scribed for the dibromo analogue; mp 229–232 °C dec (decomposition varies greatly with the rate of heating).

Anal. Calcd for $C_{21}H_{14}Cl_3NO_2$: C, 60.24; H, 3.34; N, 3.35. Found: C, 60.21; H, 3.41; N, 3.61.

Deblocking of 2,7-Dihalo-Substituted (9-Fluorenyl)methyl Carbanilates. A stock solution containing 42.6 mg (0.5 mequiv) of piperidine in 10 mL of toluene was prepared. To each of three 1-mL aliquots of this solution was added 0.005 mequiv of the corresponding Fmoc derivative. The reaction was followed by TLC on silica gel (Eastman Chromagram plates) with development by toluene in the case of the dihalo derivatives and ethyl acetate–toluene (10% v/v) in the case of the unsubstituted compound. Urethane consumption was complete in about 45 min in the case of the dibromo derivative and in about 85 min for the dichloro analogue. The dihalo derivatives were insoluble in toluene at the concentrations used, and part of the difference between the dibromo and dichloro compounds may have been due to this factor. In the case of the parent Fmoc derivative the first evidence for the formation of *p*-chloroaniline was observed only after about 12 h, and the urethane did not completely disappear until after 5.5 days. Similar tests in pyridine as both solvent and deblocking agent gave evidence for the appearance of *p*-chloroaniline immediately after mixing in the case of the dihalo derivatives and for complete consumption of urethane after about 24 h. In the case of the parent Fmoc system the first evidence of dibenzofulvene formation appeared only after about 10 h, and urethane was still present after 8 days, when the test was termninated.

Acknowledgment. This work was supported by a grant from the National Institutes of Health (GM-09706).

Registry No. 1, 24324-17-2; **2**, 20615-64-9; **3** (X = Br), 74316-23-7; **3** (X = Cl), 74808-81-4; **4**, 74808-82-5; fluorene, 86-73-7; ethyl formate, 109-94-4; 2,7-dibromofluorene, 16433-88-8; 2,7-dichlorofluorene, 7012-16-0; (2,7-dichloro-9-fluorenyl)methyl acetate, 74808-83-6; 9-fluorenylmethyl chloroformate, 28920-43-6; 2,7-dibromo-9-fluorenylmethyl *N*-(*p*-chlorophenyl)carbamate, 74808-84-7; *p*-chlorophenyl isocyanate, 104-12-1; *p*-chloroaniline, 106-47-8; 2,7-dichloro-9-fluorenylmethyl *N*-(*p*-chlorophenyl)carbamate, 74808-85-8.

An Improved Synthesis of Carbocyclic and Heterocyclic Arene Imines

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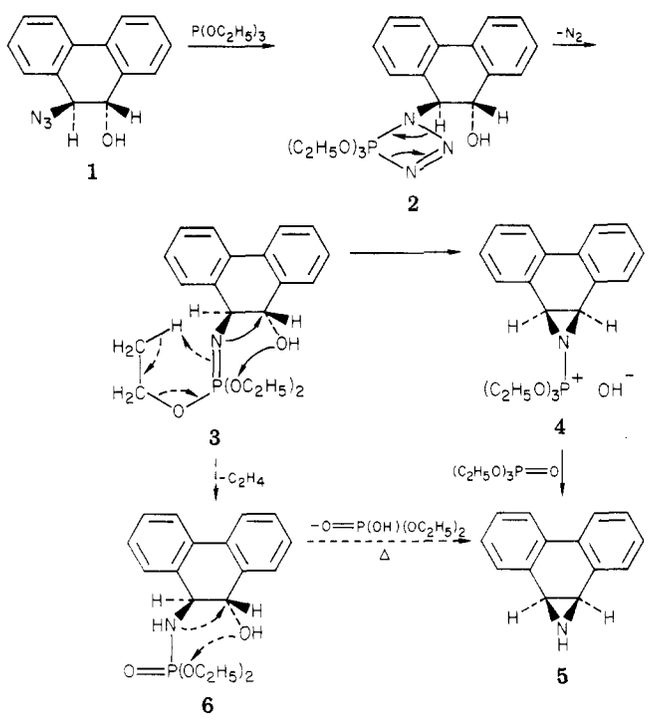
Recently we reported the synthesis of phenanthren-9,10-imine (**5**) from *trans*-10-azidodihydrophenanthren-9-ol (**1**) and a tertiary phosphine.[1] The method proved useful for the preparation of K-region imine derivatives of benz[*a*]anthracene, benzo[*a*]pyrene, and dibenz[*a*]-anthracene.[2] This synthesis has, however, two disadvantages: (i) the resulting imines decompose on prolonged treatment with excess phosphine; (ii) the separation of the polycyclic aziridines from phosphine oxides and other phosphorus-containing products is often tedious and associated with heavy losses.

We now describe an improved synthesis of polycyclic arene imines in which the tertiary phosphine is substituted by triethyl phosphite. This method does not suffer from the disadvantages and permits facile preparation of **5**, benz[*a*]anthracen-5,6-imine (**10**), and 1a,7b-dihydroazirino[5,6]benzo[1,2-*c*:3,4-*c*']dithiophene (**9**). The latter compound is the first imine of an aromatic heteropolycyclic structure.

Scheme I



When, e.g., azido alcohol **1** is treated with 1.5–2.5 equiv of $P(OC_2H_5)_3$, the exothermic reaction that takes place yields molecular nitrogen (confirmed by GLC) and 82% imine **5**. The reaction is less vigorous when the synthesis is conducted in boiling methylene chloride and the yield is essentially quantitative after 20 min. In benzene, at or below 30 °C, the interaction of **1** and triethyl phosphite leads to the formation of a phosphorus-containing compound, which is formulated as structure **6** by virtue of the elemental analysis and the spectral data. Two distinguishing bands at 3290 and 3390 cm^{-1} reveal the existence of the NH and OH groups. The 270-MHz ^1H NMR spectrum (in $CDCl_3$) shows two CH_3 triplets at 1.266 and 1.316 ppm ($J_{CH_2CH_3}$ = 6.2 Hz) and two superimposed ^{31}P-split quartets centered at 4.086 ppm. The NH resonance at 3.179 (dd, J_{NHH_9} = 10.5 Hz, J_{NHP} = 14 Hz) and the broad OH peak at 3.3 ppm[3] disappear upon addition of D_2O. The benzylic protons (α to NH and α to OH, respectively) show up at 4.353 (AB q, $J_{H_9H_{10}}$ Hz, J_{NHH_9} = 10.5 Hz) and 4.671 ppm (d, $J_{H_9H_{10}}$ = 10.0 Hz). The most indicative fragment ions in the high-resolution mass spectrum given in the experimental section are the molecular ion and its dehydration product (*m/e* 347, 329), the phosphorus containing fragments of *m/e* 302, 301, 300, 274, 255, 256, and the fluorenyl base peak which is characteristic of most 9,10-dihydrophenanthrene derivatives.[4] Fragments such as $C_{14}H_9NOP$ (*m/e* 238) and $C_4H_{11}NO_3P$ (*m/e* 152) confirm the existence of a P–N bond in **6**.

In analogy to phenanthrene-9,10-imine formation from **1** and tertiary phosphines[1] the present synthesis is assumed to follow the steps outlined in Scheme I (full arrows). The

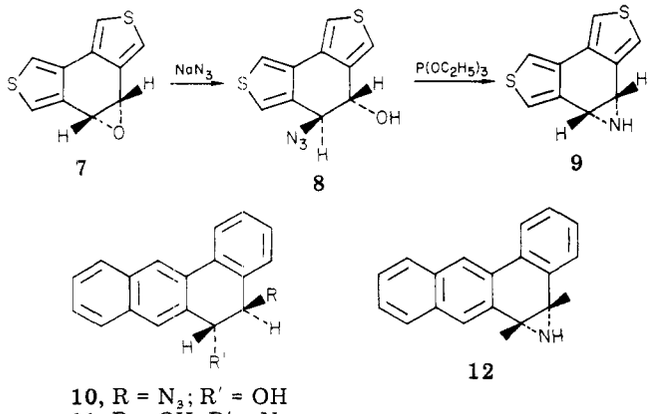
(1) Ittah, Y.; Sasson, Y.; Shahak, I.; Tsaroom, S.; Blum, J. *J. Org. Chem.* **1978**, *43*, 4271.
(2) Blum, J.; Yona, I.; Tsaroom, S.; Sasson, Y. *J. Org. Chem.* **1979**, *44*, 4178.
(3) Owing to hydrogen bonding the location of the OH peak varies considerably when the concentration of **6** in $CDCl_3$ is changed. In our experience it appeared between 3 and 8 ppm.
(4) Eland, J. H. D.; Danby, C. T. *J. Chem. Soc.* **1965**, 5935.

0022-3263/80/1945-4252$01.00/0

sequence of transformations 1 → 2 → 3 is supported by the studies of Kabachnik and Giljanov[5] who investigated the interaction of azides with several alkyl phosphites.

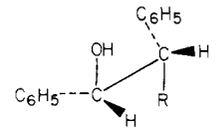
Since the amidophosphate 6 has been shown to decompose in 60–80% yield into 5 upon thermolysis at 180 °C, we considered this compound as a possible intermediate in the reaction 1 → 5. Kinetic measurements indicated, however, that this is not the case. In boiling methylene chloride or benzene solution 6 is not affected at all and is hardly consumed in boiling xylene even in the presence of hydrogen chloride, sodium hydride, or triethyl phosphite. Furthermore, during the normal course of the imine synthesis, N_2 is the only gas evolved in the reaction, while at low temperature at which transformation 1 → 6 prevails ethylene is obtained as well. GLC and volumetric gas analysis indicated that the moles of C_2H_4 are equal to the molar amount of 6 formed. The intermediacy of 6 can be excluded also on account of the observation that the mother liquor of 5 (see Experimental Section) is neutral and contains $P(O)(OC_2H_5)_3$ rather than $P(O)(OH)(OC_2H_5)_2$.[6]

The utility of the above synthesis for other aromatic aziridines is illustrated by preparation of the K-region imine of a dithiophene analogue of phenanthrene 9 and of the previously reported benz[*a*]anthracen-5,6-imine (12).[2] The reaction of oxide 7[7] with sodium azide gave *trans*-7,8-dihydrobenzo[1,2-*c*:3,4-*c'*]dithiophen-7-ol 8 in 88% yield. Treatment of a benzene solution of 8 with excess triethyl phosphite gave, after 15 min at 78 °C, 46% imine 9. Application of our previous method[1] for the

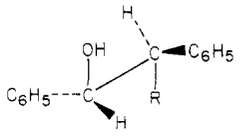


preparation of 9, i.e., treatment of 8 with tri-*n*-butylphosphine, led to much less satisfactory results. Imine 12 was obtained in 48% yield in an exothermic reaction when a 1:1 mixture of 10 and 11[2] was covered with excess phosphite followed by treatment with cold hexane.

In contrast to our previous imine synthesis,[1] the present method seems not to be applicable to aliphatic aziridines. When, e.g., *threo*-2-azido-1,2-diphenylethanol (13) (prepared from *cis*-stilbene oxide)[1] is treated with $P(OC_2H_5)_3$ only the amidophosphate 14 is formed. A temperature of 180 °C is needed to initiate (slow) decomposition of 14 into *cis*-2,3-diphenylaziridine. The *erythro*-azido alcohol 15 reacts likewise with $P(OC_2H_5)_3$, but the resulting amidophosphate 16 is resistant to pyrolysis even at 220 °C. The formation of both 14 and 16 is accompanied by evolution of 1 mol of N_2 and 1 mol of C_2H_4 per each mole of amidophosphate.



13, R = N_3
14, R = $NHP(O)(OC_2H_5)_2$



15, R = N_3
16, R = $NHP(O)(OC_2H_5)_2$

Experimental Section

Phenanthren-9,10-imine (1a,9b-Dihydro-1*H*-phenanthro[9,10-*b*]azirine, 5). A. To 6.0 g of powdered *trans*-10-azido-9,10-dihydrophenanthren-9-ol (1)[8] was added under argon with vigorous stirring and external cooling (ice water) 10 mL of triethyl phosphite. When the initial exothermic reaction ceased, stirring was continued for 15 min at room temperature. Upon addition of cold ether (0 °C) 5 precipitated as long colorless needles. Filtration and washing with petroleum ether afforded 4.0 g (82%) of pure imine, mp 150–151 °C (from cyclohexane). The compound obtained by this manner proved to be an allotropic form of the previously reported imine of mp 163–164 °C.[1,9] Recrystallization of a mixture of the two forms gave the imine of the higher melting point.

When the triethyl phosphite was substituted by triisopropyl phosphite the reaction was even more vigorous and difficult to control. On the other hand when trimethyl phosphite was employed the reaction proceeded slowly and most of the starting compound was recovered.

B. A solution of 4.00 g of 1 in 80 mL of CH_2Cl_2 was treated with 6 mL of $P(OC_2H_5)_3$ and refluxed under argon for 20 min. The methylene chloride solution was concentrated in vacuo and the residue digested with excess hexane for 3 days at 0 °C to yield 3.02 g (93%) of the imine.

C. A solution of 1.00 g of 1 and 2 mL of $P(OC_2H_5)_3$ in 50 mL of dry benzene was refluxed for 20 min. Addition of excess hexane afforded 0.611 g (75%) of analytically pure 5. When the mother liquor was evaporated to dryness and then heated with 150 mL of dry ether some further less pure imine was obtained. After 4 days at 25 °C 0.117 g (8%) of phosphorus-containing 6, described below, separated.

Diethyl (9,10-Dihydro-10-hydroxyphenanthren-9-yl)-amidophosphate (6). To a solution of 1.00 g of 1 in 25 mL of dry benzene was added 1 mL of $P(OC_2H_5)_3$, with external cooling. The mixture was heated to 30 °C during 1.5 h. The solution was concentrated under reduced pressure (bath temperature <40 °C) to a volume of 7 mL. After addition of 7 mL of dry ether the mixture was allowed to settle for 10 min. Traces of 5 were filtered off, and the filtrate was diluted with 75 mL of ether. During 2 days at 25 °C 0.922 g (63%) of colorless crystals separated: mp 134 °C (from cyclohexane); mass spectrum (70 eV, 80 °C), *m/e* (relative intensity) 347 (M^+·, <0.1[10]), 329 (M^+· − H_2O, 8), 302 ($C_{16}H_{17}NO_3P^+$, 2), 301 ($C_{16}H_{16}NO_3P^+$·, 10), 300 ($C_{16}H_{15}NO_3P^+$, 2), 274 ($C_{14}H_{13}NO_3P^+$, 6), 273 ($C_{14}H_{12}NO_3P^+$·, 7), 272 ($C_{14}H_{11}NO_3P^+$, 2), 256 ($C_{14}H_{11}NO_2P^+$, 8), 255 ($C_{14}H_{10}NO_2P^+$·, 10), 238 ($C_{14}H_9NOP^+$, 1), 237 ($C_{14}H_8NOP^+$·, 5), 210 ($C_{14}H_{12}NO^+$, 4), 208 ($C_{14}H_{10}NO^+$, 3), 194 ($C_{14}H_{10}N^+$, 100), 192 ($C_{14}H_8N^+$, 9), 180 ($C_{14}H_{12}^+$·, 21), 178 ($C_{14}H_{10}^+$·, 14), 176 ($C_{10}H_8^+$·, 4), 167 ($C_{13}H_{11}^+$, 14), 165 ($C_{13}H_9^+$, 99), 154 ($C_{12}H_{10}^+$·, 98), 152 ($C_4H_{11}NO_3P^+$, 16), 138 ($C_4H_{11}O_3P^+$·, 5). Anal. Calcd for $C_{18}H_{22}NO_4P$: C, 62.2; H, 6.3; N, 4.0; P, 8.9. Found: C, 62.2; H, 6.3; N, 4.2; P, 9.0.

***trans*-8-Azido-7,8-dihydrobenzo[1,2-*c*:3,4-*c'*]dithiophen-7-ol (8).** To a solution of 2 g of sodium azide and 50 μL of H_2SO_4 in 50 mL of acetone and 25 mL of water was added 103 mg of 1a,7b-dihydrooxireno[5,6]benzo[1,2-*c*:3,4-*c'*]dithiophene (7).[7] The mixture was stirred under N_2 at room temperature for 48 h. Evaporation of the acetone afforded 110 mg (88%) of 8 as cream-colored crystals: mp 128–130 °C (from benzene); IR (Nujol)

(5) Kabachnik, M. I.; Giljarov, V. A. *Otd. Khim. Nauk* **1956**, 760.
(6) Since the two phosphates have almost identical ^{31}P chemical shifts (see: Mark, V.; Dungan, C. H.; Crutchfield, M. M.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, 5, 227–457) the compounds were analyzed by thin-layer chromatography (SiO_2–CH_3OH).
(7) MacDowell, D. W. H.; Maxwell, M. H. *J. Org. Chem.* **1970**, *35*, 799.
(8) Shudo, K.; Okamoto, T. *Chem. Pharm. Bull.* **1976**, *24*, 1013.
(9) Denis, J. N.; Krief, A. *Tetrahedron* **1979**, *35*, 2901.
(10) At 140 °C the relative intensity of M^+· rises to 0.25%. The exact masses of ambiguous fragment ions were established by high-resolution mass spectral measurements ($R = M/\Delta M > 10000$).

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.

Acknowledgment. We are grateful to the Israel Commission for Basic Research, the Israel Academy of Sciences and Humanities, for financial support of this study.

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.

0022-3263/80/1945-4254$01.00/0