2120 (N_3), 3280 cm^{-1} (OH); 100-MHz ^1H NMR ($CDCl_3$) δ 2.281 (br s, 1, OH), 4.623 (d, 1 $J_{H_7H_8}$ = 7.5 Hz), 4.820 (br, decouples into sharp d by D_2O, 1, $J_{H_7H_8}$ = 7.5 Hz), 7.393 (s, 4); mass spectrum (70 eV, 60 °C), *m/e* (relative intensity) 240 (M^+·, 12), 221 (M^+· - N_2, 6), 220 ($C_{10}H_6NO^+$, 4), 206 ($C_{10}H_6O^+$·, 5), 192 ($C_9H_6NS_2^+$, 40), 191 ($C_{10}H_7S_2^+$, 7), 190 ($C_{10}H_6S_2^+$·, 5), 177 ($C_9H_5S_2^+$, 11), 160 ($C_9H_6NS^+$, 100), 159 ($C_{10}H_6S^+$·, 7), 148 ($C_8H_6S^+$·, 6), 146 ($C_8H_4S^+$·, 5), 121 ($C_7H_5S^+$, 20). Anal. Calcd for $C_{10}H_7N_3OS$: C, 48.2; H, 2.8; N, 16.9. Found: C, 47.8; H, 2.6; N, 17.3.

1a,7b-Dihydroazirino[5,6]benzo[1,2-*c*:3,4-*c'*]dithiophene (9). A solution of 397 mg of **8** and 2.5 mL of $P(OC_2H_5)_3$ in 15 mL of dry benzene was refluxed under N_2 for 15 min. A further 1 mL of the reagent was added and reflux continued for 5 min. The benzene was removed under reduced pressure and the residue triturated with cold ether and hexane to yield 156 mg (46%) of **9** as cream-colored crystals: mp 160–162 °C (from $CHCl_3$); IR (Nujol) 3190 cm^{-1} (NH); 100-MHz ^1H NMR ($CDCl_3$) δ 3.504 (s, 2), 7.395, 7.445 (AB q, 4); mass spectrum (70 eV, 50 °C), *m/e* (relative intensity) 205 (M^+·, 100), 204 ($C_{10}H_6NS_2^+$, 42), 190 ($C_{10}H_6S_2^+$·, 10), 177 ($C_9H_5S_2^+$, 10), 172 ($C_{10}H_6NS^+$, 16). Anal. Calcd for $C_{10}H_7NS_2$: C, 58.5; H, 3.4; N, 6.8. Found: C, 58.7; H, 3.5; N, 6.4.

Benz[*a*]anthracene-5,6-imine (1a,11b-Dihydro-1*H*-benz[3,4]anthra[1,2-*b*]azirine) (12). To 1.00 g of a 1:1 mixture of azido alcohols **10** and **11**[2] was added 0.8 mL of $P(OC_2H_5)_3$. Brief heating to 35 °C initiated an exothermic reaction that lasted a few minutes. To the cooled mixture were added 10 mL of ether and 50 mL of hexane and the solution was allowed to stand for 3 days in the refrigerator. The pale yellow precipitate of 0.406 g (48%) of **12** proved to be analytically pure, mp 157 °C dec.[2]

***threo*-Diethyl (2-Hydroxy-1,2-diphenylethyl)amidophosphate (14).** A mixture of 500 mg of *threo*-2-azido-1,2-diphenylethanol (**13**)[1] and 1.5 mL of $P(OC_2H_5)_3$ was heated briefly (50 °C) to initiate the evolution of N_2 and C_2H_4. The reaction mixture was then cooled for a few minutes with ice water until the evolution of gas ceased. The heavy precipitate (695 mg, 95%) was filtered, washed with hexane, and recrystallized from benzene–hexane: mp 135 °C; IR (KBr) 3400, 3250 cm^{-1}; 60-MHz ^1H NMR ($CDCl_3$) δ 0.96 (t, 3, J = 8 Hz), 1.22 (t, 3, J = 3 Hz), 3.35–3.83 (m, 4), 4.22 and 4.41 (unresolved d, 2), 4.93 (br, 1), 7.26 (m, 10); mass spectrum (70 eV, 150 °C), *m/e* (relative intensity) 331 (M^+· - H_2O, 1.7), 304 ($C_{16}H_{19}NO_3P^+$, 1.0), 303 ($C_{16}H_{18}NO_3P^+$·, 1.0), 276 ($C_{14}H_{15}NO_3P^+$, 1.3), 275 ($C_{14}H_{14}NO_3P^+$·, 1.6), 274 ($C_{14}H_{13}NO_3P^+$, 1.3), 258 ($C_{14}H_{13}NO_2P^+$, 1.5), 243 ($C_{14}H_{14}NOP^+$·, 34.7), 242 ($C_{14}H_{13}NOP^+$, 89.5), 240 ($C_{14}H_{11}NOP^+$, 1.4), 214 ($C_9H_{13}NO_3P^+$, 36.9), 197 ($C_{14}H_{13}O^+$, 18.5), 196 ($C_{14}H_{12}N^+$, 13.6), 195 ($C_{14}H_{11}N^+$·, 7.4), 194 ($C_{14}H_{10}N^+$, 12.9), 186 ($C_7H_9NO_3P^+$, 100), 179 ($C_{14}H_{11}^+$, 18.5), 178 ($C_{14}H_{10}^+$·, 85.2), 169 ($C_7H_8NO_2P^+$·, 19.8), 168 ($C_7H_7NO_2P^+$, 60.0), 167 ($C_{13}H_{11}^+$, 6.7), 165 ($C_{13}H_9^+$, 11.5), 152 ($C_4H_{11}NO_3P^+$, 7.1). Anal. Calcd for $C_{18}H_{24}NO_3P$: C, 61.9; H, 6.9; N, 4.0; P, 8.9. Found: C, 61.6; H, 7.1; N, 4.2; P, 9.2.

***erythro*-Diethyl (2-hydroxy-1,2-diphenylethyl)amidophosphate (16)** was obtained in the same manner as **14** in 92% yield from *erythro*-2-azido-1,2-diphenylethanol (**15**)[1]: mp 150 °C (from benzene–hexane); IR (KBr) 3410, 3320 cm^{-1}; 60-MHz ^1H NMR ($CDCl_3$) δ 1.03 (t, 3, J = 8 Hz), 1.66 (t, 3, J = 8 Hz), 3.88 (q, 4, J = 8 Hz), 4.30 and 4.51 (unresolved d, 2), 7.18 (m, 10); mass spectrum (70 eV, 150 °C), *m/e* (relative intensity) 331 (M^+· - H_2O, 1.1), 304 ($C_{16}H_{19}NO_3P^+$, 3.2), 276 ($C_{14}H_{15}NO_3P^+$, 1.2), 275 ($C_{14}H_{14}NO_3P^+$·, 1.0), 258 ($C_{14}H_{13}NO_2P^+$, 1.0), 243 ($C_{14}H_{14}NOP^+$·, 36.5), 242 ($C_{14}H_{13}NOP^+$, 100), 240 ($C_{14}H_{11}NOP^+$, 1.2), 214 ($C_9H_{13}NO_3P^+$, 35.6), 197 ($C_{14}H_{13}O^+$, 10.6), 196 ($C_{14}H_{12}N^+$, 8.2), 195 ($C_{14}H_{11}N^+$·, 5.8), 194 ($C_{14}H_{10}N^+$, 9.4), 186 ($C_7H_9NO_3P^+$, 83.4), 179 ($C_{14}H_{11}^+$, 11.4), 178 ($C_{14}H_{10}^+$·, 51.0), 169 ($C_7H_8NO_2P^+$·, 12.6), 168 ($C_7H_7NO_2P^+$, 35.8), 167 ($C_{13}H_{11}^+$, 3.8), 165 ($C_{13}H_9^+$, 6.1), 152 ($C_4H_{11}NO_3P^+$, 3.8). Anal. Calcd for $C_{18}H_{24}NO_3P$: C, 61.9; H, 6.9; N, 4.0; P, 8.9. Found: C, 61.7; H, 7.0; N, 4.5; P, 9.2.

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Registry No. 1, 53581-32-1; **5**, 74684-57-4; **6**, 74684-58-5; **7**, 74684-59-6; **8**, 74684-60-9; **9**, 74684-61-0; **10**, 71382-38-2; **11**, 71382-41-7; **12**, 74684-62-1; **13**, 74684-63-2; **14**, 74684-64-3; **15**, 74684-65-4; **16**, 74684-66-5; triethyl phosphite, 122-52-1.

Silica Gel Assisted Synthesis of Thiiranes[1]

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We report a convenient method for converting epoxides into thiiranes based on the use of silica gel either as a support for potassium thiocyanate or as a catalyst.[2] This method proceeds with high stereospecificity and requires only filtration and solvent evaporation for product isolation.

Attempted synthesis of 1-decene sulfide from 1-decene oxide (10 mmol) using finely ground potassium thiocyanate suspended in toluene at 90 °C yielded no detectable product after 16 h.[3] In contrast, a similar reaction carried out in which the inorganic reagent was first crushed with (reagent **1**) or coated onto (reagent **2**) silica gel produced a quantitative conversion (GLC). After filtration and solvent removal (reduced pressure), a 95% isolated yield of 1-decene sulfide was obtained as a colorless liquid which was spectroscopically identical with an authentic sample. Empirical testing of **1** and **2** prepared under different drying conditions revealed that small but finite amounts of water were required for high activity and that both reagents were equally effective in this new thiirane synthesis.[4,5] Procedures used for preparing optimum reagents are described in the Experimental Section.

Table I summarizes the results obtained for a variety of epoxides. In general, high yields of monosubstituted episulfides were produced in reasonably short time periods; disubstituted epoxides reacted much more slowly. The conversion is highly stereospecific as evidenced by the fact that *trans*-5-decene oxide and *cis*-5-decene oxide afford only the corresponding trans and cis episulfides, respectively. This new thiirane synthesis represents an attractive modification of current KSCN procedures.[2] Products can be isolated in good to excellent yields by simple filtration and solvent evaporation, and no extraction steps are required. The principal limitation of this method is that reaction rates are generally slow.

Experimental Section

General Methods. Unless stated otherwise, all reagents and chemicals were obtained commercially and were used without further purification. Silica gel (Bio Sil A, 100–200 mesh) was purchased from Bio-Rad Laboratories, Richmond, CA. Benzene and toluene were dried by distillation from sodium and benzophenone under a nitrogen atmosphere. All ^1H NMR and IR spectra were recorded with Varian A-60 and Beckman Acculab 7 spectrometers, respectively; chemical shifts were recorded in δ values (ppm) from internal tetramethylsilane. Product mixtures

(1) Supported by the National Science Foundation (Grant No. CHE-77-28366).

(2) Reviews of thiiranes: Reynolds, D. D.; Fields, D. L. In "Heterocyclic Compounds with Three and Four-Membered Rings"; Weissberger, A., Ed.; Interscience: New York, 1964; Part I, 576; Goodman, L.; Reist, E. J. In "The Chemistry of Organic Sulfur Compounds"; Kharasch, N., Meyers, C. Y., Eds.; Pergamon Press: New York, 1966; Vol. 2, p 93; Sander, M. *Chem. Rev.* **1966**, *66*, 297; Fokin, A. V.; Kolomeits, A. F. *Russ. Chem. Rev.* **1975**, *44*, 138. For typical KSCN procedures, see: Schuetz, R. D.; Jacobs, R. L. *J. Org. Chem.* **1961**, *26*, 3467.

(3) The solubility of KSCN in toluene at 90 °C is ca. 8×10^{-4} M (atomic emission).

(4) Menger et al. have noted that water plays an important role in permanganate-coated reagents: Menger, F. M.; Lee, C. *J. Org. Chem.* **1979**, *44*, 3446.

(5) Experimentally **1** and **2** are equally convenient to use.

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Table I. Conversion of Epoxides to Thiiranes[a]

reactant	product	reagent	temp, °C	time, h	isolated yield, %
cyclohexene oxide	cyclohexene sulfide	1	80	20	65[b]
1-decene oxide	1-decene sulfide	1	90	13	90
1-decene oxide[c]	1-decene sulfide	1	90	22	70[d]
1-decene oxide	1-decene sulfide	2	90	16	95
1-dodecene oxide	1-dodecene sulfide	1	90	13	89
1-dodecene oxide	1-dodecene sulfide	1	25	240	85
1-tetradecene oxide	1-tetradecene sulfide	1	90	13	91
1,2,7,8-octadiene bisepoxide	1,2,7,8-octadiene bisepisulfide	1	90	13	36
cis-5-decene oxide	*cis*-5-decene sulfide	1	90	124	65
trans-5-decene oxide	*trans*-5-decene sulfide	1	90	528	48
2,3-epoxypropyl *p*-methoxyphenyl ether	[(*p*-methoxyphenoxy)methyl]thiirane	1	90	19	68
p-chlorophenyl 2,3-epoxypropyl ether	[(*p*-chlorophenoxy)methyl]thiirane	1	90	19	55
p-*tert*-butylphenyl 2,3-epoxypropyl ether	[(*p*-*tert*-butylphenoxy)methyl]thiirane	1	90	19	63
2-methyl-1-hexene oxide	2-methyl-1-hexene sulfide	1	90	28	81[d]
cyclododecene oxide	cyclododecene sulfide	1	90	44	<5[d]
cyclooctene oxide	cyclooctene sulfide	1	90	44	<5[d]

[a] Reaction of 10 mmol of epoxide in 30 mL of toluene with 10 g of reagent. All products were identified either by comparison of their IR and ^{1}H NMR spectra with those of suthentic sample or by complete characterization. [b] Benzene was used as the solvent. [c] 3 g of reagent was used. [d] GLC yield.

were analyzed by GLC on a Hewlett-Packard Model 5830 A flame-ionization instrument (2 ft × 0.125 in. UCW-982 on Chromosorb W column). Elemental analysis was performed by Midwest Microlab Ltd., Indianapolis, IN.

KSCN/Silica Gel, Reagent 1. Into a 50-mL culture tube containing 5.0 g of dry silica gel (20 h, 110 °C (0.1 mm)) was added 0.375 g of water. The tube was sealed and shaken mechanically at room temperature for 4 h and the contents was then ground together with 5.0 g (52 mmol) of dry KSCN (60 °C, 24 h (0.1 mm)), using a mortar and pestle.

KSCN/Silica Gel, Reagent 2. A solution of 5.0 g (52 mmol)) of KSCN in 2.2 mL of water was added to 5.0 g of silica gel. The resulting "wet reagent" was then dried under vaccum (65 °C, 24 h (1 mm)).

General Procedure for Thiirane Synthesis. Procedures similar to that described for the conversion of 1-decene oxide to 1-decene sulfide were used for all of the reactions described in Table I. A 100-mL round-bottomed flask was charged with 10 g of reagent 1 plus 1.56 g (10 mmol) of 1-decene oxide dissolved in 30 mL of toluene. A Teflon-coated $^1/_2 \times {}^3/_4$ in. egg-shaped stirring bar was added and the mixture stirred vigorously at 90 °C for 13 h. Analysis by GLC indicated the complete disappearance of epoxide. The product mixture was filtered through Celite, and the spent and unused reagents were washed with 10 mL of toluene. Removal of solvent from the combined filtrate under reduced pressure yielded 1.55 g (90%) of 1-decene sulfide as a colorless liquid having ^{1}H NMR and IR spectra identical with those of an authentic sample, n^{25}_D 1.4695 (lit.[6] n^{20}_D 1.4720). The purity was >97% (GLC).

***trans*-5-Decene Oxide.** Into a stirred solution of *m*-chloroperbenzoic acid (15.0 g, 87 mmol) in 150 mL of $CHCl_3$ (0 °C) was added 10.0 g (70 mmol) of *trans*-5-decene dissolved in 50 mL of $CHCl_3$ over a 30-min period. The mixture was stirred overnight at room temperature, filtered, washed with 10% $NaHCO_3$, and dried (anhydrous Na_2SO_4). The solvent was removed by rotary evaporation and the epoxide distilled under reduced pressure, affording 9.6 g (88%) of *trans*-5-decene oxide having bp 71–72 °C (12 mm) [lit.[7] bp 85 °C (20 mm)]; ^{1}H NMR ($CDCl_3$) 0.97 (t, 6, CH_3), 1.45 (m, 12, CH_2), 2.63 (m, 2, CHO).

***cis*-5-Decene Oxide.** The procedure used for epoxidizing 10 g (70 mmol) of *cis*-5-decene oxide was similar to that used for the trans isomer. The yield of epoxide obtained was 8.4 g (77%), having bp 89–91 °C; ^{1}H NMR ($CDCl_3$) 0.98 (t, 6, CH_3), 1.46 (m, 12, CH_2), 2.88 (m, 2, CHO). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90; O, 10.24. Found: C, 76.57; H, 13.15; O, 10.48.

***cis*-5-Decene Sulfide.** By use of a procedure similar to that described for the preparation of 1-decene sulfide, 1.56 g (10 mmol) of *cis*-5-decene oxide was converted into the corresponding episulfide. Reaction for 124 h at 90 °C led to 70% conversion (GLC). The episulfide was separated from the epoxide by chromatography (silica gel) using benzene as the eluting solvent, yielding 1.13 g (66%) of *cis*-5-decene sulfide as a colorless liquid: bp 53–55 °C (0.3 mm); IR (neat) 1463 (m), 1457 (m), 1378 (w), 733 (w), 670 (w), 603 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.99 (t, 6, CH_3), 2.55 (m, 12, CH_2), 2.94 (m, 2, CHS). Anal. Calcd for $C_{10}H_{20}S$: C, 69.70; H, 11.70; S, 18.60. Found: C, 69.87; H, 11.45, S, 18.45. The stereochemical purity of the product was established by reacting it with excess triphenylphosphine in toluene (90 °C); only *cis*-5-decene was produced.[8]

***trans*-5-Decene Sulfide.** By use of a procedure similar to that described for the preparation of *cis*-5-decene sulfide, 1.56 g of *trans*-5-decene oxide was converted into 0.84 g (48%) of *trans*-5-decene sulfide: bp 46–47 °C (0.19 mm); IR (neat) 1465 (m), 1459 (m), 1381 (w), 1015 (w), 680 (w), 642 (w), 610 (w), cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.99 (t, 6, CH_3), 2.47 (m, 12, CH_2), 2.62 (m, 2, CHS). Anal. Found: C, 69.95; H, 11.66; S, 18.37. Reaction of the episulfide with excess triphenylphosphine in toluene at 90 °C afforded only *trans*-5-decene; none of the cis isomer was detected.

Registry No. Cyclohexene oxide, 286-20-4; cyclohexene sulfide, 286-28-2; 1-decene oxide, 2404-44-6; 1-decene sulfide, 13748-26-0; 1-dodecene oxide, 2855-19-8; 1-dodecene sulfide, 1078-74-6; 1-tetradecene oxide, 3234-28-4; 1-tetradecene sulfide, 26072-89-9; 1,2,7,8-octadiene bisepoxide, 2426-07-5; 1,2,7,8-octadiene bisepisulfide, 7763-82-8; *cis*-5-decene oxide, 36229-64-8; *cis*-5-decene sulfide, 57205-64-8; *trans*-5-decene oxide, 2165-61-9; *trans*-5-decene sulfide, 74930-08-8; 2,3-epoxypropyl *p*-methoxyphenyl ether, 2211-94-1; [(*p*-methoxyphenoxy)methyl]thiirane, 3210-68-2; *p*-chlorophenyl 2,3-epoxypropyl ether, 2212-05-7; [(*p*-chlorophenoxy)methyl]thiirane, 3210-75-1; *p*-*tert*-butylphenyl 2,3-epoxypropyl ether, 3101-60-8; [(*p*-*tert*-butylphenoxy)methyl]thiirane, 3210-65-9; 2-methyl-1-hexene oxide, 1713-33-3; 2-methyl-1-hexene sulfide, 7272-23-3; cyclododecene oxide, 286-99-7; cyclododecene sulfide, 74947-53-8; cyclooctene oxide, 286-62-4; cyclooctene sulfide, 286-63-5; *trans*-5-decene, 7433-56-9; *cis*-5-decene, 7433-78-5.

(6) Lautenschlager, F.; Schwartz, N. V. *J. Org. Chem.* **1969**, *34*, 3991. Suhara, Y. *Yukagaku* **1973**, *22*, 9.

(7) Pankova, M.; Sicher, J. *Collect. Czech. Chem. Commun.* **1965**, *30*, 388.

(8) Denney, D. B.; Boskin, M. J. *J. Am. Chem. Soc.* **1960**, *82*, 4736.