2,3,4,5-Tetrahydro-1*H*-2-benzazepin-1-one (8e). The crude product obtained from the preparation of **5e** (143 mg, 0.668 mmol) was purified by preparative chromatography on silica gel eluting with benzene–ethyl acetate (1:2) to give colorless pillars (44 mg, 41%) which were recrystallized from ether–petroleum ether, furnishing **8e**: mp 100–104.5 °C; MS *m/e* 161 (M^+), 132, 131, 104, 77; IR ν_{max} (Nujol) 3250, 1660, 1600, 1460 cm^{-1}; NMR ($CDCl_3$) δ 1.75–2.3 (m, 2 H), 2.90 (t, J = 7 Hz, 2 H), 3.20 (t, J = 7 Hz, 2 H), 7.1–7.5 (m, 5 H, aromatic).

The acidic extract of the reaction mixture was made alkaline with K_2CO_3, and the basic solution was extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated to give 14 mg (10%) of the starting material.

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Registry No.—**9,** 65185-62-8; **10,** 65185-63-9; **11,** 65185-64-0; **12,** 65185-65-1; **13,** 65185-66-2; **14,** 15115-58-9; **15** (R = H), 55223-26-2; **15** (R = CH_2Ph), 65185-67-3; **16,** 54311-89-6; **16** picrate, 54311-90-9; benzylamine, 100-46-9; *o*-bromobenzaldehyde, 6630-33-7; nitromethane, 75-52-5; *o*-bromo-β-nitrostyrene, 65185-68-4; benzaldehyde, 100-52-7; $Pd(OAc)_2$, 33571-36-7.

References and Notes

(1) Part 6: *J. Chem. Soc., Perkin Trans. 1,* submitted for publication. (a) M. Mori and Y. Ban, *Tetrahedron Lett.*, 1803, 1807 (1976); (b) M. Mori, K. Chiba, and Y. Ban, *ibid.*, 1037 (1977); (c) M. Mori, S. Kudo, K. Chiba, and Y. Ban, Abstracts, 24th Symposium on Organometallic Chemistry, Kyoto, Japan, 1976, p 145.

(2) P. N. Pylander, "Organic Syntheses with Noble Metal Catalysts", Academic Press, New York and London, 1973, p 215.

(3) A. Schoenberg and R. F. Heck, *J. Org. Chem.*, **39,** 3327 (1974).

(4) S. Gabriel, *Ber.*, **45,** 713 (1912).

(5) N. Umino, T. Iwakuma, and N. Itoh, *Tetrahedron Lett.*, 763 (1976).

(6) The spectral data (IR, NMR, and mass) of this amine (**16**) and elemental analysis of its picrate support this structure, but the melting point of this picrate (mp 132 °C) did not agree with that of the literature (mp 149–150 °C); A. Rieche and E. Hoeft, *J. Prakt. Chem.*, **17,** 293 (1962).

(7) J. von Braun and H. Reich, *Justus Liebigs Ann. Chem.*, **445,** 246 (1925).

(8) M. Hidai, M. Kokura, and Y. Uchida, *J. Organomet. Chem.*, **52,** 431 (1973).

(9) A. Matsuda, T. Mitsuyasu, and Y. Nakamura, *Kogyo Kagaku Zasshi*, **72,** 1751 (1969).

(10) D. E. Worrall, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1956, p 413.

(11) F. Mayer, H. Philipps, F. W. Ruppert, and A. T. Schmitt, *Ber.*, **61,** 1966 (1928).

Synthesis of Thiols and Polysulfides from Alkyl Halides, Hydrogen Sulfide, Ammonia, and Sulfur

James E. Bittell* and John L. Speier

Dow Corning Corporation, Midland, Michigan 48640

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Alkyl thiols and silyl-substituted alkyl thiols have been synthesized from the corresponding alkyl halides by the action of hydrogen sulfide and ammonia or alkyl amines under autogenous pressures in methanol. Alkyl halides converted to thiols in greater than 90% yield include hexyl, dodecyl, benzyl, trimethoxysilylpropyl, and methyldimethoxysilylpropyl chlorides, and 1,2-dibromoethane. Exceptionally low yields (~1%) of dialkyl sulfides were observed. Cyclohexyl bromide gave chiefly cyclohexene with a low yield of thiol. Dialkyl disulfides and polysulfides were prepared from hexyl and trimethoxysilylpropyl chlorides by the action of hydrogen sulfide, sulfur, and ammonia.

The reaction of alkyl halides and alkali metal hydrogen sulfides to prepare alkyl thiols is well known and industrially important.[1,2] In some cases, this route gives an acceptable yield of thiol, although it always leads to formation of sulfides. Even with excess hydrogen sulfide under pressure the formation of sulfides is not completely suppressed. For example, the amount of sulfides formed from dihalides is usually such that dithiols are best prepared otherwise.[1]

The reaction of alkyl halides with hydrogen sulfide and ammonia was studied as a more economical route to anhydrous preparations of alkyl thiols than the use of relatively expensive anhydrous sodium hydrosulfide. The procedure was easily extended to the preparation of disulfides and mixtures of polysulfides by adding sulfur to the mixture of reagents.

Ammonia and hydrogen sulfide combine to form unstable salts, ammonium hydrosulfide and ammonium sulfide. While these salts have received little attention in recent literature, early reports indicate that ammonium sulfide melts at −18 °C and has a vapor pressure of 760 mm at 0 °C. The more stable ammonium hydrosulfide melts at 118 °C and has a vapor pressure of 80 mm at 0 °C.[3,4] The reaction of ammonium hydrosulfide with dihalides to prepare dithiols was reported in 1947 by Simpson.[5] The yields of dithiols were poor (10–47%) and no better than those obtained with sodium hydrosulfide, so the reaction apparently received no further study.

Dodecyl thiol, $(MeO)_3Si(CH_2)_3SH$ (**1**), and $(MeO)_2MeSi(CH_2)_3SH$ (**2**) were prepared in high yield by heating the corresponding chlorides in an autoclave with a 10–20% molar excess of hydrogen sulfide and ammonia. Normally 15–25% methanol was used as solvent. For example, thiol **1** was obtained in 88.3% isolated yield by heating the corresponding chloride with hydrogen sulfide and ammonia in a molar ratio of 1:1.2:1.2 for 18.5 h at 100 °C. The rate of reaction increased with greater excess ammonia. Thiol **2** was obtained in 90.3% yield after 4 h at 100 °C when the molar ratio of chloride, hydrogen sulfide, and ammonia was 1:1:1.8. With a large excess of ammonia the yield of $[(MeO)_2MeSi(CH_2)_3]_2S$ (**3**) was only 1%.

Very little alkylation of ammonia occurred. Only 1–2% of $(MeO)_2MeSi(CH_2)_3NH_2$ (**4**) was detected in the products. Amine **4** was separated by distillation. Some loss of thiol resulted from oxidation of the thiol by air to disulfide. Oxygen must be excluded as far as possible during the reaction and workup since ammonia and amines catalyze the oxidation of thiols.

Amines and hydrogen sulfide also reacted with alkyl halides to form thiols. Conversion of 1-chlorohexane to the corresponding thiol was 80% after 6 h at 95 °C in a sealed tube with a solution of hydrogen sulfide, triethylamine, and methanol. The yield of thiol was 99% with only 0.9% of sulfide.

1,2-Dibromoethane in a solution of dipropylamine, hydrogen sulfide, and methanol at room temperature and at-

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mospheric pressure gave a 95% yield of 1,2-ethanedithiol in 4 h. However, 1,4-dichlorobutane gave a nearly quantitative yield of tetrahydrothiophene.

Benzyl chloride in a solution of ammonia, hydrogen sulfide, and methanol at 0 °C formed chiefly thiol with dibenzyl sulfide in 6–10% yield as the only other product. Bromocyclohexane in solution with methanol, triethylamine, and hydrogen sulfide at 75 °C for 24 h gave cyclohexene and cyclohexyl thiol in a ratio of 2.5:1. Bromocyclohexane and potassium hydrosulfide also gave cyclohexene as the major product.[1]

This system produced less sulfide than has been observed when alkali hydrosulfides were used. The low yield of sulfide probably is a result of dissociation of ammonium sulfide according to eq 1.[3,4] Under the conditions of the reactions this dissociation may be nearly complete so that very little sulfide was present. Similarly, ammonium alkyl thiolate formation was not favored at the temperatures of reaction, so little sulfide resulted.

$$(NH_4)_2S \rightleftarrows NH_4SH + NH_3 \qquad (1)$$

The preparation of disulfides from alkyl halides was accomplished by the use of sulfur in similar solutions. 3-Chloropropyltrimethoxysilane (**5**) with hydrogen sulfide, ammonia, and sulfur in a mole ratio of 2:1:4:1 after 2 h at 70 °C gave bis(trimethoxysilylpropyl) disulfide (**6**) in 95% yield with less than 2% of thiol **1** or bis(trimethoxysilylpropyl) sulfide (**7**). With 3 mol of sulfur the product was a mixture of polysulfides with an average rank of 3.4 in a di-/tri-/tetra-/pentasulfide ratio of 1:2.3:1.1:1.1.[6] As with alkali metal polysulfide solutions, the average rank of the resulting organic polysulfide is lower than the original solution.[7]

The mechanism of formation of polysulfides from alkyl chlorides in a mixture of excess ammonia, hydrogen sulfide, and sulfur has not been determined. The mechanism may involve rapid initial formation of ammonium polysulfides, which then react with the alkyl halides to form the organic polysulfides. Alternatively, alkyl thiols may be formed initially and then oxidized by sulfur to a mixture of polysulfides.[8]

Experimental Section

NMR spectra of carbon tetrachloride solutions were recorded on a Varian A-60-A or T-60 spectrometer. Gas–liquid chromatographic analysis were carried out on a S&M Model 720 gas chromatograph using 10% DC-200 (6 ft) on Chromasorb W and 5% DC-200 (8 ft) on Anakrum ABS columns. The thiol equivalent weights were determined by titration of aqueous ethanol solutions with a standard ethanolic iodine solution.

Preparation of Alkyl Thiols. General Procedure for Preparing Alkyl Thiols from Halides. A 3-L stainless steel Aminco rocking autoclave was evacuated (50 mm) and charged with weighed portions of NH_3 and H_2S. Alkyl halide and solvent were pumped into the autoclave which was maintained at 100 or 125 °C until 98% of the halide had reacted as determined by GLC. The pressure was released from the autoclave, and a volatile mixture of H_2S, NH_3, and solvent was trapped. The contents of the autoclave were filtered by nitrogen pressure through a coarse sintered glass filter. The filtrate and hexane washes of the filter cake were combined and distilled.

1-Dodecanethiol. Dodecyl chloride (819 g, 4.0 mol) in methanol (120 mL), NH_3 (78.4 g, 4.6 mol), and H_2S (171 g, 5.0 mol) was converted to the thiol in 22 h at 120 °C. The yield by GLC was 98%. The mixture of products was added to hexane (500 mL), washed free of salts with water, and distilled to obtain 655 g (81%) of 1-dodecanethiol: bp 120–125 °C (5 mm); n^{25} 1.4558 [lit.[2] bp 124 °C (5 mm), $n^{25}{}_D$ 1.4558]. Thiol equiv wt calcd for $C_{12}H_{26}S$: 202.4. Found: 203.9

A high boiling residue (27 g, 3.3%) remained after distillation. The major component of the residue was identified by GLC as dodecyl disulfide.

3-Mercaptopropyltrimethoxysilane. Chloride **5** (938 g, 4.68 mol) in methanol (150 mL), NH_3 (95.9 g, 5.64 mol), and H_2S (192 g, 5.65 mol) gave by GLC a 97 area % yield of thiol in 18.5 h at 100 °C. The pressure at 100 °C was 195 psi, which decreased to 85 psi. The GLC area of bis(trimethoxysilylpropyl) sulfide was less than 1% in the product. Distillation afforded the thiol in 88.3% yield: bp 93–94 °C (10 mm); $n^{25}{}_D$ 1.4412; $d^{25}{}_4$ 1.0503; NMR (CCl_4) δ 3.42 (s, 9, CH_3O), 2.45 (t, CH_2S), 1.6 (m, 3, CH_2, SH), 0.67 (m, 2, CH_2Si). Thiol equiv wt calcd for $C_6H_{16}O_3SSi$: 196.3. Found: 196.4.

3-Mercaptopropylmethyldimethoxysilane. 3-Chloropropylmethyldimethoxysilane (593 g, 3.25 mol) in methanol (200 mL), NH_3 (100 g, 5.88 mol), and H_2S (127.5 g, 3.25 mol) gave by GLC a 99 area % yield of thiol in 4 h at 100 °C. The GLC area of sulfide **3** was 1% in the product. Distillation afforded the thiol **2** in 90.3% yield: bp 72–74 °C (4 mm); $n^{25}{}_D$ 1.4478; $d^{20}{}_4$ 0.996; mass spectrum, *m/e* (relative intensity) 165 (3.6), 148 (54.7), 133 (72), 105 (100). Thiol equiv wt calcd for $C_6H_{16}O_2SSi$: 180.3. Found: 183.9.

1-Hexanethiol. A mixture of *n*-hexyl chloride (3.49 g, 0.029 mol) and 15 mL of a 2.2 M H_2S (0.033 mol) solution in equal volumes of Et_3N and methanol was heated in a sealed glass tube at 75 °C for 6 h. Analysis by GLC indicated that the reaction was 80% complete with the products being 99.1% 1-hexanethiol and 0.9% dihexyl sulfide.

1,2-Ethanedithiol. 1,2-Dibromoethane (10.9 g, 0.058 mol) in a solution of dipropylamine (13.5 g, 0.133 mol) and methanol (10 mL) saturated with H_2S at room temperature precipitated Pr_2NH_2Br within minutes. After 4 h at room temperature, GLC showed only one product in 95% yield (based on methanol as an internal standard). About 200 mL of water was added to the mixture, and the product (more dense than water) was separated and dried over Na_2SO_4. The IR spectrum of the product was identical with the reported spectrum of 1,2-ethanedithiol: IR (neat) 2550 (S–H) and 693 (C–S) cm^{-1}.[9]

Benzyl Mercaptan. A solution of NH_3 (3.3 g, 0.19 mol) and methanol was saturated with H_2S at 0 °C. Benzyl chloride (20.9 g, 0.165 mol) was added to the solution at 0 °C while slowly bubbling H_2S through the solution. The reaction was complete in 1 h with benzyl mercaptan (92% GLC area) and dibenzyl sulfide (8% GLC area) as the only detectable products.

Cyclohexanethiol. An H_2S saturated solution of triethylamine (9.4 g, 0.093 mol), methanol (20 mL), and bromocyclohexane (13.2 g, 0.08 mol) was heated at 75 °C in sealed glass tubes for 24 h. Triethylamine hydrobromide precipitated from the solution. Cyclohexene and cyclohexanethiol were identified by coinjection on GLC with authentic samples. GLC analysis with methanol as the internal standard indicated that the products were cyclohexene and cyclohexanethiol in a ratio of 2.5:1.

Preparation of Alkyl Polysulfides. General Procedure for Preparing Alkyl Polysulfides from Halides. Polysulfides were prepared by the same general procedure as the thiols except that sulfur was added to the autoclave before it was evacuated. The pressure observed during the reactions was minimal (<150 psig). When the polysulfides were not stable to distillation, semiquantitative analyses were performed by NMR spectroscopy based on the relative areas of the methylene protons adjacent to the sulfur atoms as described by Grant and Van Wazer.[6]

Bis(trimethoxysilylpropyl) Disulfide. Chloride **5** (794 g, 4.0 mol) in methanol (187 mL), sulfur (64 g, 2.0 mol), H_2S (72 g, 2.1 mol), and NH_3 (135 g, 7.9 mol) reacted completely in 2 h at 70 °C. The filtrate and hexane washes of the NH_4Cl filter cake were stripped on a rotary evaporator to 50 °C at 20 mm to give 757 g (97%) of light yellow disulfide **6:** $n^{25}{}_D$ 1.4662; NMR (CCl_4) δ 3.53 (s, 9, CH_3O), 2.67 (t, 2, CH_2S), 1.75 (m, 2, $-CH_2$), 0.67 (t, 2, CH_2Si).

The product was identical with an authentic sample of disulfide **6** prepared from 3-mercaptopropyltrimethoxysilane by iodine oxidation.[10] The product contained 1.7 wt % of $(MeO)_3Si(CH_2)_3SH$ as determined by iodine titration. Sulfide **7** was not detected by NMR spectroscopy or GLC.

Bis(trimethoxysilylpropyl) Polysulfide. Chloride **5** (993, 5 mol) in methanol (250 mL), sulfur (240 g, 7.5 mol), H_2S (87 g, 2.56 mol), and NH_3 (119 g, 7.0 mol) reacted completely in 2.5 h at 70 °C. The filtrate and hexane washes of the NH_4Cl filter cake were stripped to 60 °C at 10 mm to give 1,074 g of a cloudy yellow mixture of polysulfides, $[(MeO)_3Si(CH_2)_3]_2S_x$: NMR (CCl_4) δ 3.52 (s, 9, CH_3O), 2.66 (t, 0.36, CH_2S_2), 2.86 (t, 0.84, CH_2S_3), 2.94 (t, 0.4, CH_2S_4), 2.98 (t, 0.4, CH_2S_5), 1.87 (m, 2, CH_2), 0.70 (m, 2, CH_2Si).

Anal. Calcd for $C_{12}H_{30}O_6S_3Si_2$: S, 22.7. Found: S, 22.0.

The product contained 0.15 wt % of thiol **1** as determined by iodine titration.

Dihexyl Disulfide. 1-Chlorohexane (362 g, 3 mol), methanol (250 mL), sulfur (48 g, 1.5 mol), H_2S (51 g, 1.5 mol), and ammonia (103 g, 6 mol) gave 95% conversion in 2 h at 70 °C. Dihexyl sulfide was not detected by GLC (<0.3%). The product was distilled to yield 293 g (87.6%) of dihexyl disulfide: bp 120–122 °C (1 mm); $n^{25}{}_D$ 1.4864; $d^{25}{}_4$ 0.9145.

Anal. Calcd for $C_{12}H_{26}S_2$: C, 61.5; H, 11.2; S, 27.4. Found: C, 61.6; H, 11.2; S, 27.3.

Registry No.—**1**, 4420-74-0; **2**, 31001-77-1; **5**, 2530-87-2; **6**, 35112-74-4; 1-dodecanethiol, 112-55-0; dodecyl chloride, 112-52-7; dodecyl disulfide, 2757-37-1; 3-chloropropylmethyldimethoxysilane, 18171-19-2; 1-hexanethiol, 111-31-9; *n*-hexyl chloride, 544-10-5; 1,2-ethanedithiol, 540-63-6; 1,2-dibromoethane, 106-93-4; benzyl mercaptan, 100-53-8; benzyl chloride, 100-44-7; cyclohexanethiol, 1569-69-3; bromocyclohexane, 108-85-0; bis(trimethoxysilylpropyl) polysulfide, 40550-17-2; dihexyl disulfide, 10496-15-8; 1-chlorohexane, 544-10-5.

References and Notes

(1) S. Patai, Ed., "The Chemistry of the Thiol Group", Wiley, New York, N.Y., 1974, Vol 1, pp 180–182.
(2) E. E. Reid, "Organic Chemistry of Bivalent Sulfur", Chemical Publishing Co., New York, N.Y., 1958, Vol 1, pp 25–29, 66.
(3) L. Scheflin and C. R. McCrosky, *J. Am. Chem. Soc.*, **54**, 193 (1932).
(4) J. Walker and J. S. Lumsden, *J. Chem. Soc.*, **71**, 428 (1897).
(5) S. D. Simpson, *Can. J. Res., Sect. B*, **25**, 20 (1947).
(6) D. Grant and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 3012, (1964).
(7) Arthur V. Tobolsky, Ed., "The Chemistry of Sulfides", Wiley, New York, N.Y., 1968, p 224.
(8) B. D. Vineyard, *J. Org. Chem.*, **31**, 601 (1966).
(9) D. Welti and D. Whittaker, *J. Chem. Soc.*, 4372 (1962).
(10) G. A. Gornowicz and J. L. Speier, *Mech. React. Sulfur Compd.*, **3**, 53 (1968).

Synthetic Applications of Arylselenenic and Arylseleninic Acids. Conversion of Olefins to Allylic Alcohols and Epoxides

T. Hori and K. B. Sharpless*[1]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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A new direct (one reaction vessel) route from olefins to rearranged allylic alcohols has been developed. It involves electrophilic addition of phenylselenenic acid (PhSeOH) to the olefin. The phenylselenenic acid is generated in situ by comproportionation of phenylseleninic acid ($PhSeO_2H$) and diphenyl diselenide (PhSeSePh). The addition of PhSeOH to trisubstituted olefins is highly regioselective. A new procedure for the oxidation/elimination of alkyl phenyl selenides is described. It employs *tert*-butyl hydroperoxide in place of hydrogen peroxide and avoids the secondary epoxidation process which can be a problem with the latter oxidant. Arylseleninic acids were found to be effective catalysts for the epoxidation of olefins with hydrogen peroxide. However, attempts to achieve asymmetric epoxidations by employing optically active arylseleninic acids as catalysts met with failure. A simple procedure for generating DMAC solutions of sodium selenocyanate by direct reaction of sodium cyanide with selenium metal is described. NaSeCN so generated is used in the preparation of *o*-nitrophenyl selenocyanate.

Olefins to Allylic Alcohols

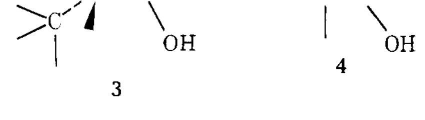
We report here a new procedure for the conversion of an olefin to a rearranged allylic alcohol. The process involves addition of the olefin to a methylene chloride solution containing both phenylseleninic acid (**1**) and diphenyl diselenide (**2**). As shown in Scheme I a β-hydroxyphenyl selenide adduct **3** is produced,[2,3] and subsequent oxidation of this adduct, in the same reaction vessel, leads to the allylic alcohol **4** in good yield. The adduct **3** probably arises by electrophilic addition of phenylselenenic acid (**5**)[4] to the olefin.

The putative intermediate **5** is thought to be generated in situ by the redox reaction between seleninic acid **1** and diselenide **2**. Going from left to right, as shown in Scheme I, this process is formally a comproportionation. The equilibrium is apparently driven by capture of the selenenic acid **5** by the olefin.

The addition of aromatic selenenic acid derivatives (ArSeX) to olefins was discovered by Hölzle and Jenny.[5] Our group,[6] Reich's group,[7] and Clive[8] demonstrated the utility of such additions for synthesis of allylically functionalized alkenes. However, the direct addition of "PhSeOH" to olefins had not been accomplished.[9] In addition to producing allylic alcohols directly, the new procedure offers high regioselectivity (Table I, entries 4 and 5) in circumstances where the earlier reagents (e.g. CH_3CO_2SePh[6] and CF_3CO_2SePh[7,8]) afford almost 1:1 mixtures of regioisomers.

Scheme I

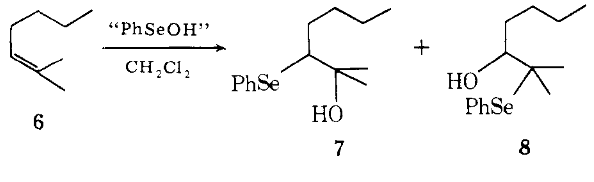
$$\underset{\mathbf{1}}{PhSeO_2H} + \underset{\mathbf{2}}{PhSeSePh} + H_2O \rightleftharpoons \underset{\mathbf{5}}{[3PhSeOH]}$$



3 **4**

The general procedure employed for addition of "PhSeOH" to olefins calls for generation of phenylseleninic acid (**1**) in situ by addition of the appropriate (i.e., that required to generate an ~1:1 mixture of **1** and **2**) amount of 30% hydrogen peroxide to a methylene chloride solution of diphenyl diselenide (**2**).[10] When this initial oxidation is complete anhydrous $MgSO_4$ is added to sequester most of the excess water. The addition of $MgSO_4$ has two important, if unanticipated, effects on the course of the subsequent reaction with the olefin: (1) both the rates of formation and the yields of the adducts **3** are increased; (2) in the case of trisubstituted olefins the Markownikoff regioselectivity is complete (whereas when anhydrous $MgSO_4$ is omitted some of the anti-Markownikoff regioisomer is also formed). For example, as shown in Scheme II addition of "PhSeOH" to 2-methyl-2-heptene (**6**) in the presence of anhydrous $MgSO_4$ gave adduct **7** exclusively, whereas when

Scheme II



with $MgSO_4$ 100:0
without $MgSO_4$ 85:15

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