45.2 and 50.8 (4,6-$CH_2$, *t*-Bu), 85.9 (C-2), 125.2 and 133.9 (C-3, C-5); EI-MS, *m/z* (relative intensity) 334 (2, M), 278 (11), 277 (55), 71 (36), 57 (77), 43 (100).

Anal. Calcd for $C_{21}H_{34}SO$: C, 75.45; H, 10.18. Found: C, 75.14; H, 10.11.

**Oxidation of Benzo[*b*]thiete (11).** In a 25-mL round-bottom flask equipped with a magnetic stir bar and argon atmosphere was placed 0.14 g (0.001 14 mol) of benzo[*b*]thiete (11)[11] in 5 mL of dry methylene chloride. After the mixture was cooled to 0 °C in an ice bath, 0.35 g (0.001 14 mol) of 2-(phenylsulfonyl)-3-(*p*-nitrophenyl)oxaziridine (9, Ar = *p*-$NO_2Ph$)[22] was added dropwise and the reaction mixture allowed to warm to room temperature. After the mixture was stirred for 0.5 h, the solvent was removed under vacuum to afford a yellow-green solid. This material was purified by preparative TLC (silica gel), eluting first with methylene chloride followed by ether, to give 0.095 g (68%) of a white solid, mp 171–180 °C, identified as 6*H*,12*H*-dibenzo[*b*,*f*]-1,5-dithiocin disulfoxide (14), 58:42 mixture of diastereomers by HPLC, identical in properties with an authentic sample prepared as described below.

**6*H*,12*H*-Dibenzo[*b*,*f*]-1,5-dithiocin Disulfoxide (14).** In a 25-mL round-bottom flask equipped with magnetic stir bar, dropping funnel, and argon atmosphere was placed 0.15 g (0.000 61 mol) of 6*H*,12*H*-dibenzo[*b*,*f*]-1,5-dithiocin[11] in 5 mL of methylene chloride. At room temperature 2-(phenylsulfonyl)-3-(p-nitrophenyl)oxaziridine (9, Ph = *p*-$NO_2Ph$;[22] 0.19 g, 0.000 61 mol) in 10 mL of methylene chloride was added dropwise and the solvent removed under vacuum to afford a solid that was purified by preparative TLC (silica gel) as described above to give 0.17 g (98%) of disulfoxide 14, as a 70:30 mixture of diastereomers by HPLC. Compound 14 had the following properties: mp 170–180 °C dec; IR (KBR) 1055 $cm^{-1}$ (sulfoxide); $^1H$ NMR ($CDCl_3$) δ 3.8–4.4 (AB q, *J* = 14.8 Hz, 4 H), 7.0–7.5 (m, 8 H); $^{13}C$ NMR ($CDCl_3$) δ 58.86 ($CH_2$); EI-MS, *m/z* (relative intensity) 276 (4.2, molecular ion), 138 (96), 137 (100), 109 (31).

Anal. Calcd for $C_{14}H_{12}O_2S_2 \cdot H_2O$: C, 57.14; H, 4.76. Found: C, 57.14; H, 4.59.

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**Registry No.** 4, 86563-40-8; 5, 86563-37-3; 7, 86563-38-4; 8, 86563-39-5; 9 (Ar = Ph), 63160-13-4; 10, 86563-41-9; 11, 63559-01-3; *cis*-14, 71635-63-7; *trans*-14, 86563-42-0.

# Reductions of Esters, Acyl Halides, Alkyl Halides, and Sulfonate Esters with Sodium Borohydride in Polyethylene Glycols: Scope and Limitation of the Reaction[1]

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Sodium borohydride in ethylene glycol oligomers (PEGs) has been explored as a novel reducing system for esters, acyl chlorides, alkyl halides, and sulfonate esters. The selectivity of the system is exemplified by its inertness toward nitrogen-containing functional groups such as amides, azides, nitriles, and nitroalkanes. Both hydroxy groups of the oligomeric diols have been established to be necessary for the above reducing system. The nature of the reductant formed by $NaBH_4$ in excess PEG 400 is discussed. Furthermore, an alkoxyborohydride, $Na[(PEG)_2BH_2]$, can be prepared by reaction of 1 mol of $NaBH_4$ and 2 mol of PEG 400. In THF the reagent reduces halides and tosylates rapidly to hydrocarbons in good yields.

Polyethylene glycols (PEGs) are oligomeric diols of general formula $HO(CH_2CH_2O)_nH$ in which the two terminal hydroxy groups are separated by several oxyethylene units ($CH_2CH_2O$). An average molecular weight $\bar{M}$ indicates approximately the numbers of such oxyethylene units. PEGs can be regarded as open-chain crown ethers as they are able to form complexes with alkaline and alkaline-earth cations in protic and aprotic solvents.[3] From preliminary studies, PEG 400 seems to most successful candidate for applications to organic synthesis.[4]

Sodium borohydride in PEG 400 exhibits a reactivity completely different from that shown by the borohydride in the presence of crown ethers in similar systems such as PEG ethers.[5] In fact, sodium borohydride in PEG 400 smoothly reduces carbonyl compounds at room temperature,[4] in this respect behaving similarly to $NaBH_4$ in hydroxylic solvents. Under the same conditions as above esters were unaffected, but when the temperature was

Table I. Reduction of 1 by 0.6 M $NaBH_4$ in Various PEGs at 80 °C[a]

| solvent | time, h | yield,[b] % |
|---|---|---|
| PEG 200 | 3 | 85 |
| PEG 300 | 5 | 80 |
| PEG 400 | 8 | 90 |
| PEG 600 | 5 | 85 |
| PEG methyl ether[c] | 16 | |

[a] Molar ratio of $NaBH_4$/1 of 3:1. [b] Yield of isolated benzyl alcohol. [c] From Aldrich.

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(2) Research Fellow from Istituto di Endocrinologia, Facoltà di Farmacia, Università di Milano.
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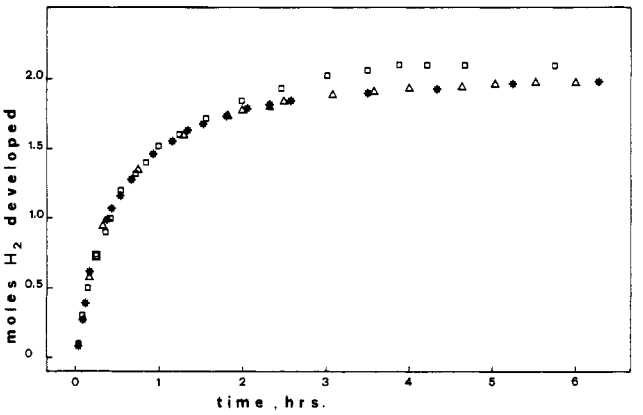


**Figure 1.**

raised to 65–80 °C evolution of hydrogen was observed, and complete reduction of esters to alcohols occurred.[6] We have now investigated more extensively the system and report here the results of this study.

**Effect of Number of the Oxyethylene Units.** We examined low-$\bar{M}$ PEGs (from 200 to 600), since these possess low enough viscosities to be useful as solvents, and the studies were limited to the most interesting reaction so far found, namely, reduction of esters.

Irrespective of molecular weight of the solvent, methyl benzoate (1) is completely reduced at 80 °C to benzyl alcohol (2) in 80–90% yields of isolated product (Scheme I and Table I). Products were readily obtained by using

**Scheme I**

$$\underset{1}{C_6H_5COOCH_3} \xrightarrow[80\ ^\circ C,\ 3\text{–}8\ h]{NaBH_4,\ PEG} \underset{2}{C_6H_5CH_2OH}$$

PEGs up to 400, but above this weight (i.e., 600) separation via extraction with water was only partially successful.

It is well-known that when in sodium borohydride the ionic pair is well separated the reducing activity of the reagent is lowered.[5] Although a correlation does not seem to exist between number of oxyethylene units and reducing power, complexation of the sodium cation by the polymeric chain of the PEGs probably does not significantly separate the ions. The flexibility of the helical conformation of PEG in the liquid state[7] could contribute to explain this behavior.

**Role of Hydroxy Groups.** It has been reported that PEG ethers retard the reduction of carbonyl compounds by sodium borohydride in THF.[5] This was explained by considering that cooperative coordination of the oxygen atoms of PEG ethers with alkali cations could promote ion-pair dissociation, which seems unfavorable to the reducing activity of borohydride. Furthermore, an insoluble complex was apparently formed between $NaBH_4$ and PEG ether.[5] This complex was unable to reduce acetophenone at 30 °C, whereas benzophenone was reduced in 24% under the same conditions (80 and 50 h, respectively). The attempted reduction of 1 by means of $NaBH_4$ in PEG monomethyl ether afforded no benzyl alcohol even under forcing conditions. This result strongly suggests that both hydroxy groups are necessary for reduction.

**Reaction between $NaBH_4$ and PEG 400.** We had previously observed that sodium borohydride reacts with excess PEG 400 at 65–80 °C with the evolution of 2 molar equiv of hydrogen within 1 h.[6] However, repetition of these experiments indicated that the rate of the evolution of hydrogen depends on the purity of $NaBH_4$. We have, therefore, determined the amount of hydrogen evolved by treating PEG 400 with variable molar equivalents of $NaBH_4$ (Ventron, 98% pure) at different temperatures. The results of these titrations at 80–90 °C are collected in Figure 1.

The general feature of the reaction between PEG 400 and $NaBH_4$ is that 2 molar equiv of hydrogen is produced when the ratios of PEG 400 and $NaBH_4$ were 2:1, 3:1, 4:1. When the ratio was lower than 2:1 results were erratic, due to the high viscosity and heterogeneity of the mixture. Apparently the ratio 2:1 represents the stoichiometry of the reaction, since increase of the molar ratio of PEG with respect to $NaBH_4$ does not influence the molar equivalents of hydrogen evolved. This suggests that the active species has the formula $NaBH_2[(OCH_2CH_2)_9OH]_2$, the corresponding oligomers not being excluded. On the other hand it cannot be excluded that the reactive specie(s) present in part may be intermolecular polymeric borohydride(s).

In the reducing system formed with a ratio PEG 400/$NaBH_4$ higher than 2:1, the remaining mole(s) of PEG may act as solvent for the reducing species and the substrate. For these reasons, we have used a 4:1 ratio of PEG 400/$NaBH_4$ for the following experiments.

**Reduction of Halides.** In view of the unusual capability of $NaBH_4$ in PEG to reduce esters of carboxylic

Table II. Reduction of Halides and Tosylates to Hydrocarbons by $NaBH_4$ in PEG 400 at 70 °C[a]

| substrate | $NaBH_4$/substrate molar ratio | time, h | yield,[b] % |
|---|---|---|---|
| 3a | 5 | 12 | 90 |
| 3b | 5 | 12 | 82 |
| 3c | 10 | 16 | 78 |
| 3d | 3 | 3 | 82 |
| 3e | 3 | 3 | 90 |
| 3f | 2 | 5[c] | 75 |
| 3g | 2 | 10 | 88 |
| 3h | 2 | 12 | 80 |
| 3i | 5 | 2 | 76 |
| 3j | 3 | 3 | 80 |
| 3k | 3 | 3 | 82 |
| 3l | 5 | 12 | 80 |
| 3m | 5 | 12 | 80 |

[a] Purity of products established by microanalysis and usual analytical (GC) and spectroscopic (IR, NMR) methods. [b] Yields refer to isolated compounds. [c] When a molar ratio 5:1 was used, the reaction was complete (GC) in 1 h.

Scheme II

$$\underset{3}{R\text{-}CHX\text{-}R'} \xrightarrow[70\ ^\circ C]{NaBH_4,\ PEG\ 400} \underset{4}{RCH_2R'}$$

a, R = $C_{15}H_{31}$; R′ = H; X = Br
b, R = $C_9H_{19}$; R′ = H; X = Br
c, R = $C_9H_{19}$; R′ = H; X = Cl
d, R = $C_9H_{19}$; R′ = H; X = I
e, R = $C_{15}H_{31}$; R′ = H; X = I
f, R = $C_6H_5$; R′ = H; X = Br
g, R = $p$-$NO_2C_6H_4$; R′ = H; X = Br
h, R = $p$-$CH_3OC_6H_4$; R′ = H; X = Br
i, R = $p$-$ClC_6H_4$; R′ = H; X = Cl
j, R = $C_{15}H_{31}$; R′ = H; X = OTs
k, R = $C_9H_{19}$; R′ = H; X = OTs
l, R = $C_{10}H_{21}$; R′ = $CH_3$; X = Br
m, R = $C_9H_{19}$; R′ = $C_4H_9$; X = Br
n, R = $C_{10}H_{21}$; R′ = $CH_3$; X = OTs
o, R = $C_9H_{19}$; R′ = $C_4H_9$; X = OTs

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Table III. Reduction of Acyl Chlorides to Alcohols by $NaBH_4$ and PEG 400 at 80 °C[a]

| RCOCl (5) | time, h | yield,[b] % |
|---|---|---|
| a, R = $C_{15}H_{31}$ | 5 | 86 |
| b, R = $C_9H_{19}$ | 5 | 80 |
| c, R = $C_6H_5$ | 3 | 82 |
| d, R = $p$-$BrC_6H_4$ | 3 | 84 |

[a] Molar ratio of $NaBH_4$/acyl chloride of 3:1. [b] Yields refer to isolated products.

acids, we investigated the reductive displacement of halides by this reagent. Such reduction by $NaBH_4$ in a variety of polar protic solvents ($Me_2SO$, sulfolane, HMPA, DMF, or diglyme) was reviewed by Hutchins.[8] We report here that primary alkyl halides **3a–e** and benzyl halides **3f–i** are reduced to the corresponding hydrocarbons **4** at 70 °C in good yields by a reducing system formed by PEG 400 and $NaBH_4$ in a molar ratio of 4:1 (Scheme II and Table II). The reaction is performed by preparing a mixture of the halide, $NaBH_4$, and PEG 400 at room temperature and raising the temperature to 70 °C. In general, an excess of $NaBH_4$ was required, and the highest molar ratio of $NaBH_4$/halide was with alkyl chlorides (10:1). As expected, iodides reacted faster than bromides, and alkyl chlorides showed the slowest reactivity, whereas benzyl halides are readily reduced under the same conditions. Also, in the case of secondary bromides **3l** and **3m**, the reduction proceeds smoothly to the corresponding alkanes **4l** and **4m** with no alkene formation as ascertained by GC. Furthermore, the nitro group is inert under the reaction conditions (entry **3g** of Table II). In all the cases the workup is straightforward, and the purity of the products and recovery are good. The process appears to be effective even when solubility of the substrates is limited (i.e., **3a**) and the reaction is heterogeneous.

**Reduction of Tosylates.** In analogy to halides, primary alkyl tosylates **3j** and **3k** are reduced to the corresponding alkanes **4a** and **4b** in good yields at 70 °C by PEG 400/sodium borohydride (molar ratio 4:1). The ratio of borohydride/tosylate was 3:1. Surprisingly, secondary tosylates such as **3n** and **3o** failed to afford the corresponding alkanes. This lack of reactivity can be rationalized in terms of steric hindrance of the reducing system.

**Reduction of Acyl Chlorides.** Acyl chlorides can be reduced to the corresponding alcohols by sodium borohydride in inert solvents such as dioxane,[9] since in hydroxylic media they mainly react with the solvent.[10] However, we have found that acyl chlorides **5a–d** are smoothly reduced to the corresponding alcohols by 3 molar equiv of $NaBH_4$ in a reducing system obtained by reaction of PEG 400 with $NaBH_4$ (ratio 4:1) at 80 °C in 3–5 h (Table III).

**Selectivity of $NaBH_4$ in PEG 400.** The above system failed to react with nitrogen-containing groups such as nitriles, (RCN, R = alkyl or aryl), azides ($RN_3$, R = alkyl), amides ($RCONH_2$, R = alkyl), and nitroalkanes ($RNO_2$, R = alkyl) also after 3 days at 80 °C.

**Formation and Reactivity of $Na[(PEG)_2BH_2]$.** We have prepared the so called dialkoxyborohydride $NaBH_2[(OCH_2CH_2)_9OH]_2$ ($Na[(PEG)_2BH_2]$ for the sake of brevity) by reaction of 2 equiv of PEG 400 with $NaBH_4$ at 80 °C. Addition of 2 mol of PEG 400 to the prepared reducing species allows the preparation of a solution capable of effecting the same reductions as described for the above substrates. $Na[(PEG)_2BH_2]$ can be an useful reducing reagent also in different media since it is also fairly soluble in tetrahydrofuran.[11] Solutions (0.5–0.6 M) of $Na[(PEG)_2BH_2]$ in THF can reduce carbonyl compounds at room temperature and alkyl bromides at 70 °C in 4–6 h. Interestingly, the reduction of bromides **3a** and **3b** was much faster than that carried out with $NaBH_4$ in PEG 400. Most importantly, only 1 molar equiv of $Na[(PEG)_2BH_2]$ is necessary for the completion of the reaction, and yields of isolated products were very good. Also tosylates **3j** and **3k** could be easily reduced in THF at 75 °C by 1 molar equiv of $Na[(PEG)_2BH_2]$.[12]

**Conclusions.** From the reported data it appears that reaction of $NaBH_4$ with PEG of various molecular weights can generate a novel reducing agent, which exhibits an enhanced reactivity with respect to $NaBH_4$ in the usual hydroxylic solvents. Our results demonstrate that the presence of two hydroxy groups for molecule of PEG is necessary to ensure this peculiar reactivity. At 80 °C the reaction between PEG 400 and $NaBH_4$ causes the evolution of 2 molar equiv of hydrogen for a ratio of PEG 400/$NaBH_4$ from 2:1 to 4:1. This reaction and the particular reactivity of the reducing system generated thereof seem to be correlated to the possible formation of a dialkoxyborohydride more reactive than $NaBH_4$. Reaction of PEG 400 and $NaBH_4$ (molar ratio 2:1) at 80 °C affords the supposed dialkoxyborohydride, $Na[(PEG)_2BH_2]$, which is soluble either in PEG 400 itself and in other solvents such as tetrahydrofuran.

In the reducing system prepared by reacting PEG 400 and $NaBH_4$ in a ratio of 4:1, 2 mol of PEG apparently act as solvent for both the reducing species and the substrate. Reductions of carboxylic acid esters and chlorides, alkyl halides, and sulfonate esters can be accomplished in good yields with PEG 400 and $NaBH_4$ in the above ratio.

In tetrahydrofuran, the reducing species $Na[(PEG)_2BH_2]$ appears capable to smoothly reduce bromides and tosylates with a defined stoichiometry.

Finally, in the light of the results here reported the reducing system seems to be intermediate between sodium borohydride and lithium aluminum hydride.

## Experimental Section

Infrared spectra were recorded for solutions in chloroform or as Nujol mulls. NMR spectra were taken on a Varian HA-100 as chloroform-*d* solutions. The mass spectra were determined on a Varian MAT 112 S spectrometer by direct inlet methods. The progress of all reactions was monitored by TLC on silica gel ($HF_{254}$) plates or by GC analyses on a 2-m silanized column of 1% SE-30 on Gas Chrom Q, operating at 70–200 °C. Distillations were performed with a Büchi 500 glass oven.

**Reduction of Methyl Benzoate (1) with Sodium Borohydride in Different PEGs.** A mixture of methyl benzoate (1; 0.68 g, 5 mmol), PEG (25 mL), and sodium borohydride (0.57 g, 15 mmol) was stirred and the solution slowly brought to 80 °C. After 3–8 h the reaction was cooled to room temperature and acidified with 2 N HCl solution. The product was extracted with diethyl ether (3 × 20 mL) and the organic solution washed with water (3 × 20 mL) and dried ($Na_2SO_4$). Diethyl ether was distilled off at ambient pressure and benzyl alcohol (2) collected at 93 °C (10 torr). The results of each experiment are reported in Table I.

**Reduction in PEG 400 as Solvent. (A) Hexadecane (4a) from 1-Bromohexadecane (3a).** To a mixture of bromohexadecane (**3a**; 1.53 g, 5 mmol) in PEG 400 (40 mL) was added

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(11) No difference was noticed in the use of commercial or rigorously anhydrous tetrahydrofuran.
(12) The same results were also observed when $Na[(PEG)_2BH_2]$ was prepared from equimolar amounts of $NaBH_4$ and PEG 400 at 80 °C.

sodium borohydride (0.95 g, 25 mmol) at room temperature with stirring. The temperature was slowly raised to 70 °C, during which evolution of hydrogen was observed. The solution was kept at 70 °C for 12 h, cooled to room temperature, and acidified with 2 N HCl solution. The solution was extracted with diethyl ether (3 × 20 mL), and the organic solution was washed with water (3 × 20 mL) and dried ($Na_2SO_4$). Diethyl ether was distilled off at ambient pressure and hexadecane (**4a**) collected (90% yield) at 10 torr (149 °C) [lit.[13] bp 152 °C (15 torr)].

**(B) Reduction of 1-[(*p*-Tolylsulfonyl)oxy]hexadecane (3j).** To a mixture of 1-[(*p*-tolylsulfonyl)oxy]hexadecane (**3j**; 1.98 g, 5 mmol) in 25 mL of PEG was added sodium borohydride (0.57 g, 15 mmol) at room temperature with stirring. After 3 h at 70 °C the reaction was terminated by addition of 2 N HCl to an acidic pH. After the usual workup hexadecane (**4a**) was obtained (0.9 g, 80% yield) in >95% purity by GC.

**(C) Reduction of Benzoyl Chloride (5c).** A solution of sodium borohydride (0.57 g, 15 mmol) in PEG 400 (25 mL) was prepared at room temperature and then kept at 80 °C (2 h). After the mixture cooled to room temperature, **5c** (0.682 g, 5 mmol) was added and the temperature of the solution raised again to 80 °C. After 3 h the reaction was terminated and worked up as described previously. Benzyl alcohol (**2**) was obtained (0.42 g, 78%) in >95% purity by GC.

**Preparation of $Na[(PEG)_2BH_2]$.** The alkoxyborohydride, $Na[(PEG)_2BH_2]$, was prepared by addition of sodium borohydride (0.38 g, 10 mmol) to PEG 400 (8 g, 20 mmol) and the resulting solution kept at 80 °C for 5 h. During this time 2 molar equiv of hydrogen was evolved, and the freshly prepared alkoxyborohydride was used for the reduction of different substrates in tetrahydrofuran: IR $\nu_{max}$ 3300, 2850, 2250 $cm^{-1}$.

**Reductions with $Na[(PEG)_2BH_2]$ in Tetrahydrofuran. Typical Procedure. (A) Reduction of 1-Bromohexadecane (3a).** A solution of **3a** (1.22 g, 4 mmol) in tetrahydrofuran[11] (5 mL) was added to freshly prepared $Na[(PEG)_2BH_2]$ (4 mmol) and the temperature raised to 70 °C. During the time of reaction (4 h), the formation of a white solid was observed, which made the stirring difficult. After the mixture cooled to room temperature, 2 N HCl solution was added and the solvent removed under reduced pressure. Extractions with diethyl ether and the usual workup furnished hexadecane (**4a**) in 80% yield.

**(B) Reduction of 1-[(*p*-Tolylsulfonyl)oxy]hexadecane (3j).** A solution of **3j** (1.98 g, 5 mmol) in tetrahydrofuran (10 mL) was added to freshly prepared $Na[(PEG)_2BH_2]$ (5 mmol) at room temperature with stirring. After 1 h at 75 °C the reaction was quenched with 2 N HCl and the solvent removed under reduced pressure. After the usual workup hexadecane (**4a**) was obtained (0.81 g, 72% yield) in >95% purity by GC.

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**Registry No.** **1**, 93-58-3; **3a**, 112-82-3; **3b**, 112-29-8; **3c**, 1002-69-3; **3d**, 2050-77-3; **3e**, 544-77-4; **3f**, 100-39-0; **3g**, 100-11-8; **3h**, 2746-25-0; **3i**, 104-83-6; **3j**, 6068-28-6; **3k**, 5509-08-0; **3l**, 13187-99-0; **3m**, 86436-68-2; **5a**, 112-67-4; **5b**, 112-13-0; **5c**, 98-88-4; **5d**, 586-75-4; $NaBH_4$, 16940-66-2; PEG, 25322-68-3; $Na[(PEG)_2BH_2]$, 86436-69-3.

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# Selenosulfonation of Acetylenes: Preparation of Novel β-(Phenylseleno)vinyl Sulfones and Their Conversion to Acetylenic and β-Functionalized Sulfones[1a]

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The 1,2-additions of *Se*-phenyl *p*-tolueneselenosulfonate (**1**) to acetylenes under mild conditions afford β-(phenylseleno)vinyl sulfones **3**, generally in high yields. The reaction is highly regioselective (anti-Markovnikov) and stereoselective (anti) and proceeds via a free-radical chain mechanism initiated by the thermolysis of the selenosulfonate. The oxidation of β-(phenylseleno)vinyl sulfones with *m*-chloroperbenzoic acid generates the corresponding selenoxides **4**, which undergo syn or base-catalyzed elimination to furnish acetylenic sulfones **5**. Base-catalyzed alcoholyses of selenoxides **4** in methanol or ethylene glycol produce β-keto sulfone ketals **8** or **10**, respectively. Free β-keto sulfones **11** are formed by the acid-catalyzed hydrolysis of the corresponding β-(phenylseleno)vinyl sulfones **3**.

We recently reported[2] that *Se*-phenyl areneselenosulfonates (e.g., **1**) undergo electrophilic (eq 1a) or thermal free-radical additions (eq 1b) to olefins to afford, with complementary regiospecificity, the corresponding β-(phenylseleno)alkyl sulfones **2**. Gancarz and Kice[3a,b] have independently shown that the free-radical reactions can also be photoinitiated. The selenosulfonation of olefins, followed by oxidation and stereospecific selenoxide syn elimination, thus provides a regio- and stereocontrolled route to synthetically useful vinyl sulfones.

As an extension of these studies we,[4] and independently Miura and Kobayashi,[5] have observed that *Se*-phenyl *p*-tolueneselenosulfonate (**1**) also undergoes thermally induced 1,2-additions to acetylenes, producing novel β-

(1) (a) We thank the Natural Sciences and Engineering Research Council of Canada and the Research Corp. for financial support. (b) Recipient of an NSERC Postgraduate Scholarship and an Honorary Killam Scholarship. (c) Undergraduate summer research assistant.

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