was hydrogenated over 10% palladium on carbon (0.2 g) at 50 lb/in.^{2} at room temperature overnight. After filtration and washing of the catalyst, the crude product was obtained by precipitation with cold acetonitrile after removal of the solvent in vacuo.

The product (0.79 g) in chloroform was applied to a SilicAR CC-7 column (130 g, 2 in. i.d.), which was then eluted with chloroform and then 0.5% methanol in chloroform. The pure product obtained from the latter eluate weighed 0.67 g (53.8%); R_f 0.17 in chloroform–ethyl acetate–methanol (89:10:1). IR and NMR data agreed with the expected structure for IV. Anal. Calcd for $C_{51}H_{98}O_7P_2$: C, 69.19; H, 11.16; P, 7.00. Found: C, 68.82; H, 11.11; P, 7.07.

Phenyl [2-(4-Nitrophenyl)ethenyl](chloromethyl)phosphinate (Cis–Trans Mixture) (V). *p*-Nitrobenzaldehyde (0.1 g, 0.7 mmol) in acetonitrile (2 mL) was added dropwise to an acetonitrile solution (5 mL) of the ylide II prepared from 0.25 g (0.5 mmol) of the phosphonium salt. The reaction mixture was heated at 50 °C for 18 h under nitrogen. The solvent was evaporated and the product V was separated by HPLC, employing a spectrophotometric detector and a 10-μm RP-18 column (250 mm × 10 mm E. Merck semi-prep), using an isocratic 65:35 (v/v) MeOH–H_2O eluent with a flow rate of 2.0 mL/min; the retention times of the cis and trans olefins were 29.0 and 32.0 min, respectively. The analytically pure product, 53 mg (32%), a 1.0:1.12 cis–trans mixture, was collected. IR and NMR data agreed with the expected structure for V. Anal. Calcd for $C_{15}H_{13}NO_4PCl$: C, 53.35; H, 3.88; N, 4.15; P, 9.17. Found: C, 53.44; H, 4.03; N, 4.03; P, 9.27.

Registry No. III, 87517-94-0; IV, 80991-34-0; *cis*-V, 87517-95-1; *trans*-V, 87517-96-2; phenyl (chloromethyl)(triphenylphosphoniomethyl)phosphinate chloride, 87517-93-9; phenyl bis(chloromethyl)phosphinate, 14212-98-7; triphenylphosphine, 603-35-0; triethyl phosphite, 122-52-1; *p*-nitrobenzaldehyde, 555-16-8; (*R*)-glyceraldehyde 2,3-dioctadecyl ether, 80991-31-7.

Selenosulfonation of Disubstituted Acetylenes: Reactions of Corresponding Vinyl Selenoxides and Anomalous Formation of a Ketene Diselenoacetal[1a]

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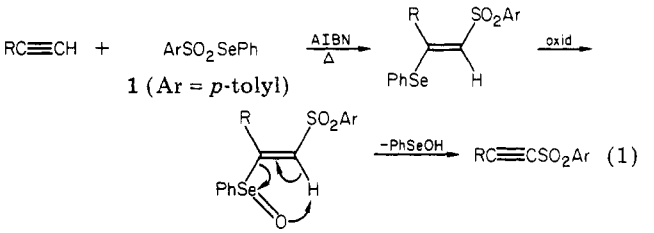
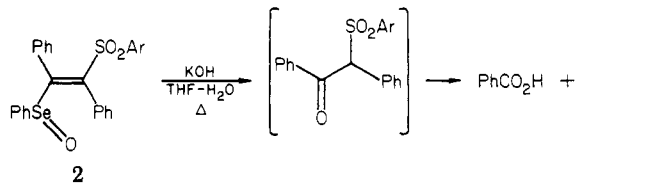
Received June 7, 1983

Se-Phenyl areneselenosulfonates ($ArSO_2SePh$) undergo 1,2-additions to olefins via electrophilic[2] or free-radical reactions,[2,3] which we have collectively named "selenosulfonations". The free-radical processes may be initiated thermally[2] or photochemically[3] and have also been performed with allenes[4] and diazomethane[5] as substrates. Several synthetic applications of olefin selenosulfonations have subsequently appeared.[6]

We,[7] and independently Miura and Kobayashi,[8] have recently extended these studies to acetylenes. *Se*-Phenyl *p*-tolueneselenosulfonate (1) adds regio- and stereoselectively to various acetylenes under thermal free-radical conditions, which can be initiated with azobis(isobutyronitrile) (AIBN).[7] The adducts can be oxidized to selenoxides which, when derived from terminal acetylenes, readily undergo syn-[7,8] or base-catalyzed[7a] elimination of benzeneselenenic acid[9] (PhSeOH) to afford high yields of acetylenic sulfones (eq 1; the symbol Ar will indicate the *p*-tolyl group throughout this work).



1,2-Adducts can also be prepared from disubstituted acetylenes, but the behavior of the corresponding selenoxides has only been investigated in one isolated case.[7a] Clearly, such compounds cannot react according to eq 1 as no vinylic hydrogen atom is available for elimination. Selenoxide **2** was found to be stable and isolable but fragmented under base-catalyzed conditions according to eq 2.[7a] In order to determine whether such behavior is



2

general or atypical, we prepared three other selenoxides from disubstituted acetylenes and subjected them to pyrolytic or hydrolytic conditions. We now report that two other reaction modes have been identified and that the fate of such selenoxides is largely dependent on the nature of the substituents in the original acetylenes. We also describe an unexpected and anomalous selenosulfonation reaction observed when 1-(trimethylsilyl)propyne was treated with **1**.

Selenoxide **4**, derived from the known[7a] selenide **3** by oxidation with *m*-chloroperbenzoic acid (MCPBA) in THF, was treated with 3 M aqueous potassium hydroxide solution in the presence of 18-crown-6 at room temperature. Neither the β-keto sulfone **5** nor products derived from its further hydrolysis were isolated. Instead, the allylic alcohol **6** was formed in 65% yield. When deuterium oxide was used in place of water, the product was deuterated exclusively (within the limits of detection by ^1H NMR spectroscopy) at the vinylic position. These results indicate that a base-catalyzed isomerization of the double bond occurs to form an allylic selenoxide intermediate **8** (Scheme I). This species rapidly rearranges via a [2,3] sigmatropic shift[9] to provide, after hydrolysis of the initially formed

(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.

(2) (a) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249. (b) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, *21*, 2215.

(3) (a) Gancarz. R. A.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899. (b) Gancarz, R. A.; Kice, J. L. *Tetrahedron Lett.* **1980**, *21*, 4155.

(4) Kang, Y.-H.; Kice, J. L. *Tetrahedron Lett.* **1982**, *23*, 5373.

(5) Back, T. G. *J. Org. Chem.* **1981**, *46*, 5443.

(6) (a) Paquette, L. A.; Kinney, W. A. *Tetrahedron Lett.* **1982**, *23*, 5127. (b) Paquette, L. A.; Crouse, G. D. *J. Org. Chem.* **1983**, *48*, 141.

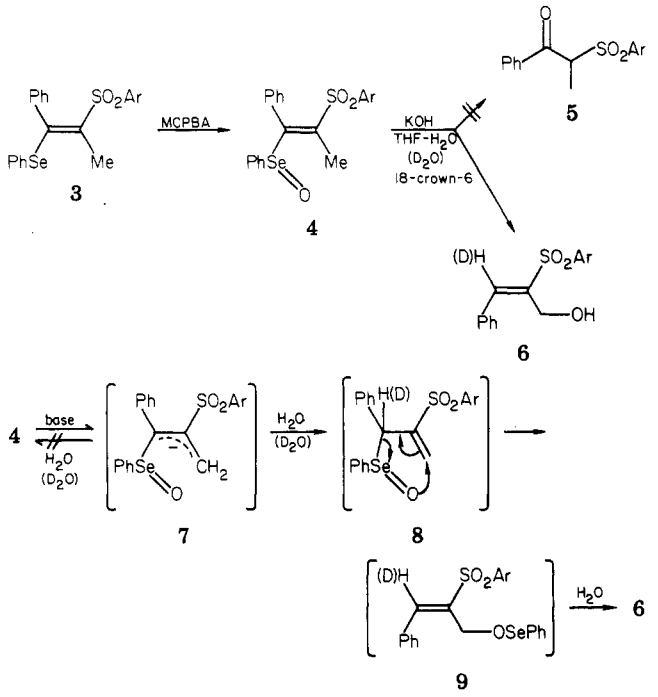
(7) (a) Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, *48*, 3077. (b) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1981**, *22*, 5111.

(8) Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438.

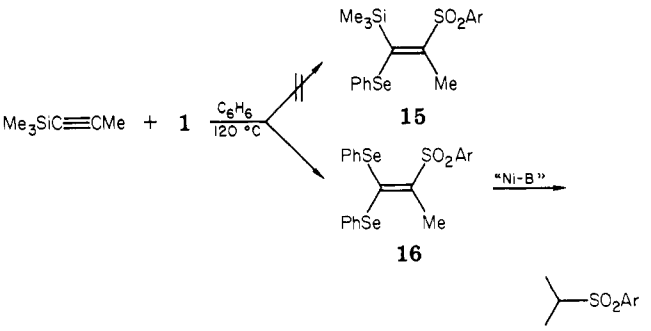
(9) For reviews of selenoxide eliminations and sigmatropic rearrangements, see: (a) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22. (b) Reich, H. J. In "Oxidation in Organic Chemistry. Part C"; Trahanovsky, W., Ed.; Academic Press: New York, 1978; p 1. (c) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049.

0022-3263/83/1948-4776$01.50/0

Scheme I

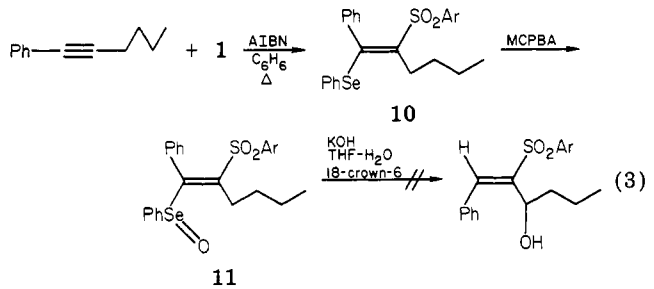


Scheme II



selenenic ester **9**, the observed product **6**. It is interesting to note that the selenoxide-stabilized anion **7** must be protonated or deuterated with high selectivity at the position α to the selenoxide moiety, in order to account for the result of the labeling experiment. The above process represents a rare, though not unique,[10] example of a vinyl selenoxide undergoing an allylic rearrangement promoted by base-catalyzed double bond isomerization.

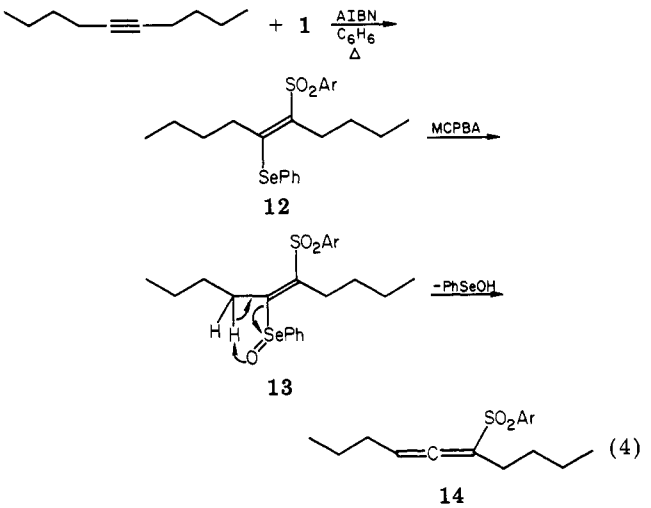
Selenosulfonation of 1-phenyl-1-hexyne provided the 1,2-adduct **10**, which was oxidized to selenoxide **11** in the usual way (eq 3). The latter selenoxide proved remarkably



resistant to either hydrolysis to its β-keto sulfone as in eq 2 or to allylic rearrangement as in Scheme I. It was recovered in 70% yield even after refluxing for 26 h with 3 M potassium hydroxide in THF–water in the presence of 18-crown-6. The greater stability of selenoxide **11** compared to that of **4** is attributed to the decreased acidity of the secondary allylic protons in the former compound compared to the primary allylic ones on the latter, thus preventing the formation of the required anionic intermediate (analogous to **7** in Scheme I). The less likely possibility that the rearrangement fails because of completely reversible proton abstraction from the allylic position of **11**, in lieu of the reprotonation α to the selenoxide, is ruled out by the failure of the allylic protons to exchange in deuterium oxide under similar conditions.[11]

Similarly, hydrolysis to the corresponding β-keto sulfone is less facile than in the case of selenoxide **2**. This can be explained by the inability of the *n*-butyl substituent in **11** (compared to the phenyl group in **2**) to assist in stabilizing the adjacent carbanion which is formed by the addition of hydroxide ion to the carbon α to the selenoxide moiety in the initial stage of the hydrolysis.

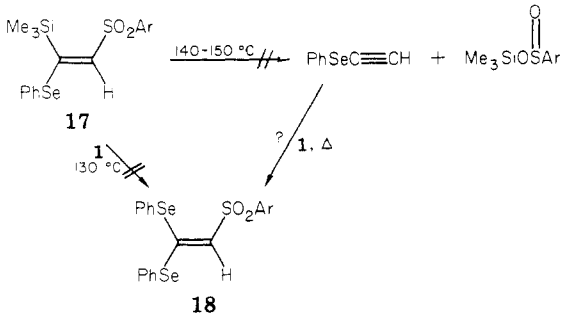
Selenoxide **13**, obtained from 5-decyne via the 1,2-adduct **12**, was also studied. Unlike selenoxides **2**, **4**, or **11**, this compound has β-hydrogens available for selenoxide elimination. Not unexpectedly, the allene[12] **14** was obtained in nearly quantitative yield when **13** was pyrolyzed in refluxing chloroform (eq 4). (*p*-Tolylsulfonyl)allenes such as **14** may prove of synthetic interest in Diels–Alder cycloadditions.[13]



The present experiments, taken in conjunction with our previous observations,[7a] permit the following conclusions to be made regarding the behavior of selenoxides derived from the selenosulfonation and oxidation of acetylenes. When a vinylic β-hydrogen is available for elimination (i.e., a monosubstituted acetylene is the precursor), then the acetylenic sulfone is generally formed in good yield via eq 1. The presence of allylic β-hydrogens does not result in competing allene formation. If a vinylic β-hydrogen is unavailable (i.e., a disubstituted acetylene is employed) but allylic ones are present, then allene formation is facile, as in eq 4. The absence of both types of β-hydrogens precludes elimination in either direction and results in selenoxides which are remarkably stable thermally. Such compounds may, however, undergo base-catalyzed fragmentation by either of two modes to afford either products

(10) Reich, H. J.; Shah, S. K. *J. Am. Chem. Soc.* **1977**, *99*, 263.
(11) Several attempts to effect the allylic rearrangement of **11** with stronger bases than KOH (e.g., *t*-BuOK) were made but resulted in its extensive decomposition instead of in the formation of the corresponding allylic alcohol.
(12) The formation of acetylenes and/or allenes has been observed from certain other vinyl selenoxides: Reich, H. J.; Willis, W. W., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 5967.
(13) Barbarella, G.; Cinquini, M.; Colonna, S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1646.

Scheme III



derived from a β-keto sulfone intermediate (eq 2) or from rearrangement to an allylic alcohol (Scheme I).

Finally, we report that the selenosulfonation of 1-(trimethylsilyl)propyne with **1** in benzene at 120 °C in a sealed glass tube did not form the expected 1,2-adduct **15** but rather the ketene diselenoacetal **16** in 90% yield (based on **1**). In order to unambiguously assign the structure of the product as **16** instead of as its *cis*- or *trans*-diphenylseleno isomer, the product was subjected to hydrogenation of the double bond and hydrogenolysis of the phenylseleno residues with nickel boride.[14] Isopropyl *p*-tolyl sulfone was isolated in 54% yield while its *n*-propyl counterpart was not observed, thus confirming the structural assignment (Scheme II). The formation of **16** is especially unexpected since we had previously found that the selenosulfonation of (trimethylsilyl)acetylene provided the usual 1,2-adduct **17** in 94% yield,[7a] albeit under milder conditions (80 °C vs. 120 °C).

We considered the possibility that the higher temperature of 120 °C might result in the further pyrolysis of the initially formed 1,2-adduct **15** to produce 1-(phenylseleno)propyne. Selenosulfonation of the latter compound in the usual fashion would then produce the observed product **16**. In order to test this hypothesis, we heated the similar adduct **17** at an even higher temperature of 140–150 °C in perchloroethene in a sealed NMR tube and monitored its decomposition. After 2 days there was no sign of (phenylseleno)acetylene formation and the starting material remained largely intact. Similarly, no ketene diselenoacetal **18** was produced when **17** was heated with selenosulfonate **1** in chlorobenzene at 130 °C for 4 days (Scheme III). Thus, either the putative intermediate **15** is far more thermally labile than the less substituted analogue **17** or the ketene diselenoacetal **16** is formed by some other pathway. Unfortunately there is presently insufficient evidence to permit an unequivocal conclusion regarding the mechanism.

Experimental Section

Melting points were obtained on an A. H. Thomas hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 467 spectrometer. NMR spectra were obtained on a Hitachi Perkin-Elmer R24B instrument at 60 MHz or on a Varian XL-200 spectrometer at 200 MHz. All NMR spectra were obtained in $CDCl_3$ solution unless otherwise noted and are reported in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra were recorded on a Varian MAT CH5 spectrometer and, along with elemental analyses, were obtained by Drs. R. Yamdagni and W. S. Lin. Preparative TLC was performed with Analtech 20 × 20 cm plates coated with 1000 μm of silica gel GF. MCPBA (Aldrich Chemical Co.) was purified by treatment with a pH 7.5 phosphate buffer and was assumed to be 100% pure.[15] Previously described procedures were employed for the preparation of selenosulfonate **1**[16] and adducts **3** and **17**.[7a] All other reagents were purchased from commercial sources.

3-Phenyl-2-(*p*-tolylsulfonyl)-2-propen-1-ol (6).[17] Selenide **3** (298 mg, 0.70 mmol) and MCPBA (144 mg, 0.84 mmol) were stirred for 5 min in 10 mL of THF. Five milliliters of 3 M aqueous KOH and a catalytic amount of 18-crown-6 were then added, and the mixture was stirred vigorously for 18 h at room temperature. It was then diluted with ether, washed with water (2 × 10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, and evaporated in vacuo. The residue was separated by preparative TLC (hexane–ethyl acetate, 4:1; R_f 0.09) to afford **6**: 130 mg (65%); mp 95.5–96.5 °C (from ether–hexane); IR ($CHCl_3$) 3574, 1613, 1595, 1300, 1139 cm^{-1}; NMR (60 MHz) 7.74 (s, 1 H) superimposed on 7.65 (d, J = 8 Hz, 2 H), 7.5–7.0 (complex, 7 H), 4.23 (d, J = 6 Hz, collapsed to s upon exchange with D_2O, 2 H), 2.53 (t, J = 6 Hz, exchanged with D_2O, 1 H), 2.30 (s, 3 H); mass spectrum, m/e 288 (M^+). Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59; S, 11.12. Found: C, 66.50, H, 5.73; S, 11.05.

The experiment was repeated with D_2O instead of H_2O, and the product was isolated as above. The NMR signal at δ 7.74 was no longer evident, whereas the doublet at δ 4.23 appeared unchanged; mass spectrum, m/e 289 (M^+).

1-Phenyl-1-(phenylseleno)-2-(*p*-tolylsulfonyl)-1-hexene (10). Selenosulfonate **1** (326 mg. 1.05 mmol), 1-phenylhexyne (166 mg, 1.05 mmol), and AIBN (8 mg. 0.05 mmol) were refluxed 46 h in 2 mL of benzene under nitrogen. Preparative TLC (hexane–ethyl acetate, 24:1; R_f 0.14) of the concentrated solution afforded 390 mg (80%) of **10**: mp 75–76 °C (from dichloromethane–hexane); IR (Nujol), 1590, 1568, 1310, 1153 cm^{-1}; NMR (200 MHz) 7.25–6.6 (complex, 14 H), 2.90 (crude t, J = 8.1 Hz, 2 H), 2.33 (s, 3 H), 1.80 (m, 2 H), 1.53 (m, 2 H), 1.03 (t, J = 7.3 Hz, 3 H); mass spectrum, m/e 470 (M^+, ^{80}Se), 468 (M^+, ^{78}Se). Anal. Calcd for $C_{25}H_{26}O_2SSe$: C, 63.95; H, 5.58; S, 6.83. Found: C, 64.13; H, 5.64; S, 6.56.

1-Phenyl-1-(phenylseleno)-2-(*p*-tolylsulfonyl)-1-hexene *Se*-Oxide (11). Selenide **10** (235 mg, 0.50 mmol) in MCPBA (105 mg, 0.61 mmol) were stirred in 4 mL of THF. After 30 min at room temperature, the solution was diluted with 10 mL of ether, washed twice with aqueous KOH and twice with saturated brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to afford 214 mg (88%) of the title selenoxide: mp 149–151 °C (from dichloromethane–hexane); IR (Nujol) 1591, 1309, 1149, 839 cm^{-1}; NMR (200 MHz) 7.36–7.00 (complex, 14 H), 3.16 (t, J = 8 Hz, 2 H), 2.34 (s, 3 H), 1.7–1.5 (m, 4 H), 1.08 (t, J = 7.3 Hz, 3 H); mass spectrum, m/e 470 (M^+ – 0, ^{80}Se); 468 (M^+ – 0, ^{78}Se). Anal. Calcd for $C_{25}H_{26}O_3SSe$: C, 61.84; H, 5.40; S, 6.60. Found: C, 61.72; H, 5.48; S, 6.09.

Attempted Hydrolysis of Selenoxide 11. Selenide **10** (238 mg, 0.51 mmol) was oxidized with MCPBA (103 mg, 0.60 mmol) in 8 mL of THF. After 25 min, 5 mL of 3 M aqueous KOH solution was added along with a catalytic amount of 18-crown-6. The mixture was refluxed 26 h and then worked up as in the preparation of **11** to afford 170 mg (70%) of the recovered selenoxide, identified by its melting point and IR and NMR spectra.

5-(Phenylseleno)-6-(*p*-tolylsulfonyl)-5-decene (12). Selenosulfonate **1** (311 mg, 1.00 mmol), 5-decyne (138 mg, 1.00 mmol), and AIBN (5 mg, 0.03 mmol) were refluxed for 42 h in 5 mL of benzene under nitrogen. Concentration of the reaction mixture, followed by preparative TLC (hexane–ethyl acetate, 4:1; R_f 0.66) provided 284 mg (63%) of compound **12**: mp 86–87 °C (from chloroform–hexane); IR (Nujol) 1590, 1567, 1285, 1160, 1141 cm^{-1}; NMR (200 MHz) 7.75 (d, J = 8.1 Hz, 2 H), 7.6–7.25 (complex, 7 H), 2.60 (m, 4 H), 2.43 (s, 3 H), 1.7–1.1 (complex, 8 H), 0.92 (t,

(14) For leading references and descriptions of the use of this reagent in related desulfurizations, see: (a) Boar, R. B.; Hawkins, D. W.; McGhie, J. F.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1973**, 654. (b) Schut, J.; Engberts, J. B. F. N.; Wynberg, H. *Synth. Commun.* **1972**, *2*, 415.

(15) Schwartz, N. N.; Blumbergs, J. H. *J. Org. Chem.* **1964**, *29*, 1976.

(16) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, *21*, 2213.

(17) Only one geometrical isomer of allylic alcohol **6** was isolated. The absence of significant allylic coupling between the vinyl and methylene protons suggests the *E* configuration, as transoid coupling constants are generally smaller than cisoid ones (see: Jackman, L. M.; Sternhell, S. In "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; p 316). However, the unavailability of the other isomer for purposes of comparison makes this assignment tentative.

J = 7.1 Hz, 3 H), 0.61 (t, J = 7.2 Hz, 3 H); mass spectrum, m/e 450 (M^+, ^{80}Se), 448 (M^+, ^{78}Se). Anal. Calcd for $C_{23}H_{30}O_2SSe$: C, 61.45; H, 6.73; S, 7.13. Found: C, 61.14; H, 6.87; S, 6.84.

6-(*p*-Tolylsulfonyl)-4,5-decadiene (14). Selenide **12** (225 mg, 0.50 mmol) and MCPBA (94 mg, 0.55 mmol) were refluxed 2.5 h in 10 mL of chloroform. The solution was then concentrated and preparative TLC (hexane–ethyl acetate, 4:1; R_f 0.59) furnished 140 mg (96%) of allene **14**: bp (bulb-to-bulb) 150–160 °C (0.25 mm); IR (film) 1946, 1592, 1304, 1153 cm^{-1}; NMR (200 MHz) 7.75 (d, J = 7.7 Hz, 2 H), 7.31 (d, J = 7.7 Hz, 2 H), 5.76 (m, 1 H), 2.43 (s, 3 H), 2.26 (m, 2 H), 2.07 (m, 2 H), 1.5–1.2 (complex, 6 H), 0.92 (t, J = 7.6 Hz, 3 H), 0.84 (t, J = 7.5 Hz, 3 H); mass spectrum, m/e 292 (M^+, faint). Anal. Calcd for $C_{17}H_{24}O_2S$: C, 69.82; H, 8.27; S, 10.97. Found: C, 69.62; H, 8.27; S, 10.75.

1,1-Bis(phenylseleno)-2-(*p*-tolylsulfonyl)propene (16). Selenosulfonate **1** (311 mg, 1.00 mmol), 1-(trimethylsilyl)propyne (112 mg, 1.00 mmol) and AIBN (8 mg, 0.05 mmol) were dissolved in 0.5 mL of benzene in a sealed glass tube and heated for 4 days at an oil-bath temperature of 120 °C. The contents were then separated by preparative TLC (hexane–ethyl acetate, 4:1; R_f 0.24) to furnish 227 mg (90%) of **16**: mp 122.5–123.5 °C (from ether–hexane); IR (KBr) 1592, 1572, 1303, 1152, 830, 817 cm^{-1}; NMR (60 MHz) 7.86 (d, J = 8 Hz, 2 H), 7.4–6.75 (complex, 12 H), 2.31 (s, 3 H), 2.23 (s, 3 H); mass spectrum, m/e 508, 506, and 504 (M^+ of $^{80}Se_2$, ^{80}Se–^{78}Se, and $^{78}Se_2$, respectively). Anal. Calcd for $C_{22}H_{20}O_2SSe_2$: C, 52.18; H, 3.98; S, 6.33. Found: C, 52.38; H, 3.90; S, 6.36.

Deselenization of Ketene Diselenoacetal 16. The title compound **16** (128 mg, 0.25 mmol) was dissolved in 20 mL of methanol–THF (3:1), and the solution was added to $NiCl_2{\cdot}6H_2O$ (684 mg, 2.5 mmol) in 5 mL of methanol. Sodium borohydride (284 mg, 7.5 mmol) was then added in portions with continuous stirring. The reaction mixture was filtered through Celite, concentrated, and separated by preparative TLC (hexane–ethyl acetate, 4:1; R_f 0.16) to afford 27 mg (54%) of isopropyl *p*-tolyl sulfone [mp 76–79 °C (lit.[18] mp 80 °C)], identified by its IR and NMR spectra.

Registry No. **1**, 68819-94-3; (*E*)-**2**, 86410-04-0; (*E*)-**3**, 86409-90-7; (*E*)-**4**, 87517-76-8; (*E*)-**6**, 87517-77-9; (*E*)-**6-*d***, 87517-84-8; (*E*)-**10**, 87517-78-0; (*E*)-**11**, 87517-79-1; (*E*)-**12**, 87517-80-4; (*E*)-**13**, 87517-81-5; **14**, 87517-82-6; **16**, 87517-83-7; 1-phenyl-1-hexyne, 1129-65-3; 5-decyne, 1942-46-7; 1-(trimethylsilyl)propyne, 6224-91-5; isopropyl *p*-tolyl sulfone, 51751-71-4.

(18) Tröger, J.; Uhde, R. *J. Prakt. Chem.* **1899**, *59*, 336.

Deacylation and Deformylation of Pyrroles

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Received May 23, 1983

Introduction

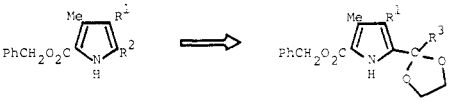
Unsubstituted positions on pyrrole rings tend to be reactive and hence often require protection during synthetic sequences.[1] Such positions in monopyrroles and porphyrins are usually protected with halogen atoms that can be removed, with variable success,[2] using catalytic hydrogenation. We recently communicated[3] that 3-acetylpyrroles and acetylporphyrins can be deacetylated by heating with ethanedithiol/BF_3 in acetic acid, and thus exploited the acetyl group as a porphyrin protecting group

Scheme I. Deacetylation, Deformylation, and Acetal Formation with Pyrroles Using Ethanedithiol and Boron Trifluoride

	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4	Yield
1	$PhCH_2$	Me	COMe	Me	5	$PhCH_2$	Me	H	Me	(95%)
2	$PhCH_2$	H	COMe	Me	6	$PhCH_2$	H	H	Me	(55%)
3	Et	Me	CHO	Me	7	Et	Me	H	Me	(45%)
4	$PhCH_2$	Me	CO_2Me	CHO	8	$PhCH_2$	Me	CO_2Me		(64%)

Scheme II. Deacetylation, Deformylation, and Acetal/Ketal Formation with Pyrroles Using Ethylene Glycol and *p*-Toluenesulfonic Acid

	R^1	R^2	R^3		R^1	R^2	Yield
1	$PhCH_2$	Me	COMe	5	$PhCH_2$	Me	(95%)
3	Et	Me	CHO	7	Et	Me	(83%)
10	Et	CH_2CO_2Et	CHO	11	Et	CH_2CO_2Et	(35%)



	R^1	R^2		R^1	R^3	Yield
12	Me	COMe	13	Me	Me	(84%)
14	$CH_2CH_2CO_2Me$	CHO	17	$CH_2CH_2CO_2Me$	H	(86%)
15	Et	CHO	18	Et	H	(80%)
16	CO_2Me	CHO	19	CO_2Me	H	(96%)

in a partial synthesis of dehydrocoproporphyrin (S-411 porphyrin).[4] In this paper we give full details of the deacylation process in pyrrole systems, modify it so that less obnoxious reagents are used, and extend the method to deformylation. The process of deacetylation is important in pyrrole synthetic chemistry since acetylpyrroles are readily available via standard ring fabrication routes,[5,6] but unsubstituted pyrroles, in contrast, are not nearly so accessible.

Scheme I shows the results of attempts to deacetylate and deformylate pyrroles **1–4** with use of ethanedithiol and BF_3 in acetic acid, and a general method is given in the Experimental Section. The 3-acetylpyrroles **1** and **2** were efficiently transformed, under these conditions, into the corresponding 3-unsubstituted pyrroles **5** and **6**. Likewise, the 3-formylpyrrole **3** was deformylated in 45% yield to give pyrrole **7**. Attempts to deformylate the pyrrole **4** bearing three electron-withdrawing substituents were unsuccessful, and the corresponding acetal **8** was obtained in 64% yield.

Owing to the obnoxious nature of ethanedithiol, the deacetylations and deformylations were also attempted

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