to the literature procedures[30, 31].

1a: Method A, Yield 84%, m.p. 136-137°C (Lit. 135°C[30]); **1b**: Method B, Yield 91%, m.p. 107-108°C (Lit. 110°C[30]); **1c**: Method B, Yield 88%, m.p. 163-164°C (Lit. 166°C[30]).

Method A[30]: The acid was transformed to the corresponding acid chloride with 1.2 eq. oxalyl chloride and one drop of DMF in benzene followed by the reaction with 1.0 eq. *N*-hydroxy-2-thiopyridone in the presence of 1.2 eq. triethylamine.

Method B[31]: The acid (1.0 eq.) and *N*-hydroxy-2-thiopyridone (1.0 eq.) were dissolved in dry methylene chloride and treated with 0.95 eq. N,N'-dicyclohexyl carbodiimide. The precipitated urea was removed by filtration after 3 hrs and the acyl derivatives were then recrystallized from methylene dichloride/hexanes.

General procedure for the radical addition of the acyl derivatives **1** to tosylcyanide **4a**: All operations were performed under argon using degased dichloromethane as solvent. The photolyses were done using two 150W tungsten lamps from a distance of about 20 cm. A 0.2-0.25 M solution of the mixed anhydride was added in portions, 0.2eq each time, into the irradiated solution of tosylcyanide (**4a**) (0.3 M) in dichloromethane at 0°C. The consumption of the anhydride was indicated by the decoloration of the solution and/or by t.l.c. After the consumption of all the anhydride the solvent was removed under reduced pressure at room temperature and the ^{1}H NMR spectrum of the crude mixture was recorded. Silica gel separation and/or distillation can be employed for the isolation of the produced nitriles **5**.

Preparation of the authentic nitriles **5**. *Typical procedure*: The appropriate acid (0.02mol) in dry benzene containing one drop of DMF was treated at room temperature with oxalyl chloride (2.8 g, 0.022 mol). After stirring for 3 hr the solvent and the rest of oxalyl chloride were removed and the resulting pale yellow acid chloride was dissolved in dry dichloromethane (20 ml) and treated at about 5°C (ice bath) with gaseous ammonia for 10 min. Stirring was continued at room temperature for 1 hr. Removal of most of the solvent and gradual

addition of hexanes affords pure the corresponding amide in 90-95% yield. Treatement of the amide (0.01 mol) with phosphorus pentoxide[32] (1.28 g, 0.009 mol) at 150°C for 8 hr affords after extraction with water and dichloromethane, drying the organic layer with magnesium sulfate and removal of the solvent the title compounds in good yield.

Linoleic nitrile **15**:[33, 34] Yield: 97%; IR ($CHCl_3$) 2249 (CN), 1418, 1255 cm^{-1}; ^1H NMR (δ, ppm): 0.85-0.90 (t, 3H), 1.2-1.5 (m, 14H), 1.6-1.7 (m, 2H), 1.95-2.10 (m, 4H), 2.25-2.35 (t, 2H), 2.7-2.8 (m, 2H), 5.3-5.4 (m, 4H); ^{13}C NMR (δ, ppm): 14.1, 17.3, 22.6, 25.4, 25.7, 27.2, 27.3, 28.7, 28.8, 29.0, 29.4, 29.5, 31.6, 119.9, 127.9, 128.3, 129.9, 130.3; m/z(%): 261 (10), 218 (5), 148 (25), 134 (30), 67 (100).

Oleic nitrile **16**:[33, 34] Yield: 95%; IR ($CHCl_3$) 2247 (CN), 1457 cm^{-1}; ^1H NMR (δ, ppm): 0.86 (t, 3H), 1.2-1.45 (m, 20H), 1.6-1.65 (m, 2H), 2.00-2.10 (m, 4H), 2.30 (t, 2H), 5.3-5.4 (m, 2H); ^{13}C NMR (δ, ppm): 14.1, 17.1, 22.7, 25.4, 27.1, 27.3, 28.7, 28.8, 29.0, 29.3, 29.4, 29.6, 29.7, 29.8, 32.0, 119.8, 129.6, 130.2; m/z(%): 263 (10), 220 (16), 122 (48), 55 (100).

Hydrolysis of the nitriles to the corresponding acids. *General procedure* [35, 36]:

The nitrile **5** (1.0 mmol) was dissolved in ethanol (3 ml) and this solution was then treated with sodium hydroxide (1.3 mmol, 52 mg in 2 ml of water). The reaction mixture then was brought to the boil and kept at this temperature for 40 hrs under argon. The reaction was monitored by tlc. After the completion of the reaction the solvents were removed in vacuum and the residue was then carefully neutralized with a 5% aqueous sulfuric acid solution. The free acid was extracted into methylene chloride and this solution was then dried over anhydrous magnesium sulfate and evaporated in vacuum to furnish the pure acid.

Independent preparation of the 2-mercaptopyridine p-toluenesulfonate **7a** (R' = p-Tol): Under continiously purged with argon atmosphere (1.1 g, 0.01 mol) of 2-mercaptopyridine and (1.95 g, 0.01 mol) tosyl chloride in 10 ml of dry dichloromethane, were treated at 0°C with (1.1 g, 0.011 mol) of freshly distilled triethylamine. The reaction mixture was stirred at 0°C for 2hr and then warmed up to room temperature where stirring continued for 2 hr. The precipitated triethylamine hydrochloride was then removed by gravity filtration and the solvent was distilled under reduced pressure. Recrystalisation from ether/hexanes afforded the title compound in 86% yield as colorless crystals, mp. 50-51°C; IR ($CHCl_3$) 1331, 1143 cm^{-1}; ^1H NMR (δ, ppm): 2.43 (3H, s), 7.26 (2H, d, J = 8Hz), 7.38 (1H, m), 7.58 (2H, d, J = 8Hz), 7.78 (2H, m), 8.54 (1H, m); ^{13}C

NMR (δ, ppm): 21.8, 125.0, 127.6, 129.7, 132.0, 137.9, 141.4, 145.2, 150.8, 151.3; m/z(%): 220 (6.2), 200 (100), 91 (100); calcd. for $C_{12}H_{11}NO_2S_2$: C: 54.32, H: 4.18, N: 5.28; found: C: 54.27, H: 4.18, N: 5.26%.

2-mercaptopyridine methanesulfonate **7b** (R' = Me): mp. 59-60°C; IR ($CHCl_3$) 1329, 1130 cm^{-1}; ^1H NMR (δ, ppm): 3.53 (s, 3H), 7.39-7.42 (m, 1H), 7.64-7.84 (m, 2H), 8.6 (m, 1H); ^{13}C NMR (δ, ppm): 50.3, 125.0, 131.2, 138.4, 150.9, 151.3; m/z(%): 189 (20), 111 (100); calcd. for $C_6H_7NO_2S_2$: C: 38.08, H: 3.73, S: 33.88; found: C: 38.17, H: 3.77, S: 33.93%.

p-Toluenesulfonyl isothiocyanate **8a** (R' = p-Tol):[19] Yield 51%, b.p. 119°C (0.5 mmHg), ^1H NMR (δ, ppm): 2.47 (s, 3H), 7.40 (d, 2H, J = 8 Hz), 7.85 (d, 2H, J = 8 Hz); ^{13}C NMR (δ, ppm): 21.6, 127.1, 130.0, 136.1, 146.1, 155.8.

Methanesulfonyl isothiocyanate **8b** (R' = Me):[19] Yield 45%, b.p. 115°C (24 mmHg), IR ($CHCl_3$) 1905 (NCS), 1363 and 1164 cm^{-1} (SO_2); ^1H NMR (δ, ppm): 3.29 (s, 3H), ^{13}C NMR (δ, ppm) 43.3, 155.9. This compound dimerizes upon storage. Therefore it has been used immediately after distillation.

β-Phenylethyl thiocyanate **9a**:[20] This compound was also prepared independently from β-phenylethyl bromide and excess KSCN in DMF in 71% yield. IR ($CHCl_3$) 2156 (SCN), 694 cm^{-1} (C-S); ^1H NMR (δ, ppm) 3.1-3.2 (m, 4H), 7.2-7.35 (m, 5H); ^{13}C NMR (δ, ppm) 35.0, 35.9, 112.0, 127.1, 128.5, 128.7, 137.5.

Cyclohexyl thiocyanate **9b**:[21] This compound was also prepared independently in 41% yield. IR ($CHCl_3$) 2153 (SCN); ^1H NMR (δ, ppm) 1.3-1.9 (m, 8H), 2.1-2.2 (m, 2H), 3.25 (m, 1H); ^{13}C NMR (δ, ppm) 24.7, 25.7, 33.4, 47.7, 111.4.

1-Adamantyl thiocyanate **9c**: This compound was prepared according to the published procedure.[22]

General Procedure for the Addition of Sulfonyl Cyanides to Olefins.

The corresponding sulfonyl cyanide **4** (3 mmol) was dissolved in dry methylene chloride (5.0 ml) and the olefin (10 eqs., 30 mmol) was added to this solution. The flask was then placed under argon in an ice bath and subjected to visible light photolysis with two tungsten lamps (GE, 150 W each). The acyl derivative **1a** (0.2 eq., 0.6 mmol, 0.1550 g) was dissolved in dry methylene chloride (2.0 ml) and injected into the reaction mixture in 0.5 ml portions at 20 min. intervals. The reaction was monitored by ^1H NMR. After the completion of the addition the reaction mixture was washed with water, dried over magnesium sulfate and the solvent evaporated in vacuum. The residue containing the adduct **12** was then either crystallized or purified on a silica column with hexanes/ether 1:1.

1-Cyano-1-ethoxy-2-p-toluenesulfonyl-ethane **12a** (R' = p-Tol, X = OEt): Obtained in 81% yield. m.p. 76-77°C (Et_2O/hexanes); IR ($CHCl_3$) 2304 (CN), 1329, 1146 (SO_2); ^1H NMR (δ, ppm) 1.1 (t, 3H, J = 7 Hz), 2.48 (s, 3H), 3.4 - 3.8 (m, 4H), 4.7 (dd, 1H, J_1 = 4 Hz, J_2 = 6 Hz), 7.4 (d, 2H, J = 8 Hz), 7.8 (d, 2H, J = 8

Hz); ^{13}C NMR (δ, ppm) 14.2, 21.6, 58.4, 63.6, 66.7, 115.7, 128.1, 129.8, 136.3, 145.4; m/z (%) 253 (1), 156 (42), 91 (100); calcd. for $C_{12}H_{15}NO_3S$: C: 56.90, H: 5.97, found: C: 56.81, H: 5.96%.

1-Cyano-1-ethoxy-2-methanesulfonyl-ethane **12b** (R' = Me, X = OEt): Obtained in 91% yield. m.p. 73-74°C (CH_2Cl_2/hexanes); IR ($CHCl_3$) 2250 (CN), 1310, 1139 (SO_2); ^1H NMR (δ, ppm) 1.3 (t, 3H, J = 7 Hz), 3.0 (s, 3H), 3.38 (m, 1H), 3.6 - 3.7 (m, 2H), 3.9 - 4.0 (m, 1H), 4.75 (dd, 1H, J_1 = 3 Hz, J_2 = 10 Hz); ^{13}C NMR (δ, ppm) 14.3, 43.6, 56.4, 63.7, 67.1, 115.5; m/z (%) 178 (2), 151 (8), 132 (18), 98 (100); calcd. for $C_6H_{11}NO_3S$: C: 40.66, H: 6.25, found: C: 40.68, H: 6.23%.

1-p-Toluenesulfonyl-2-cyano-2-methoxy-propane **12c** (R' = p-Tol, X = OMe): Obtained in 42% yield. m.p. 57-58°C (Et_2O/hexanes); IR ($CHCl_3$) 2302 (CN), 1325, 1140 (SO_2); ^1H NMR (δ, ppm) 1.8 (s, 3H), 2.47 (s, 3H), 3.36 (s, 3H), 3.61 (s, 2H), 7.4 (d, 2H, J = 8 Hz), 7.8 (d, 2H, J = 8 Hz); ^{13}C NMR (δ, ppm) 23.7, 52.9, 53.3, 62.0, 71.1, 116.9, 128.0, 129.6, 136.9, 145.0; m/z (%) 253 (1), 200 (65), 91 (100); HRMS calcd. for $C_{12}H_{15}NO_3S$: 253.3222, found: 253.3240.

1-Methanesulfonyl-2-cyano-2-methoxy-propane **12d** (R' = Me, X = OMe): Obtained in 85% yield. m.p. 49-50°C (Et_2O/hexanes); IR ($CHCl_3$) 2255 (CN), 1321, 1141 (SO_2); ^1H NMR (δ, ppm) 1.8 (s, 3H,), 3.06 (s, 3H), 3.45 (d, 2H, J = 2 Hz), 3.54 (s, 3H); ^{13}C NMR (δ, ppm) 23.1, 44.0, 53.5, 61.6, 71.3, 117; m/z (%) 162 (4), 98 (30), 84 (100); calcd. for $C_{12}H_{15}NO_3S$: C: 40.66, H: 6.25, N: 7.90, found: C: 40.61, H: 6.26, N: 7.92%.

1-Cyano-1-phenylthio-2-p-toluenesulfonyl-ethane **12e** (R' = p-Tol, X = SPh): Obtained in 81% yield. m.p. 82-83°C (Et_2O/hexanes); IR ($CHCl_3$) 2303 (CN), 1327, 1146 (SO_2); ^1H NMR (δ, ppm) 2.47 (s, 3H), 3.5 (d, 2H, J = 7 Hz), 3.5 (d, 2H, J = 7 Hz), 4.15 (t, 1H, J = 7 Hz), 7.4-7.6 (m, 7H), 7.8 (d, 2H, J = 8 Hz); ^{13}C NMR (δ, ppm) 21.6, 30.7, 57.7, 116.2, 128.0, 128.3, 129.7, 130.2, 130.5, 134.9, 135.5, 145.9; m/z (%) 317 (1), 161 (100); calcd. for $C_{16}H_{15}NO_2S_2$: C: 60.54, H: 4.76, found: C: 60.47, H: 4.75%.

1-Cyano-1-phenylthio-2-methanesulfonyl-propane **12f** (R' = Me, X = SPh): Obtained in 91% yield. m.p. 87-88°C (Et_2O/hexanes); IR ($CHCl_3$) 2305 (CN), 1327, 1132 (SO_2); ^1H NMR (δ, ppm) 3.0 (s, 3H,), 3.4 (d, 2H, J = 7.3 Hz), 4.3 (dd, 1H, J_1 = 6.7 Hz, J_2 = 7.5 Hz), 7.4 (m, 3H), 7.7 (m, 2H); ^{13}C NMR (δ, ppm) 30.9, 42.3, 56.4, 116.9, 127.9, 129.9, 130.7, 135.6; m/z (%) 241 (3.5), 161 (100); calcd. for $C_{10}H_{11}NO_2S_2$: C: 49.77, H: 4.59, N: 5.80, found: C: 49.70, H: 4.61, N: 5.83%.

1-Cyano-1-trimethylsilyl-2-p-toluenesulfonyl-ethane **12g** (R' = p-Tol, X = $SiMe_3$): Obtained in 25% yield. m.p. 81-82°C (Et_2O/hexanes); IR ($CHCl_3$) 2291 (CN), 1331, 1149 (SO_2); ^1H NMR (δ, ppm) 0.3 (s, 9H), 2.4 (dd, 1H, J = 12 Hz), 2.49 (s, 3H), 2.9 (m, 1H), 3.5 (dd, 1H, J = 12 Hz), 7.4 (d, 2H, J = 8 Hz), 7.8 (d, 2H, J = 8 Hz); ^{13}C NMR (δ, ppm) -4.1, 15.6, 21.6, 51.3, 115.4, 128.2, 129.7, 136.4, 141.4; m/z (%) 281 (1), 91 (100); calcd. for $C_{13}H_{19}NO_2SSi$: C: 55.48, H: 6.81, found: C: 55.68, H: 6.90%.

1-Cyano-1-trimethylsilyl-2-methanesulfonyl-ethane **12h** (R' = Me, X = $SiMe_3$): Obtained in 55% yield. m.p. 87-88°C (Et_2O/hexanes); IR ($CHCl_3$) 2228 (CN), 1323, 1132 (SO_2); ^1H NMR (δ, ppm) 0.3 (s, 9H), 2.5 (dd, 1H, J = 12 Hz), 2.94 (m, 1H), 3.13 (s, 3H), 3.30 (dd, 1H, J = 12 Hz); ^{13}C NMR (δ, ppm) -3.4, 14.1,

41.5, 52.2, 119.7; m/z (%) 206 (2), 190 (5), 79 (100); HRMS calcd. for $C_7H_{15}NO_2SSi$: 205.3531, found: 205.3552

trans-1-Cyano-2-p-toluenesulfonyl-cyclohexane:[26] Obtained in 30% yield. m.p. 133-134°C (Et_2O/hexanes)(lit. m.p. 133-135°C); IR ($CHCl_3$) 2245 (CN), 1314, 1143 (SO_2); ^1H NMR (δ, ppm) 1.3-2.4 (m, 8H), 2.47 (s, 3H), 2.9 (dt, 1H, J_1 = 4 Hz, J_2 = 9 Hz), 3.2 (dt, 1H, J_1 = 4 Hz, J_2 = 9 Hz), 7.4 (d, 2H, J = 8 Hz), 7.8 (d, 2H, J = 8 Hz); ^{13}C NMR (δ, ppm) 21.6, 22.9, 23.2, 24.5, 27.6, 29.3, 62.5, 119.5, 129.0, 129.9, 133.7, 145.4; m/z (%) 263 (9), 157 (12), 108 (100).

trans-1-Cyano-2-methanesulfonyl-cyclohexane : Obtained in 41% yield. m.p. 88-89°C (Et_2O/hexanes); IR ($CHCl_3$) 2250 (CN), 1310, 1139 (SO_2); ^1H NMR (δ, ppm) 1.3-2.0 (m, 6H,), 2.2-2.4 (m, 2H), 3.15 (s, 3H), 2.9-3.2 (m, 2H); ^{13}C NMR (δ, ppm) 23.3, 23.5, 23.6, 28.7, 29.7, 41.5, 62.3, 120.4; m/z (%) 188 (0.5), 108 (100), 81 (100); calcd. for $C_8H_{13}NO_2S$: C: 51.31, H: 7.00, found: C: 51.39, H: 7.04%.

1-p-Toluenesulfonyl-2-cyano-hexane:[26] Obtained in 45% yield. m.p. 38-39°C (Et_2O/hexanes)(lit. 38-40°C); IR ($CHCl_3$) 2241 (CN), 1323, 1142 (SO_2); ^1H NMR (δ, ppm) 0.9 (t, 3H, J = 7 Hz), 1.2-1.8 (m, 6H), 2.44 (s, 3H), 3.1 (s, 3H), 3.25 (m, 1H), 3.45 (m, 1H), 7.4 (d, 2H, J = 8 Hz), 7.8 (d, 2H, J = 8 Hz); ^{13}C NMR (δ, ppm) 13.4, 21.3, 21.5, 26.0, 28.3, 31.4, 56.8, 119, 127.9, 129.9, 135.1, 145.3; m/z (%) 265 (7), 155 (88), 91 (100).

1-Methanesulfonyl-2-cyano-hexane: Obtained in 59% yield. m.p. 34-35°C (hexanes); IR ($CHCl_3$) 2246 (CN), 1319, 1133 (SO_2); ^1H NMR (δ, ppm) 0.9 (t, 3H, J = 7 Hz), 1.3-1.8 (m, 6H), 3.07 (s, 3H), 3.2 (m, 2H), 3.45 (m, 1H); ^{13}C NMR (δ, ppm) 13.5, 21.7, 26.1, 28.5, 31.5, 41.9, 55.6, 119.6; m/z (%) 190 (0.5), 110 (100); HRMS calcd. for $C_8H_{15}NO_2S$: 189.2782, found: 189.2786.

Acknowledgements: We thank the NIH and the Schering-Plough Corporation for financial support. Mr. E.A. Theodorakis is a Schering Scholar.

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