Toshiro Inubushi and Herman Yeh of this Institute for determination of ^{31}P NMR spectra.

Registry No. **1a**, 65954-94-1; **1b** triethylammonium salt, 78549-90-3; **2a**, 69504-15-0; **2b**, 72409-42-8; **2c**, 72409-47-3; **2d**, 362-75-4; **2e**, 362-76-5; **2f**, 78549-91-4; **2g**, 78549-92-5; **4a**, 78571-57-0; **4b**, 78571-58-1; **4c**, 78571-59-2; **4d**, 78549-93-6; **4e**, 78549-94-7; **4f**, 78549-95-8; **4g**, 78571-60-5; **5a**, 78571-61-6; **5b**, 78571-62-7; **6a**, 61-19-8; **6a** triethylammonium salt, 65411-70-3; **6b**, 85-32-5; **6c**, 63-37-6; **6f**, 78549-96-9; **6g**, 78549-97-0; bis(2,2,2-trichloroethyl) phosphorochloridite, 41662-41-3; 2,2,2-trichloroethyl phosphorochloridite, 78549-98-1; tetrabutylammonium fluoride, 429-41-4.

Synthesis of and Absolute Configurational Assignment to Enantiomerically Pure Unsaturated [4.4.2]Propellanes

W. Dirk Klobucar,[1] Leo A. Paquette,* and John F. Blount[2]

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210, and Research Division, Hoffmann-LaRoche Inc., Nutley, New Jersey 07110

Received April 28, 1981

The chiral unsaturated propellanes **6a**, **6b**, and **19** have been prepared by sequences which hinge upon Ramberg–Bäcklund rearrangement as a pivotal step. These hydrocarbons have been obtained in enantiomerically pure form and with established absolute configuration. The procedure involves Diels–Alder addition of (−)-*endo*-bornyltriazolinedione, followed by efficient separation of the two diastereomeric urazoles involving crystallization or high-pressure liquid chromatography techniques. Diastereomeric purity could be ascertained by ^1H NMR spectroscopy at 300 MHz, and absolute configuration was determined by X-ray crystal structure analysis. Subsequent hydrolysis or hydride reduction and oxidation of the diastereomerically pure urazoles efficiently delivered the optically pure propellanes. The relationship of the various substitution patterns to the magnitude of the observed specific rotations is briefly discussed.

Interest in propellane compounds has become rather widespread in recent years for several reasons.[3] Small-ring propellanes, for example, have tested various extreme limits of carbon hybridization and provided additional insight into the stability of highly strained systems.[4] Unsaturated propellanes have proven to be a rich source of fascination because of their often observed involvement in multifarious electrocyclic reactions, including fluxional isomerism, which stem in large part from the structurally enforced proximity of the reacting centers.[5] The existence of many naturally occurring propellanes[3] has likewise engendered interest in the control of stereochemistry within such carbocyclic frameworks.[6] While literally hundreds of propellane derivatives are now known, very few have been prepared by design in optically active form,[7] and no attention has, to our knowledge, been paid to the establishment of absolute configuration.

Our past interest in the chemistry of unsaturated [4.4.2]propellanes[8] and in the utilization of optically active triazolinediones for asymmetric transfer[9–11] has led presently to the preparation of several enantiomerically pure

(1) The Ohio State University Fellow, 1975–1976.

(2) Author to whom inquiries concerning the X-ray data should be addressed.

(3) Ginsburg, D. "Propellanes"; Verlag Chemie, Weinheim/Bergstr., West Germany, 1975.

(4) (a) Reference 3, pp 30–52. (b) Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *J. Am. Chem. Soc.* **1977**, *99*, 2297. (c) Wiberg, K. B.; Jason, M. E. *Ibid.* **1976**, *98*, 3393.

(5) Reference 3, pp 81–108.

(6) Schostarez, H.; Paquette, L. A. *J. Am. Chem. Soc.* **1981**, *103*, 722; *Tetrahedron*, in press.

(7) However, chemical transformations of propellanoid natural products have provided a number of compounds of this type: reference 3, pp 225–244.

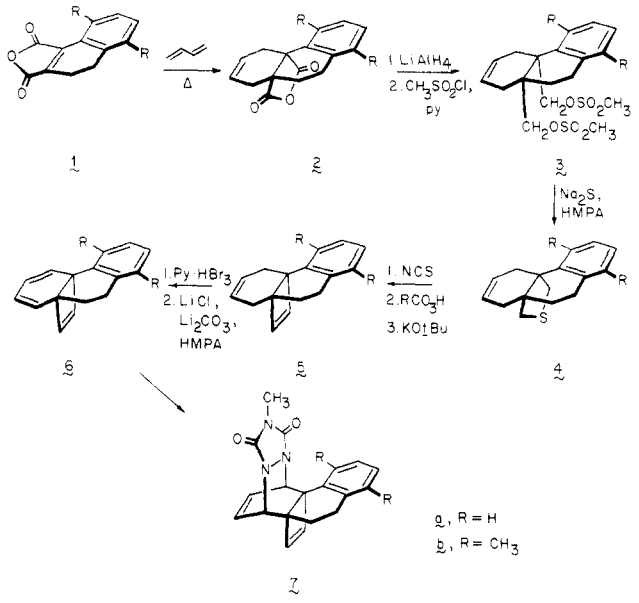
(8) (a) Paquette, L. A.; Philips, J. C. *J. Am. Chem. Soc.* **1968**, *90*, 3898. (b) Paquette, L. A.; Philips, J. C. *J. Chem. Soc., Chem. Commun.* **1969**, 680. (c) Paquette, L. A.; Philips, J. C. *J. Am. Chem. Soc.* **1969**, *91*, 3973. (d) Paquette, L. A.; Kakihana, T.; Hansen, J. F.; Philips, J. C. *Ibid.* **1971**, *93*, 152. (e) Paquette, L. A.; Wingard, R. E., Jr.; Philips, J. C.; Thompson, G. L.; Read, L. K.; Clardy, J. *Ibid.* **1971**, *93*, 4508. (f) Paquette, L. A.; Philips, J. C.; Wingard, R. E., Jr. *Ibid.* **1971**, *93*, 4516. (g) Paquette, L. A.; Houser, R. W. *Ibid.* **1971**, *93*, 4522. (h) Paquette, L. A.; Thompson, G. L. *Ibid.* **1971**, *93*, 4920. (i) Paquette, L. A.; Wingard, R. E., Jr. *Ibid.* **1972**, *94*, 4398. (j) Paquette, L. A.; Thompson, G. L. *Ibid.* **1972**, *94*, 7118. (k) Paquette, L. A.; Thompson, G. L. *Ibid.* **1972**, *94*, 7127. (l) Gleiter, R.; Heilbronner, E.; Paquette, L. A.; Thompson, G. L.; Wingard, R. E., Jr. *Tetrahedron* **1973**, *29*, 565. (m) Paquette, L. A.; Thompson, G. L. *J. Am. Chem. Soc.* **1973**, *95*, 2364. (n) Paquette, L. A.; Photis, J. M.; Fayos, J.; Clardy, J. *Ibid.* **1974**, *96*, 1217. (o) Thompson, G. L.; Heyd, W. E.; Paquette, L. A. *Ibid.* **1974**, *96*, 3177. (p) Paquette, L. A.; Wingard, R. E., Jr.; Photis, J. M. *Ibid.* **1974**, *96*, 5801. (q) Paquette, L. A.; Photis, J. M. *Tetrahedron Lett.* **1975**, 1145. (r) Paquette, L. A.; Photis, J. M.; Gifkens, K. B.; Clardy, J. *J. Am. Chem. Soc.* **1975**, *97*, 3536. (s) Kalo, J.; Photis, J. M.; Paquette, L. A.; Vogel, E.; Ginsburg, D. *Tetrahedron* **1976**, *32*, 1013. (t) Paquette, L. A.; Liao, C. C.; Burson, R. L.; Wingard, R. E., Jr.; Shih, C. N.; Fayos, J.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 6935. (u) Paquette, L. A.; Wallis, T. G.; Kempe, T.; Christoph, G. G.; Springer, J. P.; Clardy, J. *Ibid.* **1977**, *99*, 6946. (v) Birladeanu, L.; Chamot, E.; Fristad, W. E.; Paquette, L. A.; Winstein, S. *J. Org. Chem.* **1977**, *42*, 3260. (w) Paquette, L. A.; Photis, J. M.; Micheli, R. *J. Am. Chem. Soc.* **1977**, *99*, 7899. (x) Paquette, L. A.; Micheli, R. P.; Photis, J. M. *Ibid.* **1977**, *99*, 7911. (y) Paquette, L. A.; Kretschmer, G. *Ibid.* **1979**, *101*, 4655. (z) Paquette, L. A.; Chamot, E.; Browne, A. R. *Ibid.* **1980**, *102*, 637. (aa) Paquette, L. A.; Browne, A. R.; Chamot, E.; Blount, J. F. *ibid.* **1980**, *102*, 643; (bb) Paquette, L. A.; Carr, R. V. C. *Ibid.* **1980**, *102*, 7553. (cc) Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1980**, *45*, 4922.

(9) (a) Gardlik, J. M.; Paquette, L. A. *Tetrahedron Lett.* **1979**, 3597; (b) Paquette, L. A.; Doehner, R. F., Jr. *J. Org. Chem.* **1980**, *45*, 5105.

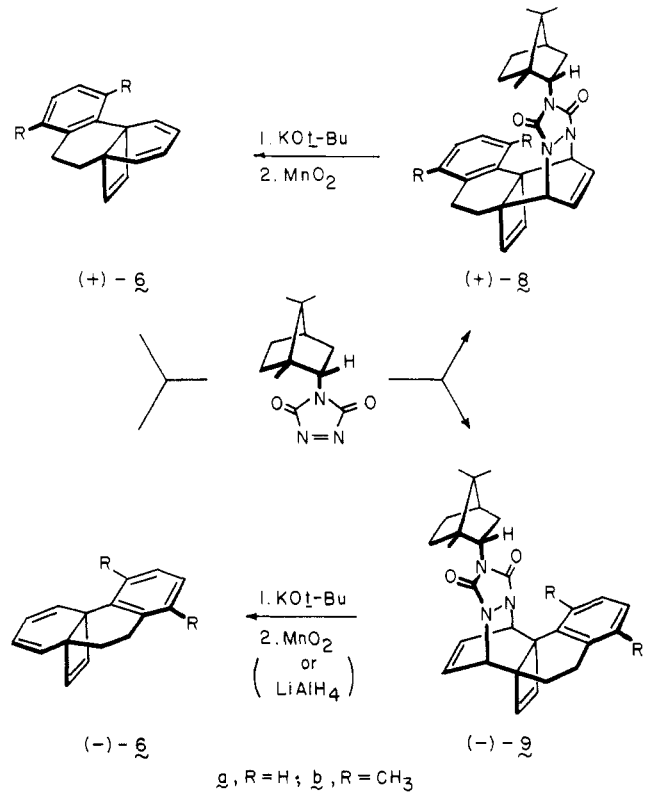
(10) (a) Paquette, L. A.; Doehner, R. F., Jr.; Jenkins, J. A.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 1188. (b) Jenkins, J. A.; Doehner, R. F., Jr.; Paquette, L. A. *Ibid.* **1980**, *102*, 2131.

0022-3263/81/1946-4021$01.25/0 © 1981 American Chemical Society

Scheme I



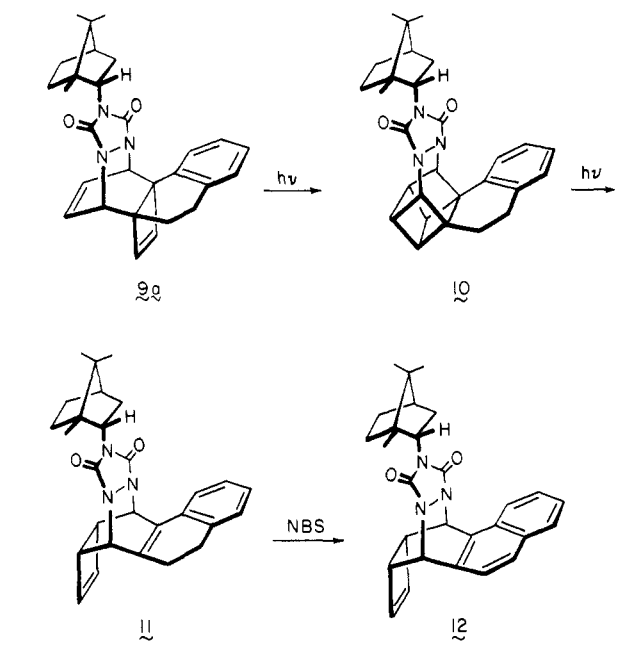
Scheme II



polycyclic hydrocarbons of established configuration. The methodology outlined herein provides a straightforward means of introducing optical activity into chiral propellanes which possess a conjugated diene unit. Central to our approach is the feasibility of separating diastereomeric urazole adducts on a preparative scale either by direct recrystallization or by high-pressure liquid chromatography. As noted earlier by others,[12-14] the benefits of chromatographic resolution include superior yields and the eventual obtention of both antipodes in enantiomerically enriched, if not pure, form.

Our synthetic approach to propellanes **6a** and **6b** was based on the efficient ring-contraction scheme developed earlier[8e,f,u,15] for the transformation of fused succinic anhydrides to annulated cyclobutene derivatives. Accordingly, attention was turned to **2a**[16] and **2b** which were readily prepared via Diels–Alder cycloaddition of the corresponding dihydro-1,2-naphthalic anhydrides (**1a**[17] and **1b**) with butadiene. By means of the three-step sequence outlined in Scheme I, the anhydrides **2** were transformed into sulfides **4** without difficulty. Submission of **4a** and **4b** in turn to α-chlorination, chemospecific oxidation at sulfur, and Ramberg–Bäcklund rearrangement[18] of the resulting epimeric α-chloro sulfones delivered hydrocarbons **5a** and **5b** efficiently. The cyclohexene ring of these intermediates could be regiospecifically brominated with pyridinium hydrobromide perbromide and subsequently didehydrobrominated with lithium chloride and lithium carbonate in anhydrous hexamethylphosphoramide.[19] The racemic bicyclooctatrienes **6a** and **6b** were stable for prolonged periods of time when stored in the cold with the exclusion of light. Expectedly, both propellanes entered rapidly into [4 + 2] cycloaddition with *N*-methyltriazolinedione at low temperature (−78 °C) to give the colorless crystalline adducts **7**.

Scheme III



(11) (a) Paquette, L. A.; Gardlik, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 5016. (b) Paquette, L. A.; Gardlik, J. M.; Johnson, L. K.; McCullough, K. J. *Ibid.* **1980**, *102*, 5026. (c) Paquette, L. A.; Hanzawa, Y.; McCullough, K. J.; Tagle, B.; Swenson, W.; Clardy, J. *Ibid.* **1981**, *103*, 2262. (d) Paquette, L. A.; Hanzawa, Y.; Hefferon, G. J., submitted for publication.

(12) (a) Pirkle, W. H.; Hoekstra, M. S. *J. Org. Chem.* **1974**, *39*, 3904. (b) Pirkle, W. H.; Sikkenga, D. L. *Ibid.* **1977**, *42*, 1370. (c) Pirkle, W. H.; Border, C. W. *Ibid.* **1978**, *43*, 1950, 2091. (d) Pirkle, W. H.; Rinaldi, P. L. *Ibid.* **1978**, *43*, 3803; **1979**, *44*, 1025. (e) Pirkle, W. H.; Adams, P. E. *Ibid.* **1980**, *45*, 4111, 4117.

(13) (a) Helmchen, G.; Nill, G.; Flockerzi, D.; Schuhle, W.; Youssef, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 62. (b) Helmchen, G.; Nill, G.; Flockerzi, D.; Youssef, M. *Ibid.* **1979**, *18*, 63. (c) Helmchen, G.; Nill, G. *Ibid.* **1979**, *18*, 65.

(14) (a) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S.; Siret, P.; Keck, G. E.; Gras, J. *J. Am. Chem. Soc.* **1978**, *100*, 8031. (b) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S.; Keck, G. E.; Gopalan, B.; Larsen, S. D.; Siret, P.; Gras, J. *Ibid.* **1978**, *100*, 8034. (c) Schmid, G.; Fukuyama, T.; Akasaka, K.; Kishi, Y. *Ibid.* **1979**, *101*, 259.

(15) Paquette, L. A.; Wallis, T. G.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 2815.

(16) Fieser, L. F.; Hershberg, E. B. *J. Am. Chem. Soc.* **1935**, *57*, 2192.

(17) Hershberg, E. B.; Fieser, L. F. "Organic Syntheses"; Wiley: New York, *Collect. Vol. II*, p 194.

(18) Paquette, L. A. *Org. React.* **1977**, *25*, 1.

(19) King, P. F.; Paquette, L. A. *Synthesis* **1977**, 279.

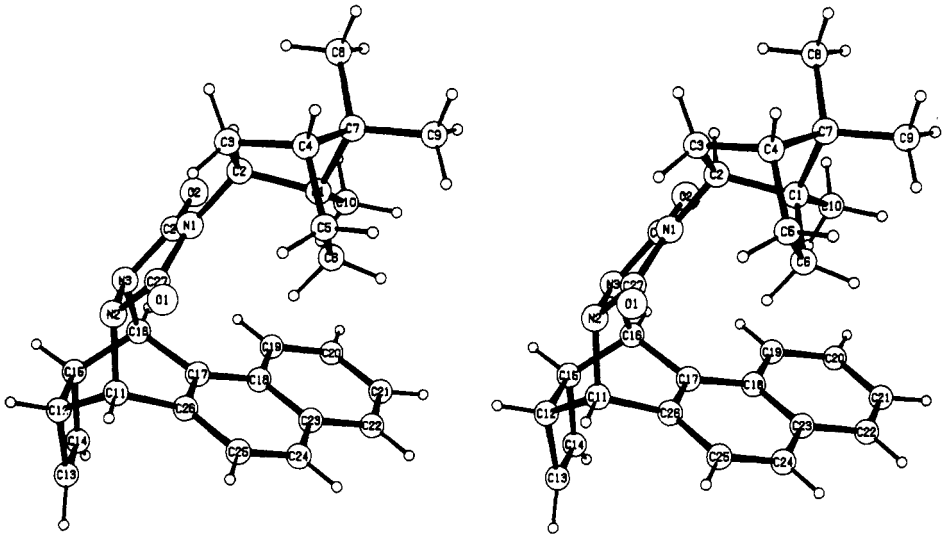


Figure 1. Structural view of (−)-**12** as determined by X-ray analysis.

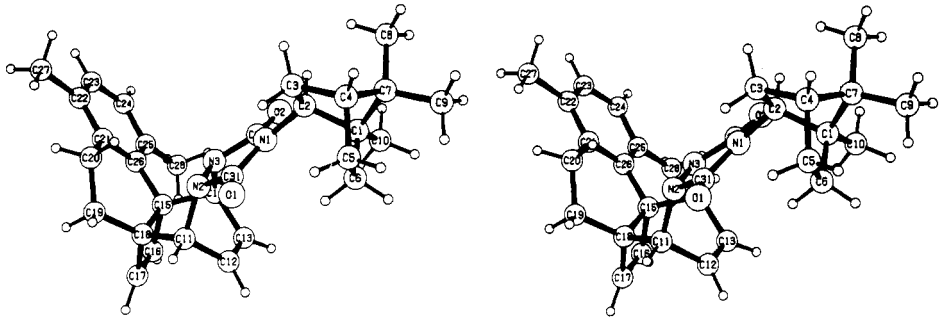


Figure 2. Structural view of (+)-**8b** as determined by X-ray analysis.

When (±)-**6a** dissolved in an equally cold 4:1 mixture of pentane and ethyl acetate was treated with an ethyl acetate solution of enantiomerically pure (−)-*endo*-bornyltriazolinedione,[9] a precipitate characterized by an $[\alpha]_{578}$ of −243° was formed. Evaporation of solvent from the filtrate yielded additional crystals: $[\alpha]_{578}$ +169°; total yield of 77%. Two additional recrystallizations of the levorotatory diastereomer provided a sample which exhibited $[\alpha]_D$ −231° and whose rotation was unaltered upon further processing (Scheme II).

Diastereomeric purity in this series could be conveniently ascertained by ^{1}H NMR spectroscopy at 300 MHz. The upfield region of a 1:1 mixture of (+)-**8a** and (−)-**9a** showed four methyl singlets at δ 0.92, 0.84, 0.74, and 0.73 in an intensity ratio of 3:3:1.5:1.5. Therefore, the 1-methyl groups of the *endo*-bornyl moiety in the two diastereomers are in sufficiently different chemical environments to be distinctive under high-resolution conditions. Since the spectrum of (−)-**9a** comprised only three methyl absorptions (δ 0.92, 0.84, and 0.74), this tool proved convenient for monitoring the degree of diastereomeric enrichment.

The absolute configuration of the levorotatory diastereomer was established as **9a** by X-ray crystal structure analysis of its subsequent transformation product **12** (Scheme III).[20] Triplet-sensitized [2 + 2] photocyclization–rearrangement[15] led via the diazabishomocubane **10** to the cyclobutene-migrated urazole **11**, $[\alpha]_D$ +112°. Dehydrogenation of this compound with *N*-bromosuccinimide in dichloromethane solution afforded **12**, $[\alpha]_D$ −230°. A structural view of (−)-**12** with its absolute configuration is provided in Figure 1. Recall that the established configuration of the *endo*-bornylamine segment requires only that the remaining configurational features be assigned in a relative sense (Tables I and II, supplementary material). The relevant bond lengths and angles of the molecule can be found in Tables III and IV (supplementary material).

Hydrolysis of diastereomerically pure **9a** with potassium *tert*-butoxide in dimethyl sulfoxide at room temperature followed by manganese dioxide oxidation gave (−)-**6a** ($[\alpha]_D$ −147°) in 51% isolated yield after silica gel chromatography. Consequently, the levorotatory antipode of this propellane has the indicated absolute stereostructure.

In light of the successes just achieved, racemic **6b** was similarly treated with (−)-*endo*-bornyltriazolinedione at −78 °C. The specific rotation of the resulting 1:1 mixture of diastereomers was $[\alpha]_D$ −5.0°. Whereas the ^{13}C NMR spectrum was of no use in distinguishing the presence of **8b** and **9b**, 300-MHz ^{1}H NMR spectroscopy once again proved highly utilitarian in this regard. Thus, the original cycloaddition mixture exhibited five methyl singlets at δ 0.93, 0.92, 0.85, 0.74, and 0.72 in a ratio of 1.5:1.5:3:1.5:1.5. Various attempts to separate **8b** from **9b** by recrystallization failed. On the other hand, preparative high-pressure liquid chromatography (Waters Prep 500) on silica gel proved successful when band-shaving techniques were implemented. The two resolved diastereomers could thereby be obtained in gram quantities. The dextrorotatory diastereomer ($[\alpha]_D$ +14.0°) from the leading edge showed three methyl signals at δ 0.92, 0.85, and 0.74. Recrystallization of this material from ethyl acetate afforded crystals which were suitable for X-ray structure analysis (Tables V and VI, supplementary material). A stereoscopic view

(20) Klobucar, W. D.; Burson, R. L.; Paquette, L. A. *J. Org. Chem.* 1981, *46*, 2680.

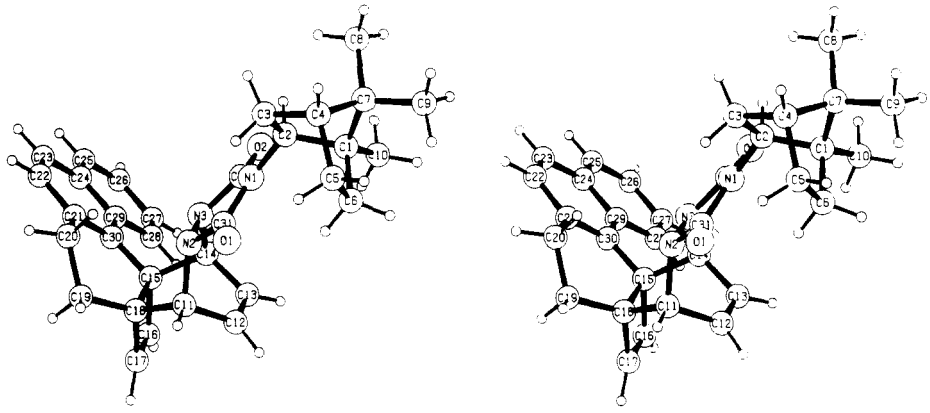
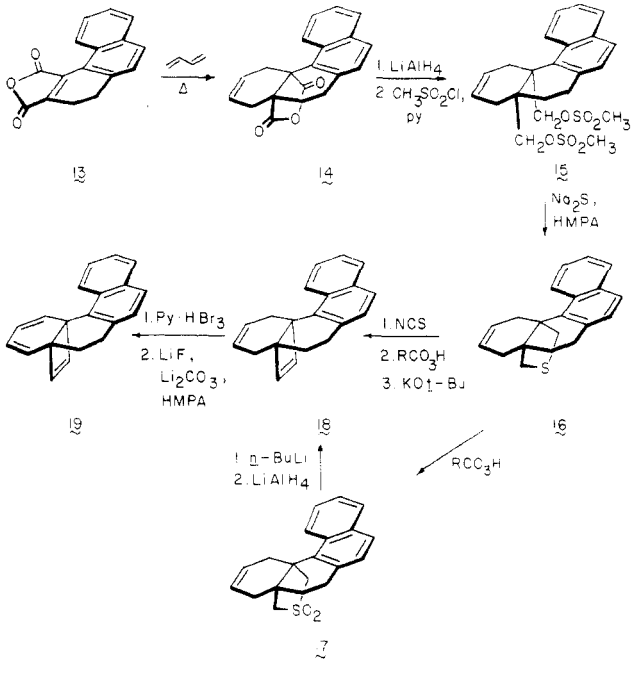
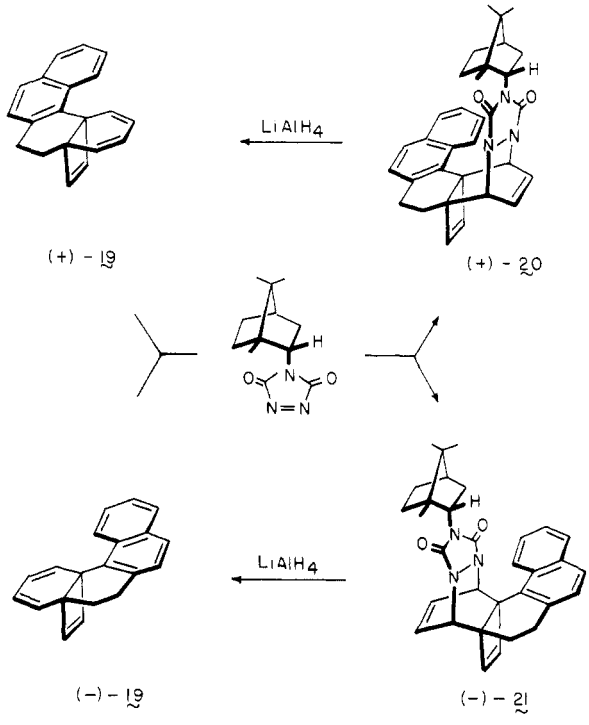


Figure 3. Structural view of (+)-**20** as determined by X-ray analysis.

Scheme IV



Scheme V



of (±)-**8b** is shown in Figure 2. Its characteristic bond lengths and angles are summarized in Tables VII and VIII (supplementary material).

The 300-MHz ^{1}H NMR spectrum of levorotatory diastereomer (−)-**9b** ($[\alpha]_D$ −19.7°) obtained from the tailing edge of the band-shaving process was identical with that of **8b** except for the location of the methyl signals at δ 0.93, 0.85, and 0.72.

Degradation of (+)-**8b** with lithium aluminum hydride in refluxing tetrahydrofuran[21] gave a dextrorotatory propellane ($[\alpha]_D$ + 487°) whose absolute configuration could be unambiguously assigned as **6b**.

To arrive at the more helix-shaped propellane **19**, we treated the known 1,2-dihydrophenanthrene-3,4-dicarboxylic anhydride (**13**)[22] with butadiene under autoclave conditions. While the increased level of steric hindrance surrounding one of the carbonyl groups in **14** caused no difficulty during the hydride reduction and mesylation steps, the added bulk did make its appearance in the sodium sulfide reaction intended to deliver cyclic sulfide **16** (Scheme IV). Although the conversion to **16** did proceed in 63% yield, the cyclic ether was formed concomitantly (12%). Two equivalents of monoperphthalic acid acted on **16** to give sulfone **17** efficiently (96%).

The availability of **16** and **17** led us to examine two routes to cyclobutene **18**. In the first, **16** was α-chlorinated, oxidized, and rearranged in strong base as before. The conversion to **18** was accomplished in 40% overall yield. Alternatively, the α-sulfonyl carbanion of **17** was prepared by treatment with 1 equiv of *n*-butyllithium and added to a refluxing slurry of lithium aluminum hydride in dioxane.[23] This method afforded **18** in 17% yield and therefore is not preferred in this situation. The subsequent elaboration of (±)-**19** and formation of the diastereomeric mixture of adducts **20** and **21** (Scheme V) were carried out in unexceptional fashion.

The specific rotation of the 1:1 mixture of these urazoles was noted to be $[\alpha]_D$ −3.4°, and the 300-MHz ^{1}H NMR spectrum once again exhibited four methyl signals for the *endo*-bornyl segments. These appeared at δ 0.91 (3 H), 0.83 (3 H), 0.73 (1.5 H), and 0.70 (1.5 H). The diastereo-

(21) (a) Barton, D. H. R.; Shiori, T.; Widdowson, D. A. *J. Chem. Soc. C* **1971**, 1968. (b) Bosworth, N.; Emke, A.; Midgley, J. M.; Moore, C. J.; Whalley, W. B.; Ferguson, G.; Marsh, W. C. *J. Chem. Soc., Perkin Trans. 1* **1977**, 805. (c) Barton, D. H. R.; Gunatilaka, A. A. L.; Nakanishi, T; Paton, H.; Widdowson, D. A.; Worth, B. R. *Ibid.* **1976**, 821.

(22) Fieser, L. F.; Hershberg, E. B. *J. Am. Chem. Soc.* **1935**, *57*, 1851.

(23) (a) Paquette, L. A.; Photis, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4936. (b) Paquette, L. A.; Photis, J. M. *Org. Synth.* **1977**, *57*, 53.

mers were nicely partitioned by application of recycling techniques on the Waters Prep 500 instrument. The pure dextrorotatory isomer ($[\alpha]_D$ +135°) was identified as being responsible for the δ 0.73 absorption and characterized as **20** by X-ray crystal structure analysis (Figure 3; Tables IX–XII, supplementary material). Upon hydride reduction, (+)-**20** was transformed back to the dextrorotatory propellane ($[\alpha]_D$ +447°) which is necessarily (+)-**19**. Comparable degradation of a 4:1 mixture of **21** and **20** gave a sample of the propellane that was commensurately enriched in (−)-**19**, $[\alpha]_D$ −266°.

By way of summary, the preparation of several chiral unsaturated propellanes has been successfully achieved, and methodology (nondestructive resolution[11]) for their ready obtention in optically pure form has been devised. The use of (−)-*endo*-bornyltriazolinedione allows for formation of separable diastereomeric urazole adducts which can be reconverted to the hydrocarbon after separation. Correlation of the elution order of the adducts from silica gel and their stereochemistry is presently obvious, that which is dextrorotatory[24] being somewhat less readily adsorbed. The diastereomeric purity of these substances could be ascertained conveniently in the absence of otherwise superfluous chiral solvating agents[25] or chiral lanthanide shift reagents[26] by means of ^{1}H NMR at 300 MHz.

Particularly revealing is the fact that the like-signed diastereomers (+)-**8a**, (+)-**8b**, and (+)-**20** share the same absolute configuration. Moreover, all three give rise to the corresponding dextrorotatory propellanes upon degradation. The capability of these hydrocarbons to rotate plane-polarized light ($[\alpha]_D$ values given) was observed to increase in the order **6a** (147°), **19** (447°), and **6b** (487°). The enhancement in specific rotation which materializes during the progression from **6a** to **19** follows from structural embellishment of the handedness of the molecular framework, a phenomenon encountered earlier in the helicene series.[27] Although the relative position of **6b** might lead one to conclude that placement of a C_5-methyl group onto **6a** has a greater effect on $[\alpha]_D$ than does C_5–C_6 benzo fusion, we point out that the contributions made by the second (C_8) methyl group in **6b** are presently unknown.

Experimental Section

Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. All optical rotations were obtained on a Perkin-Elmer Model 241 polarimeter and are expressed in mg/mL. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Proton magnetic resonance spectra were recorded with Varian A-60A, EM-360, T-60, and HA-100 spectrometers, as well as Bruker HX-90, WP-200, and WM-300 spectrometers. Carbon spectra were recorded with Bruker WP-80 and HX-90 spectrometers. Mass spectra were determined on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory.

1,4,9,10-Tetrahydro-4a,10a-phenanthrenedimethanol Dimethanesulfonate (3a). The Diels–Alder addition of butadiene to dihydro-1,2-naphthalic anhydride[17] (**1a**) according to the procedure of Fieser and Hershberg[16] constituted the source of **2a**. A solution of **2a** (70.4 g, 0.277 mol) in dry tetrahydrofuran (450 mL) was added slowly to a slurry of lithium aluminum hydride (17.0 g, 0.448 mol) in dry tetrahydrofuran (100 mL) under nitrogen. After the addition was finished, the reaction mixture was heated at reflux overnight, cooled to 0 °C, and quenched with a saturated solution of sodium sulfate (100 mL). The white salts were filtered, placed in a Soxhlet extractor, and extracted with dichloromethane for 2 days. The solvent was evaporated, and the resulting solid was recrystallized from benzene to give 64.5 g (95%) of diol as a white solid: mp 107–109 °C; IR ($CHCl_3$) ν_{max} 3550, 3270, 2900, 1490, 1475, 1450, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.6–7.0 (m, 4 H), 5.7–5.4 (m, 2 H), 4.5–3.5 (m, 6 H), 3.2–1.5 (m, 8 H); mass spectrum, no M^+, calcd for ($M^+ - H_2O$) m/e 226.1358, obsd 226.1351.

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.36; H, 8.21.

To dry pyridine (100 mL) cooled in a dry ice–carbon tetrachloride bath was added methanesulfonyl chloride (34.6 g, 0.302 mol) under nitrogen. The diol (31.1 g, 0.127 mol) in dry pyridine (100 mL) was added at a rate such that the temperature remained below −10 °C. After the addition was finished, the reaction mixture was stirred at 0 °C for 4.5 h, slowly poured into 600 mL of 4 N hydrochloric acid while cooled at 0 °C, and allowed to stand for 2.5 h. The aqueous phase was decanted. The beige gum was taken up in acetone (175 mL of solution) and cooled in an ice bath. Water was added until cloudiness persisted. Additional water (700 mL) was next introduced in one portion while the solution was stirred, and the oil that resulted solidified. The white solid was collected and dried overnight at 0.1 mm to give 47.6 g (94%) of dimesylate **3a**: mp 100–101 °C dec; IR ($CHCl_3$) ν_{max} 3200-2800, 1360, 1170, 968, 945 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.26–7.10 (m, 4 H), 5.6–5.5 (m, 2 H), 4.48 (s, 2 H), 4.29 (s, 2 H), 3.2–1.7 (m, 8 H), 2.99 (s, 3 H), 2.83 (s, 3 H).

Anal. Calcd for $C_{18}H_{24}O_6S_2$: C, 53.98; H, 6.04. Found: C, 53.89; H, 6.01.

1,4,9,10-Tetrahydro-4a,10a-methanothiomethanophenanthrene (4a). An anhydrous slurry of sodium sulfide in hexamethylphosphoramide was prepared by distillation of the water–HMPA fraction [bp 25–120 °C (30 mm)] from a mixture of sodium sulfide nonahydrate (183 g, 0.763 mol) and HMPA (1.60 L). The cooled reaction mixture was treated with dimesylate **3a** (102 g, 0.255 mol), stirred under nitrogen in an oil bath at 60–70 °C for 39 h,, cooled, diluted with water (3.0 L), and continuously extracted with ether. The combined organic layers were diluted with an equal volume of petroleum ether, washed with water, dried, filtered, and evaporated. Chromatography on alumina with benzene elution followed by recrystallization from benzene (10 mL)/petroleum ether (200 mL) gave 41.9 g (68%) of sulfide **4a** as a white solid: mp 69–71 °C; IR ($CDCl_3$) ν_{max} 3200–2800, 1490, 1450, 1180, 975 cm^{-1}; ^{1}H NMR δ 7.5–6.9 (m, 4 H), 5.7–5.4 (m, 2 H), 3.02 (s, 2 H), 3.3–1.6 (m, 10 H); mass spectrum, calcd m/e 242.1129, obsd 242.1133.

Anal. Calcd for $C_{16}H_{18}S$: C, 79.29; H, 7.49. Found: C, 79.41; H, 7.56.

1,4,9,10-Tetrahydro-4a,10a-ethenophenanthrene (5a). To sulfide **4a** (3.00 g, 13.4 mmol) and *N*-chlorosuccinimide (1.71 g, 12.8 mmol) was added dry carbon tetrachloride (35 mL). The reaction mixture was heated at reflux under nitrogen for 3 h, cooled, and filtered to remove the succinimide. The solvent was evaporated to leave a mixture of isomeric α-chloro sulfides as a clear, colorless oil. This oil was used in the next step without further purification.

A solution of the α-chloro sulfides from above in chloroform (40 mL) under nitrogen was cooled in a dry ice/carbon tetrachloride bath and treated dropwise with 37.0 mL of 0.684 N monoperphthalic acid in ether. After the addition was finished, the reaction mixture was stirred at room temperature for 7.5 h. The precipitated solid was removed, and the combined organic phases were washed with 0.5 N sodium hydroxide solution and dried. The solvent was evaporated to give the α-chloro sulfones as a beige foam which was dried overnight at 0.1 mm: mp 65–110 °C; mass spectrum, calcd m/e 308.0637, obsd 308.0642.

The isomeric α-chloro sulfones from above were taken up in dry tetrahydrofuran (50 mL), cooled in a dry ice/carbon tetrachloride bath under nitrogen, and treated with potassium *tert*-butoxide (8.00 g, 71.4 mmol). The dark brown reaction mixture was heated at reflux for 3 h, cooled, diluted with water (800 mL),

(24) Although the two diastereomers need not exhibit $[\alpha]_D$'s of opposite sign, our experience to date with propellane adducts of (−)-*endo*-bornyltriazolinedione indicates that this trend is general in this series: Klobucar, W. D. Ph.D. Thesis, The Ohio State University, 1981.

(25) (a) Pirkle, W. H.; Hoekstra, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 1832. (b) Kainosno, M.; Ajisaka, K.; Pirkle, W. H.; Beare, S. D. *Ibid.* **1972**, *94*, 5924. (c) Pirkle, W. H.; Muntz, R. L.; Paul, E. C. *Ibid.* **1971**, *93*, 2817.

(26) (a) Fraser, R. F.; Petit, M. A.; Miskow, M. *J. Am. Chem. Soc.* **1972**, *94*, 3253. (b) Goering, H. L.; Eikenberry, J. N.; Koermer, G. S. *Ibid.* **1971**, *93*, 5913. (c) Whitesides, G. M.; Lewis, D. W. *Ibid.* **1971**, *93*, 5914. (d) Whitesides, G. M.; Lewis, D. W. *Ibid.* **1970**, *92*, 6979.

(27) Martin, R. H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 649.

and continuously extracted with ether for 3 days. After drying, the solvent was removed, and the oil was chromatographed on basic alumina with hexane as eluant to give 2.02 g (81%) of **5a** as an oily yellow solid. Recrystallization from pentane gave the analytical sample as a white solid: mp 35–36 °C; IR (film) ν_{max} 3200–2800, 1480, 1470, 1440, 1200, 995, 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, 4 H), 6.0–5.7 (m, 3 H), 5.64 (d, J = 3 Hz, 1 H), 3.0–1.0 (m, 8 H); mass spectrum, calcd m/e 208.1252, obsd 208.1254.

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.91; H, 7.82.

(±)-9,10-Dihydro-4a,10a-ethenophenanthrene (6a). To a solution of **5a** (2.02 g, 9.71 mmol) in carbon tetrachloride (35 mL) and glacial acetic acid (35 mL) was added pyridinium hydrobromide perbromide (3.26 g, 10.2 mmol). The reaction mixture was stirred for 3 h at room temperature, water was added, and the organic phase was separated. The aqueous layer was extracted with carbon tetrachloride (4 × 25 mL). The combined organic layers were washed with water (2 × 25 mL), 0.5 N sodium hydroxide solution (2 × 25 mL), and water (2 × 25 mL) prior to drying and solvent evaporation. The mixture of dibromides was isolated as a yellow oil, mass spectrum, calcd m/e 365.9620, obsd 365.9624.

The crude mixture of dibromides from above was treated with lithium chloride (4.15 g, 97.9 mmol), lithium carbonate (7.25 g, 98.1 mmol), and dry HMPA (100 mL). The reaction mixture was stirred under nitrogen in an oil bath at 90 °C for 27 h, cooled, diluted with water (400 mL), filtered through Celite, and extracted with hexane (5 × 75 mL). The combined organic layers were washed with water (5 × 10 mL), dried, filtered, and eluted through an alumina column. Elution with benzene gave 1.51 g (75%) of **6a** as a yellowish solid. The analytical sample was obtained by recrystallization from pentane: mp 43.5–44 °C; IR (film) ν_{max} 3200–2800, 1490, 1460, 1440, 1375, 965, 945 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.4–6.9 (m, 4 H), 6.4–5.4 (m, 6 H), 2.9–2.5 (m, 2 H), 2.0–1.2 (m, 2 H); mass spectrum, calcd m/e 206.1095, obsd 206.1099.

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 92.80; H, 6.84.

***N*-2-Methyl-5,6-dihydro-1,4:4a,10b-diethenobenzo[*f*]phthalazine-2,3(1*H*,4*H*)-dicarboximide (7a).** A solution of **6a** in a 4:1 pentane/ethyl acetate mixture (100 mL) cooled in a dry ice/2-propanol bath was treated dropwise with a solution of *N*-methyltriazolinedione (1.24 g, 11.0 mmol) in ethyl acetate (20 mL). The reaction mixture was allowed to warm to room temperature, and the precipitated adduct was collected to give 2.70 g (77%) of urazole **7a** as a light pink solid, mp 193–194 °C. The analytical sample was obtained in colorless condition by recrystallization from benzene/cyclohexane: mp 193–193.5 °C; IR (KBr) ν_{max} 3100–2820, 1780, 1710, 1460, 1400, 1220, 1200, 790 and 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.6–7.0 (m, 4 H), 6.4–6.15 (m, 2 H), 5.99 (d, J = 3 Hz, 1 H), 5.73 (d, J = 3 Hz, 1 H), 5.62–5.37 (m, 1 H), 4.83–4.60 (m, 1 H), 3.0–2.6 (m, 2 H), 2.90 (s, 3 H), 2.2–1.8 (m, 2 H); mass spectrum, calcd m/e 319.1320, obsd 319.1324.

Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16. Found: C, 71.19; H, 5.51; N,, 12.85.

(±)- and (−)-*N*-2-Bornyl-5,6-dihydro-1,4:4a,10b-dietheno-benzo[*f*]phthalazine-2,3(1*H*,4*H*)-dicarboximides (8a and 9a). To (±)-**6a** (4.36 g, 21.1 mmol) dissolved in 4:1 pentane/ethyl acetate (150 mL) cooled in a dry ice/isopropyl alcohol bath was added dropwise a solution of (−)-*endo*-bornyl-1,2,4-triazoline-3,5-dione[9] (4.97 g, 21.1 mmol) in ethyl acetate (30 mL). The reaction mixture was stirred at room temperature for 1 h and the precipitate that formed was collected to give 3.40 g of **9a** as a white solid, $[\alpha]_{578}$ −243° (*c* 10.9, benzene). When the mixture was allowed to stand for further evaporation of solvent, an additional quantity of crystals materialized: 3.73 g (77%); $[\alpha]_{578}$ +169° (*c* 14.0, benzene). The analytical sample of optically pure **9a** was obtained by two recrystallizations from chloroform/ethyl acetate: mp 260–260.5 °C; UV (ethanol) 258 nm (ϵ 3.9 × 10^{-3}), 215 (9.7 × 10^3); $[\alpha]_D$ −231°, $[\alpha]_{578}$ −244°, $[\alpha]_{546}$ −281°, $[\alpha]_{436}$ −517° (*c* 12.8, benzene); IR (KBr) ν_{max} 3080–2800, 1765, 1700, 1420, 1390, 1395, 780, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.53–7.20 (m, 4 H), 6.34–6.29 (m, 2 H), 6.02 (d, J = 2.8 Hz, 1 H), 5.75 (d, J = 2.8 Hz, 1 H), 5.53–5.50 (m, 1 H), 4.73–4.70 (m, 1 H), 4.23–4.10 (m, 1 H), 2.90–1.1 (m, 11 H), 0.92 (s, 3 H), 0.84 (s, 3 H), 0.74 (s, 3 H); ^{13}C NMR ($CDCl_3$) 160.0, 159.4, 139.3, 138.9, 138.4, 134.4, 129.0, 127.7, 127.2 (2C), 126.7, 125.5, 59.4, 59.1, 57.0, 51.6, 51.0, 49.7, 47.8, 45.5, 29.6, 28.1, 27.2, 26.7, 25.8, 19.7, 18.7, 14.0 ppm; m/e calcd 441.2416, obsd 441.2425.

Anal. Calcd for $C_{28}H_{31}N_3O_2$: C, 76.16; H, 7.08; N, 9.52. Found: C, 75.80; H, 7.08; N, 9.49.

Separation of 8a and 9a by HPLC. This experiment relates to a mixture of diastereomers ($[\alpha]_{578}$ +113°) whose ^{1}H NMR (300 MHz) was the same as that previously reported except that there were four methyl groups (δ 0.92, 0.84, 0.74, and 0.73) arising from the *endo*-bornyl moiety instead of three. This material was subjected to band shaving on a Waters Prep 500 chromatograph with 15% ethyl acetate/petroleum ether as the eluant to give a leading edge fraction ($[\alpha]_{578}$ = +93.5°) and a tailing edge fraction ($[\alpha]_{578}$ = −128°).

(−)-9,10-Dihydro-4a,10a-ethenophenanthrene (6a). Diastereomerically pure urazole **9** (0.141 g, 0.319 mmol) was added to a solution of potassium *tert*-butoxide (0.85 g, 7.6 mmol) in dimethyl sulfoxide (10 mL). The reaction mixture was stirred at room temperature for 5 days, poured into 100 mL of ice and water, made acidic (pH ~5) with concentrated hydrochloric acid, basified with concentrated ammonium hydroxide (pH ~9), and finally extracted with ether (5 × 25 mL). The combined organic layers were washed with water and brine (5 mL), dried, filtered, and evaporated. The resulting beige foam was used below without further purification.

To this foam was added dry ether (45 mL) and manganese dioxide (0.271 g, 3.12 mmol). The reaction mixture was stirred at room temperature under nitrogen for 16 h, filtered through Celite, and freed of solvent. The resultant oil was subjected to preparative layer chromatography on silica gel (three elutions with hexane) to give 33.6 mg (51%) of a yellow oil, the NMR spectrum of which showed it to be **6a**. The rotations of the sample (33.6 mg) in 2.00 mL of chloroform were $[\alpha]_D$ −147°, $[\alpha]_{578}$ −154°, $[\alpha]_{546}$ −174°, and $[\alpha]_{436}$ −283°.

The conversion of **9** to **12** as outlined in Scheme III has been described experimentally in full.[20] In view of the X-ray crystal structure data reported herein, it is now clear that the structural formulas used above are correctly representative of the absolute configurations of the indicated compounds.

3,4-Dihydro-5,8-dimethyl-1,2-naphthalenedicarboxylic Anhydride (1b). To powdered potassium (33.8 g, 0.864 mol) in 150 mL of dry ether was added absolute ethanol (150 mL). After all of the potassium had reacted, diethyl oxalate (177 g, 1.21 mol) in dry ether (200 mL) was added dropwise. Ethyl γ-(2,5-dimethylphenyl)butyrate[28] (178 g, 0.809 mol) in absolute ether (200 mL) was added dropwise. The reaction mixture was heated at reflux for 18 h, cooled to 0 °C, and treated with cold dilute sulfuric acid. The aqueous layer was separated and extracted with ether. The combined organic layers were washed with water, dried, filtered, and evaporated. The resulting yellow oil was poured into 80% sulfuric acid (12.5 L) and stirred in an oil bath at 80–90 °C for 1.25 h. The reaction mixture was cooled to 0 °C, and the precipitate was collected, rinsed with cold methanol, and dried to give 122 g (66%) of pale yellow solid, mp 111–120 °C (lit.[28] mp 187 °C; we believe their product to be sulfonated). The product was used without further purification. The analytical sample was obtained by HPLC on silica gel (elution with 9% ethyl acetate/petroleum ether) followed by recrystallization from dichloromethane/hexane: light yellow-green needles, mp 113.5–115 °C; IR (KBr) ν_{max} 3080–2800, 1830, 1760, 1480, 1430, 1290, 1265, 1210, 1085, 910, 870, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.07 (q, J = 7.5 Hz, 2 H), 3.0–2.1 (m, 4 H), 2.48 (s, 3 H), 2.24 (s, 3 H); ^{13}C NMR ($CDCl_3$) 164.3, 162.8, 143.3, 137.6, 136.3, 135.1, 133.7, 133.3, 130.0, 125.0, 25.0, 22.1, 20.1, 18.4 ppm; mass spectrum, calcd m/e 228.0786, obsd 228.0779.

Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.75; H, 5.37.

5,8-Dimethyl-1,4,9,10-tetrahydro-4a,10a-phenanthrenedicarboxylic Anhydride (2b). A 3-L autoclave was charged with anhydride **1b** (101 g, 0.444 mol), hydroquinone (4 g), dioxane (200 mL), and butadiene (300 mL) and rocked for 29 h while being heated at 150 °C. The dioxane solution was filtered and concentrated, and the crude product was allowed to crystallize. The product was recrystallized twice from acetone to give 71.0 g (57%) of anhydride **2b** as a white solid. The analytical sample was

(28) Christiaens, L.; Renson, M. *Bull Chim. Soc. Belg.* **1969**, *78*, 359.

prepared by an additional recrystallization from acetone: mp 158.5–159 °C; IR (KBr) ν_{max} 3030–2820, 1855, 1790, 1465, 1445, 1230, 1210, 1140, 945, 895, 810, 630 cm^{-1}; ^{1}H ($CDCl_3$) δ 7.00 (s, 2 H), 5.9–5.7 (m, 2 H), 3.8–1.5 (m, 8 H), 2.49 (s, 3 H), 2.14 (s, 3 H); ^{13}C NMR ($CDCl_3$) 173.9 (s), 172.1 (s), 135.8 (s), 135.5 (s), 133.3 (s), 132.5 (s), 131.3 (d), 129.9 (d), 124.6 (d), 121.8 (d), 52.9 (s), 49.0 (s), 33.1 (t), 29.8 (t), 24.2 (t), 23.7 (t), 21.7 (q), 20.0 ppm (q); mass spectrum, calcd m/e 282.1256, obsd 282.1262.

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.78; H, 6.54.

5,8-Dimethyl-1,4,9,10-tetrahydro-4a,10a-phenanthrenedimethanol Dimethanesulfonate (3b). To a slurry of lithium aluminum hydride (15.0 g, 0.395 mol) in dry tetrahydrofuran (250 mL) under nitrogen was added dropwise a solution of anhydride **2b** (60.0 g, 0.231 mol) in dry tetrahydrofuran (1.1 L). After the addition was completed, the reaction mixture was heated at reflux overnight, cooled, and treated with saturated sodium sulfate solution (40 mL). The white solid was removed and extracted for 2 days in a Soxhlet extractor with chloroform. The extract was dried, filtered, and evaporated. The residue was recrystallized from acetone to give 42.7 g (74%) of diol as a white solid, mp 151–153 °C. The analytical sample was prepared by recrystallization from acetone: mp 152.5–153 °C; IR (KBr) ν_{max} 3630–3050, 3030, 2920, 1500, 1470, 1440, 1380, 1240, 1085, 1060, 1045, 1035, 1000, 805, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.88 (s, 2 H), 5.8–5.4 (m, 2 H), 4.4–1.5 (m, 12 H), 3.55 (q, J = 12.0 Hz, 2 H), 2.55 (s, 3 H), 2.13 (s, 3 H); ^{13}C NMR ($CDCl_3$) 138.6 (s), 136.2 (s), 135.6 (s), 133.3 (s), 131.4 (d), 128.2 (d), 125.0 (d), 122.4 (d), 66.9 (t), 65.0 (t), 46.4 (s), 38.5 (s), 34.8 (t), 32.5 (t), 29.3 (t), 24.6 (t), 24.2 (q), 20.2 ppm (q); mass spectrum calcd m/e 272.1776, obsd 272.1784.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.41; H, 8.95.

This diol (43.9 g, 0.161 mmol) in dry pyridine (180 mL) was added dropwise to a solution of methanesulfonyl chloride (44.2 g, 0.379 mol) in cold dry pyridine (150 mL) at a rate such that the reaction temperature remained below −15 °C. After the addition was finished, the reaction mixture was stirred at 0 °C for 4.5 h, slowly poured with stirring into 4 N hydrochloric acid solution (580 mL) at 0 °C, and allowed to stand for 1 h. The white precipitate was collected, rinsed with water, and dried overnight at 0.05 mm to give 68.5 g (99%) of dimesylate **3b**: mp 113–114 °C dec; IR (KBr) ν_{max} 3100–2800, 1510, 1470, 1440, 1350, 1335, 1180, 980, 970, 950 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.90 (q, J = 7.5 Hz, 2 H), 5.9–5.4 (m, 2 H), 4.67 (q, J = 10.5 Hz, 2 H), 4.3–4.14 (m, 2 H), 3.00 (s, 3 H), 2.93 (s, 3 H), 2.8–1.7 (m, 8 H), 2.52 (s, 3 H), 2.88 (s, 3 H). This material was used without further purification.

5,8-Dimethyl-1,4,9,10-tetrahydro-4a,10a-methanothiomethanophenanthrene (4b). An anhydrous slurry of HMPA and sodium sulfide was prepared by distillation of the water–HMPA fraction [25–120 °C (30 mm)] from a mixture of sodium sulfide nonahydrate (105 g, 0.438 mol) in HMPA (975 mL). After the mixture cooled, dimesylate **3b** (60.9 g, 0.142 mol) was added, and the reaction mixture was stirred in an oil bath at 70 °C for 63 h under nitrogen. After the mixture cooled, water (2.7 L) was added, and the mixture was extracted with ether (5 × 200 mL). Following the addition of petroleum ether (800 mL), the organic phase was washed with water (7 × 25 mL), dried, and evaporated. The resultant oil was chromatographed on alumina with 10% ethyl acetate/petroleum ether as eluant. Recrystallization from cyclohexane/hexane gave 23.2 g (60%) of sulfide **4b** as a light yellow solid, mp 105–107 °C. The analytical sample, prepared by recrystallization from cyclohexane, was isolated as a white solid: mp 106–108 °C; IR (KBr) ν_{max} 3030–2840, 1460, 1380, 1160, 1030, 970, 840, 805, 738, 650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.87 (s, 2 H), 5.8–5.4 (m, 2 H), 3.38 (q, J = 11.0 Hz, 2 H), 3.2–1.3 (m, 10 H), 2.50 (s, 3 H), 2.13 (s, 3 H); ^{13}C NMR ($CDCl_3$) 140.0 (s), 134.5 (s), 133.8 (s), 133.2 (s), 130.8 (d), 127.8 (d), 123.9 (d), 122.7 (d), 50.2 (s), 45.2 (s), 38.3 (t), 37.0 (t), 35.1 (t), 33.0 (t), 26.9 (t), 24.8 (t), 23.9 (q), 20.1 ppm (q); mass spectrum, calcd m/e 270.1442, obsd 270.1449.

Anal. Calcd for $C_{18}H_{22}S$: C, 79.94; H, 8.20. Found: C, 80.10; H, 8.16.

5,8-Dimethyl-1,4,9,10-tetrahydro-4a,10a-ethenophenanthrene (5b). To sulfide **4b** (23.2 g, 85.8 mmol) was added *N*-chlorosuccinimide (12.0 g, 90.2 mmol) and dry carbon tetrachloride (250 mL). The reaction mixture was heated at reflux for 3 h. After cooling, the succinimide was removed, and the solvent was evaporated to give a mixture of isomeric α-chloro sulfides as a yellow oil. This oil was used without further purification.

To the α-chloro sulfides dissolved in cold (−23 °C) chloroform (250 mL) was added dropwise 250 mL of 0.706 N monoperphthalic acid in ether. The reaction mixture was stirred at room temperature for 6 h. The precipitated phthalic acid was removed. The reaction mixture was washed with 0.5 N sodium hydroxide solution. After the mixture was dried, the solvent was removed to give the α-chlorosulfones as a beige foam which was dried at 0.05 mm overnight.

To the α-chloro sulfones dissolved in cold (−23 °C) dry tetrahydrofuran (350 mL) was added potassium *tert*-butoxide. The dark brown reaction mixture was heated at the reflux temperature under nitrogen for 3.5 h, diluted with water, and continuously extracted for 3 days with ether. The dark brown oil was chromatographed on basic alumina with 2:1 petroleum ether/benzene to give 10.7 g (53%) of **5b** as a yellowish oily solid. The analytical sample was prepared by subjecting this material to preparative TLC on silica gel followed by recrystallization from hexane: white solid; mp 102–103 °C; IR (KBr) ν_{max} 3080–2800, 1475, 1450, 1310, 1290, 1020, 850, 810, 800, 750, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.78 (s, 2 H), 6.23 (d, J = 3.0 Hz, 1 H), 5.95 (d, J = 3.0 Hz, 1 H), 5.70 (m, 2 H), 2.9–0.9 (m, 8 H), 2.23 (s, 3 H), 2.15 (s, 3 H); ^{13}C NMR ($CDCl_3$) 142.4 (s), 141.8 (d), 137.3 (s), 136.0 (d), 133.4 (s), 132.7 (s), 128.9 (d), 127.3 (d), 127.1 (d), 126.5 (d), 53.5 (s), 50.5 (s), 34.0 (t), 33.2 (t), 32.6 (t), 25.1 (t), 20.7 (q), 20.5 ppm (q); mass spectrum, calcd m/e 236.1565, obsd. 236.1572.

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.44; H, 8.53.

(±)-5,8-Dimethyl-9,10-dihydro-4a,10a-ethenophenanthrene (6b). Pyridinium hydrobromide perbromide (5.71 g, 17.9 mmol) and **5b** (4.02 g, 17.0 mmol) in carbon tetrachloride and glacial acetic acid (65 mL each) were stirred together for 3.5 h at room temperature. Water was added to the reaction mixture, the organic phases were separated, and the aqueous phase was extracted with carbon tetrachloride. The combined organic phases were washed with water, 0.5 N sodium hydroxide solution, and water. After the mixture was dried, the solvent was removed, and the yellow oil was dried at 0.05 mm for 1 h. This mixture of dibromides was used without further purification.

To this oil were added lithium chloride (7.42 g, 0.175 mol), lithium carbonate (12.6 g, 0.171 mol), and dry HMPA (200 mL). The slurry was stirred for 1 day under argon at 85–90 °C. The reaction mixture was cooled, diluted with water, filtered through Celite, and extracted with hexane. The combined organic layers were washed with water, dried, and evaporated. The brown oil was chromatographed on basic alumina (benzene elution) to give 2.42 g (61%) of **6b** as a light brown oil: IR (film) ν_{max} 3100–2800, 1470, 850, 795, 750, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.83 (s, 2 H), 6.46 (d, J = 2.7 Hz, 1 H), 6.07 (d, J = 2.7 Hz, 1 H), 6.1–5.4 (m, 4 H), 2.95–0.8 (m, 4 H), 2.37 (s, 3 H), 2.16 (s, 3 H); mass spectrum, calcd m/e 234.1408, obsd 234.1401.

***N*-2-Methyl-5,6-dihydro-7,10-dimethyl-1,4:4a,10b-diethenobenzo[*f*]phthalazine-2,3(1*H*,4*H*)-dicarboximide (7b).** To **6b** (2.42 g, 10.4 mol) dissolved in 50 mL of cold (−78 °C) 4:1 pentane/ethyl acetate was added dropwise *N*-methyltriazolinedione (1.17 g, 10.4 mmol) dissolved in ethyl acetate (14 mL). After the addition was finished, the reaction mixture was stirred for 1 h at room temperature. The slightly pink solid was collected to give 2.38 g (67%) of urazole **7b**. The analytical sample was prepared by recrystallization from benzene: white solid; mp 220–222 °C; IR (KBr) ν_{max} 3100–2800, 1770, 1705, 1450, 1390, 1380, 1190, 850, 800, 780, 740, 605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.97 (s, 2 H), 6.4–6.1 (m, 3 H), 6.12 (d, J = 2.9 Hz, 1 H), 5.10–4.75 (m, 2 H), 3.10–2.75 (m, 2 H), 2.95 (s, 3 H), 2.5–1.9 (m, 2 H), 2.35 (s, 3 H), 2.23 (s, 3 H); ^{13}C NMR ($CDCl_3$) 158.8 (s), 158.4 (s), 143.4 (d), 139.5 (d), 137.7 (s), 134.1 (s), 133.6 (s), 133.1 (s), 129.1 (d), 128.9 (d), 128.7 (d), 128.2 (d), 60.7 (2C, 2 d), 50.8 (s), 46.8 (s), 28.5 (t), 26.1 (t), 25.3 (q), 20.6 (q), 20.3 ppm (q); mass spectrum, calcd m/e 347.1634, obsd 347.1642.

Anal. Calcd for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09. Found: C, 72.71; H, 6.17.

(+)- and (−)-*N*-2-Bornyl-5,6-dihydro-7,10-dimethyl-1,4:4a,10b-diethenobenzo[*f*]phthalazine-2,3-(1*H*,4*H*)-di-

carboximides (8b and 9b). To a solution of **7b** (4.34 g, 18.5 mmol) in 100 mL of 4:1 pentane/ethyl acetate cooled at −78 °C was added dropwise (−)-*endo*-bornyl-1,2,4-triazoline-3,5-dione (4.36 g, 18.5 mmol) in ethyl acetate (20 mL). The reaction mixture was stirred at room temperature for 1.5 h. The precipitate was collected to give 5.20 g (69%) of slightly pink solid. The analytical sample was prepared by recrystallization from ethyl acetate: white solid; mp 224–225 °C; $[\alpha]_D$ −5.0° (*c* 10.4, chloroform); IR (KBr) ν_{max} 3100–2800, 1760, 1700, 1410, 1385, 1375, 800, 770 cm^{-1}; UV (ethanol) 258 nm (ϵ 5.5 × 10^3), 220 (1.7 × 10^4); ^{1}H NMR ($CDCl_3$) δ 6.96 (s, 2 H), 6.36–6.28 (m, 3 H), 6.11 (d, J = 2.93 Hz, 1 Hz), 5.05–4.97 (m, 1 H), 4.82–4.74 (m, 1 H), 4.17–4.11 (m, 1 H), 2.91–1.24 (m, 11 H), 2.36 (s, 3 H), 2.25 (s, 3 H), 0.93 (s, 1.5 H), 0.92 (s, 1.5 H), 0.85 (s, 3 H), 0.74 (s, 1.5 H), 0.72 (s, 1.5 H); ^{13}C NMR ($CDCl_3$) 160.0, 159.6, 143.2, 139.6, 137.7, 134.1, 133.6, 133.0, 128.9, 128.8, 128.6, 127.7, 61.0, 59.4, 51.7, 51.6, 50.7, 47.8, 46.8, 45.5, 29.6, 28.4, 27.1, 26.6, 26.0, 20.6, 20.3, 19.7, 18.7, 14.1 ppm; mass spectrum, calcd *m/e* 469.2729, obsd 469.2743.

Anal. Calcd for $C_{30}H_{35}N_3O_2$: C, 76.73; H, 7.51; N, 8.95. Found: C, 76.58, H, 7.49; N, 8.94.

HPLC Separation of (+)-8b and (−)-9b. Urazoles **8b** and **9b** were resolved by band-shaving techniques on a Waters Prep 500 HPLC chromatograph on silica gel (elution with 15% ethyl acetate/petroleum ether). Optimum conditions involved injection of 700 mg of the mixture dissolved in dichloromethane (8 mL) each time. Three band-shaving cycles afforded pure (+)-**8** (from leading edge). This pure diastereomer had the following rotations: $[\alpha]_D$ +14.1°, $[\alpha]_{578}$ +14.3, $[\alpha]_{546}$ +15.1°, $[\alpha]_{436}$ +13.9° (*c* 10.9, chloroform). The ^{1}H NMR spectrum (300 MHz) of this diastereomer is the same as that of the mixture except that only three methyl singlets were evidenced from the *endo*-bornyl unit at δ 0.92, 0.85, and 0.74.

The other pure diastereomer (−)-**9** (tailing edge) exhibited the following rotations: $[\alpha]_D$ −19.7°, $[\alpha]_{578}$ −20.3°, $[\alpha]_{546}$ −21.6°, $[\alpha]_{436}$ −22.2° (*c* 10.9, chloroform). The ^{1}H NMR spectrum (300 MHz) is the same as the mixture except for the appearance of only three methyl singlets at δ 0.93, 0.85, and 0.72.

(+)-9,10-Dihydro-5,8-dimethyl-4a,10a-ethenophenanthrene (6b). To dry tetrahydrofuran (10 mL) was added lithium aluminum hydride (0.121 g, 3.19 mmol) and diastereomerically pure (+)-**8b** (0.162 g, 0.345 mmol). The reaction mixture was heated at the reflux temperature for 11 h under nitrogen and for 0.75 h in the open air and then stirred in the open air for 12 h. A few drops of water were added, the solid was filtered, and the filtrate was dried and evaporated. The resulting oil was subjected to preparative layer chromatography (three elutions with hexane) to give 10.3 mg (13%) of (+)-**6b**, which was spectroscopically identical with that previously reported. This propellane sample was dissolved in $CHCl_3$ (2.00 mL), and the following rotations were observed: $[\alpha]_D$ +487°, $[\alpha]_{578}$ +516°, $[\alpha]_{546}$ +601°, $[\alpha]_{436}$ +1250.

1,4,9,10-Tetrahydro-5,6-benzo-4a,10a-phenanthrenedicarboxylic Anhydride (14). Anhydride **13**[22] (111 g, 0.444 mol), dioxane (20 mL), and 1,3-butadiene (300 mL) were heated together for 7 days in a rocking autoclave at 100 °C. The reaction vessel was cooled, the contents were removed, and the volatile organics were evaporated under vacuum. The residual oil was crystallized from benzene/petroleum ether to give a solid which was recrystallized twice from acetone. There was obtained 75.5 g (56%) of anhydride **14** as a white solid: mp 162–162.5 °C (lit.[16] mp 161.5–162 °C); IR (KBr) ν_{max} 3100–2800, 1850, 1780, 1440, 1220, 950, 915, 900, 800, 770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 173.7 (s), 172.8 (s), 133.8 (s), 133.4 (s), 131.7 (s), 129.7 (s and d), 129.2 (d), 128.3 (d), 126.6 (d), 125.8 (d), 125.5 (d), 124.9 (d), 121.8 (d), 53.4 (s), 49.6 (s), 33.5 (t), 31.3 (t), 27.4 (t), 23.4 (t).

1,4,9,10-Tetrahydro-5,6-benzo-4a,10a-phenanthrenedimethanol Dimethanesulfonate (15). To lithium aluminum hydride (13.0 g, 0.343 mol) in dry tetrahydrofuran (100 mL) under argon was added dropwise **14** (66.5 g, 0.291 mol) in dry tetrahydrofuran (1 L). The reaction mixture was heated at reflux overnight, cooled to 0 °C, and treated dropwise with saturated sodium sulfate solution (55 mL). The salts were removed, air-dried, and extracted in a Soxhlet extractor for 1 week with tetrahydrofuran. The combined organic layers were dried, filtered, and evaporated. The resulting solid was recrystallized frrom toluene to give 50.6 g (79%) of diol as a white solid, mp 119.5–121.5 °C. The analytical sample was obtained by recrystallization from acetone: mp 122–123 °C; IR (KBr) ν_{max} 3600–3100, 3010, 2990–2810, 1440, 1420, 1380, 1075, 1055, 1040, 1025, 835, 810, 775, 735, 650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.6–7.0 (m, 6 H), 6.0–5.3 (m, 2 H), 4.44 (q, J = 13.0 Hz, 2 H), 3.72 (q, J = 12.0 Hz, 2 H), 3.3–1.2 (m, 10 H); ^{13}C NMR ($CDCl_3$) 136.2 (s), 135.3 (s), 133.8 (s), 132.4 (s), 130.0 (d), 129.0 (d), 127.5 (d), 126.4 (d), 125.3 (d), 124.5 (d), 123.6 (d), 122.4 (d), 66.9 (t), 66.5 (t), 46.2 (s), 39.4 (s), 36.6 (t), 33.0 (t), 28.8 (t), 27.7 ppm (t); mass spectrum, calcd *m/e* 294.1620, obsd 294.1627.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.59; H, 7.53. Found: C, 81.54; H, 7.53.

To a stirred slush (−78 °C) of dry pyridine (130 mL) and methanesulfonyl chloride (42.0 g, 0.367 mol) under nitrogen was added dropwise a solution of the above diol (41.7 g, 0.142 mol) in dry pyridine (170 mL). After completion of the addition, the reaction mixture was warmed to −23 °C, stirred at this temperature for 6 h, and added dropwise to cold (0° C) stirred 4 N hydrochloric acid solution. The white precipitate was collected and dried on a vacuum pump at 0.05 mm overnight to give 61.8 g (97%) of dimesylate **15**: mp 92–93 °C dec; IR (KBr) ν_{max} 3100–2800, 1510, 1470, 1440, 1350, 1335, 1180, 980, 965, 950 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.3–7.1 (m, 6 H), 5.9–5.5 (m, 2 H), 4.95 (q, J = 11.1 Hz, 2 H), 4.27 (q, J = 9.6 Hz, 2 H), 3.9–1.8 (m, 8 H), 3.01 (s, 3 H), 2.47 (s, 3 H); mass spectrum, dec.

1,4,9,10-Tetrahydro-5,6-benzo-4a,10a-methanothiomethanophenanthrene (16). An anhydrous slurry of HMPA and sodium sulfide was prepared by distillation of the water–HMPA fraction [25–120 °C (30 mm)] from a mixture of sodium sulfide nonahydrate (95 g, 0.40 mol) in HMPA (900 mL). After cooling, dimesylate **15** (59.6 g, 0.132 mol) was added, and the reaction mixture was stirred in an oil bath at 55–60 °C for 4 days under nitrogen. The reaction mixture was cooled, diluted with water, and continuously extracted with ether for 4 days. The extract was washed with water, dried, filtered, and evaporated. After chromatography of the residue on alumina (elution with 31% ethyl acetate/petroleum ether), two recrystallizations from dichloromethane/hexane gave sulfide **16** as a white solid, mp 179–180 °C. The residual oil and solid were heated at 130 °C (0.1 mm) for 2 days to remove the remaining HMPA, and the mixture was further purified by HPLC (silica gel) with 5% ethyl acetate/petroleum ether to give a total of 24.3 g (63%) of sulfide **16** (after recrystallization from dichloromethane/hexane) and 4.37 g (12%) of the structurally related cyclic ether as a light yellow semisolid. The analytical sample of **16** was prepared by recrystallization from benzene/petroleum ether: mp 179.5–180.5 °C; IR (KBr) ν_{max} 3050–2800, 1510, 1450, 1420, 835, 820, 780, 755, 740, 650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.25–8.14 (m, 1 H), 7.93–7.02 (m, 5 H), 5.69–5.46 (m, 2 H), 3.67 (q, J = 11.1 Hz, 2 H), 3.04 (q, J = 10.1 Hz, 2 H), 3.09–1.18 (m, 8 H); ^{13}C NMR ($CDCl_3$) 136.8, 134.0, 133.0, 131.5, 129.6, 128.0, 127.4, 125.6, 124.6, 124.2, 123.8, 122.8, 50.1, 46.3, 38.3, 37.8, 35.1, 34.7, 27.7, 26.9 ppm; calcd *m/e* 292.1286, obsd 292.1292.

Anal. Calcd for $C_{20}H_{20}S$: C, 82.14; H, 6.89. Found: C, 82.11; H, 6.98.

The cyclic ether was obtained in a pure state as a white solid by recrystallization from cyclohexane: mp 125–127 °C; IR (KBr) ν_{max} 3080–2870, 1510, 1440, 1400, 1260, 1085, 1050, 1035, 920, 785, 750, 730, 705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.0–7.0 (m, 6 H), 6.6–6.3 (m, 1 H), 5.8–5.4 (m, 1 H), 4.52 (q, J = 8.5 Hz, 2 H), 3.73 (q, J = 8.5 Hz, 2 H), 2.94 (t, J = 7.0 Hz, 2 H), 2.3–1.5 (m, 6 H); ^{13}C NMR ($CDCl_3$) 136.4 (s), 134.2 (s), 133.2 (d), 132.4 (d), 131.4 (d), 129.6 (d), 128.1 (d), 127.1 (s), 125.8 (s and d), 125.2 (d), 124.4 (d), 80.7 (t), 74.9 (t), 49.4 (s), 43.6 (s), 28.8 (t), 27.1 (t), 26.0 (t), 21.5 ppm (t); mass spectrum, calcd *m/e* 276.1514, obsd 276.1500.

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 87.00; H, 7.28.

1,4,9,10-Tetrahydro-5,6-benzo-4a,10a-methanothiomethanophenanthrene 12,12-Dioxide (17). To sulfide **16** (3.62 g, 12.4 mmol) in chloroform (50 mL) cooled to −23 °C was added dropwise an ethereal solution of 0.667 N monoperphthalic acid (38 mL). After completion of the addition, the reaction mixture was stirred at room temperature for 48 h. The solid was removed and rinsed with chloroform (5 × 10 mL). The filtrate was washed with 0.5 N sodium hydroxide solution (3 × 10 mL), dried, filtered, and evaporated to leave a white solid. After recrystallization from

chloroform/hexane, 3.84 g (96%) of sulfone **17** was obtained as a white solid: mp 226–228 °C; IR (KBr) ν_{max} 3100–2800, 1510, 1445, 1410, 1245, 1235, 1125, 1110, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.1–7.0 (m, 6 H), 5.9–5.4 (m, 2 H), 4.05 (q, J = 12.0 Hz, 2 H), 3.4–1.4 (m, 8 H), 3.08 (q, J = 12.0 Hz, 2 H); mass spectrum, calcd m/e 324.1184, obsd 324.1191.

1,4,9,10-Tetrahydro-5,6-benzo-4a,10a-ethenophenanthrene (18). (A) Ramberg–Bäcklund Rearrangement of 16. To sulfide **16** (14.6 g, 50.0 mmol) were added *N*-chlorosuccinimide (6.72 g, 50.5 mmol) and dry carbon tetrachloride. The reaction mixture was heated at reflux under nitrogen for 29 h, cooled, filtered, and evaporated to give a mixture of isomeric α-chloro sulfides as a white solid: mass spectrum, calcd m/e 326.0896, obsd 326.0903.

To the solid from above in chloroform (200 mL) at −23 °C was added dropwise an ethereal solution of 0.624 N monoperphthalic acid (163 mL). After the addition was finished, the reaction mixture was stirred at room temperature for 9.75 h. The precipitate was removed and rinsed with chloroform. The filtrate was washed with 0.5 N sodium hydroxide solution (the cloudy solution had to be filtered through Celite), dried, and evaporated. After the mixture was dried overnight on a vacuum pump (0.1 mm), there was obtained a mixture of isomeric α-chloro sulfones as a beige foam: mass spectrum, calcd m/e 358.0794, obsd 358.0800.

The α-chloro sulfone mixture from above was dissolved in dry dioxane (250 mL) at 0 °C under nitrogen and treated with potassium *tert*-butoxide (35.1 g, 0.313 mol). The reaction mixture was heated gently at reflux for 20 h. After cooling, the dark brown reaction mixture was diluted with water and continuously extracted with ether for 2 days. Chromatography on silica gel with hexane elution gave 5.13 g (40%) of **18** as a yellow oil: IR (film) ν_{max} 3140–2700, 1510, 1480, 1380, 1215, 1200, 1185 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.2–7.0 (m, 6 H), 6.54 (d, J = 3.4 Hz, 1 H), 6.04 (d, J = 3.4 Hz, 1 H), 6.0–5.6 (m, 2 H), 3.3–0.4 (m, 8 H); mass spectrum, m/e 258.1408, obsd 258.1413.

(B) Paquette–Photis Ring Contraction of 17. To sulfone **17** (1.00 g, 3.08 mmol) in dry dioxane (40 mL) under nitrogen at 0 C was added 2.6 mL of 1.2 M *n*-butyllithium in hexane. The solution turned yellow and then brown. This solution was added via cannula to a refluxing slurry of lithium aluminum hydride (0.90 g, 24 mmol) in dioxane (25 mL). The reaction mixture was heated at reflux for 23 h, cooled, and treated with saturated sodium sulfate solution (5 mL). The solid was removed and rinsed with hexane (3 × 50 mL). The aqueous layer was removed. The combined organic phases were washed with saturated sodium chloride solution, dried, filtered, and evaporated to give a brown oil. Chromatography of this material on silica gel with petroleum ether gave 134 mg (17%) of **18** as a colorless oil.

(±)-9,10-Dihydro-5,6-benzo-4a,10a-ethenophenanthrene (19). Pyridinium hydrobromide perbromide (7.20 g, 22.5 mmol) and **18** (4.62 g, 17.9 mmol) in carbon tetrachloride and glacial acetic acid (65 mL of each) were stirred at room temperature for 24 h, diluted with water, and extracted with carbon tetrachloride. The combined organic layers were washed with water, 0.5 N sodium hydroxide solution, 10% sodium sulfite solution, and water prior to drying and solvent evaporation. The beige foam was dried under vacuum (0.1 mm) overnight and used below without further purification.

To the dibromide were added lithium fluoride (4.65 g, 0.179 mol), lithium carbonate (13.3 g, 0.180 mol), and dry HMPA (200 mL). The reaction mixture was stirred at 80–85 °C in an oil bath for 9 h under nitrogen, cooled, diluted with water, filtered through Celite, and extracted with hexane. The combined organic layers were washed with water, dried, and added to a column of basic alumina. The column was eluted with 1:1 hexane/benzene to give 4.22 g of **19** as an orange oil. This was used without further purification in the next step. A pure sample of **19** was obtained by MPLC (silica gel) with petroleum ether as the eluant: IR (film) ν_{max} 3120–2740, 1510, 1448, 1440, 1262, 1229, 1040, 923, 830, 810, 790, 750, 698, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.2–6.95 (m, 6 H), 6.70 (d, J = 2.4 Hz, 1 H), 6.02 (d, J = 2.4 Hz, 1 H), 6.2–5.4 (m, 4 H), 3.1–2.4 (m, 2 H), 2.0–1.5 (m, 2 H); mass spectrum, calcd m/e 256.1252, obsd 256.1260.

(+)- and (−)-*N*-2-Bornyl-5,6-dihydro-1,4:4a,10b-dietheno-naphtho[*f*]phthalazine-2,3(1*H*,4*H*)-dicarboximides (20 and 21). To a solution of **19** (4.22 g) in cold (−78 °C) ethyl acetate (40 mL) was added dropwise to a solution of (−)-*endo*-bornyl-1,2,4-triazoline-3,5-dione (4.00 g, 17.0 mmol) in ethyl acetate (15 mL). The reaction mixture was allowed to warm to room temperature, and the precipitate was collected to give 3.80 g of the **20**/**21** mixture (43% based on **19**) as a white solid, mp 263–265 °C. The analytical sample of the 1:1 diastereomer mixture was prepared by two recrystallizations from dichloromethane/ethyl acetate: mp 263.5–264.5 °C; UV (acetonitrile) 275 nm (ϵ 8.5 × 10^3), 230 (9.7 × 10^4); $[\alpha]_D$ −3.4° (*c* 11.9, chloroform); IR (KBr) ν_{max} 3100–2800, 1765, 1710, 1420, 1395, 1385, 815, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.91–7.23 (m, 6 H), 6.58 (d, J = 2.6 Hz, 1 H), 6.48–6.39 (m, 2 H), 6.17 (d, J = 2.9 Hz, 1 H), 5.33–5.21 (m, 1 H), 4.90–4.83 (m, 1 H), 2.92–1.26 (m, 12 H), 0.91 (s, 3 H), 0.83 (s, 3 H), 0.73 (s, 1.5 H), 0.70 (s, 1.5 H); ^{13}C NMR ($CDCl_3$) 159.9 (s), 159.7 (s), 143.9 (d), 140.3 (d), 137.3 (s), 133.5 (s), 130.8 (s), 129.6 (d), 129.1 (d), 128.9 (s), 127.9 (d), 127.6 (d), 127.4 (d), 126.0 (d), 124.6 (d), 123.4 (d), 61.3 (d), 61.1 (d), 61.0 (d), 59.3 (d), 51.7 (s), 50.5 (s), 47.7 (s), 47.5 (s), 45.4 (d), 31.0 (t), 29.5 (t), 29.3 (t), 27.1 (t), 26.6 (t), 19.6 (q), 18.7 (q), 14.1 ppm (q); mass spectrum, calcd m/e 491.2573, obsd 491.2583.

Anal. Calcd for $C_{32}H_{33}N_3O_2$: C, 78.18; H, 6.77. Found: C, 78.02; H, 6.75.

HPLC Separation of 20 and 21. Urazoles **20** and **21** were separated by band-shaving techniques on a Waters Prep 500 HPLC chromatograph using silica gel (elution with 20% ethyl acetate/petroleum ether). Due to the urazole's lack of solubility in the elution solvent, 700 mg was dissolved in 10 mL of dichloromethane and injected onto the column. Pure diastereomer **20** from the leading edge was characterized by the following rotations: $[\alpha]_D$ +128°, $[\alpha]_{578}$ +135°, $[\alpha]_{546}$ +156, $[\alpha]_{436}$ +297° (*c* 11.3, chloroform). Its ^1H NMR spectrum (300 MHz) is the same as that of the mixture except for the presence of only three methyl singlets for the *endo*-bornyl unit at δ 0.91, 0.83, and 0.73. Its ^{13}C NMR spectrum is the same as that of the mixture except for the absence of the doublet at 61.1 ppm.

(+)-9,10-Dihydro-5,6-benzo-4a,10a-ethenophenanthrene (19). To dry tetrahydrofuran (10 mL) under nitrogen was added lithium aluminum hydride (0.106 g, 2.79 mmol) followed by diastereomerically pure urazole **20** (0.170 g, 0.346 mmol). The reaction mixture was heated at reflux under nitrogen for 23 h (blackish yellow color) and then opened to the air for 1 h (turned orange). The excess hydride was quenched by the addition of a few drops of water which was added to the reaction mixture at 0° C (turned yellow). The solid was removed and rinsed with dichloromethane (5 × 10 mL). The combined filtrates were dried, filtered, and evaporated. The resulting oil was subjected to preparative layer chromatography on silica gel (two elutions with hexane) to give 14.8 mg (18%) of light yellow oil, the ^1H NMR spectrum of which showed it to be **19**. The rotations of the sample (15.8 mg) in 5.00 mL of chloroform were $[\alpha]_D$ +447°, $[\alpha]_{578}$ +474°, $[\alpha]_{546}$ +562°, and $[\alpha]_{436}$ +1282°.

(−)-9,10-Dihydro-5,6-benzo-4a,10a-ethenophenanthrene (19). A 4:1 mixture of urazoles **21** and **20** (0.172 g, 0.350 mmol) was degraded by the reductive method previously described to give 23.7 mg (26%) of a 4:1 mixture of (−)-**19** and (+)-**19** as a yellow oil. The rotations of this sample (23.7 mg) in 5.00 mL of chloroform were $[\alpha]_D$ −266°, $[\alpha]_{578}$ −281°, $[\alpha]_{546}$ −333°, and $[\alpha]_{436}$ −759°.

X-ray Crystal Structure Analysis of (−)-12. Crystals of (−)-**12** were orthorhombic, space group $P2_12_12_1$, with a = 11.225 (2) Å, b = 12.099 (3) Å, c = 17.164 (3) Å, and d_{calcd} = 1.252 g cm^{-3} for Z = 4($C_{28}H_{29}N_3O_2$, M_r = 439.56). The intensity data were measured on a Hilger-Watts diffractomerer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). A crystal measuring approximately 0.08 × 0.15 × 0.35 mm was used for data collection. A total of 1810 reflections were measured tor θ < 57°, of which 1333 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple solution procedure and was refined by full-matrix least-squares methods. In the final refinement, anisotropic thermal parameters were used for the heavier atoms, and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are R = 0.042 and R_w = 0.037 for the 1333 observed reflections. The final difference map has no peaks greater than ±0.2 eA^{-3}.

X-ray Crystal Structure Analysis of (+)-8b. The unit cell for (+)-**8b** contained two independent molecules, that is, two molecules not related by crystallographic symmetry. Normally, this only doubles the number of reflections to be measured and the number of atoms to be found, thus making the problem slightly harder to solve. In this case, however, the two molecules (designated as unprimed and primed) were nearly exactly related by a noncrystallographic rotation axis such that

$$x' = x - 0.503\ (6)$$

$$y' = 0.752\ (12) - y$$

$$z' = 0.492\ (3) - z$$

where the numbers in parentheses are the standard deviations. This noncrystallographic symmetry played havoc with the direct methods program (MULTAN) used to solve the structure, but in the end the complications were overcome.

The crystals were orthorhombic, space group $P2_12_12_1$, with $a = 13.444\ (3)$ Å $b = 14.168\ (3)$ Å, $c = 26.662\ (5)$ Å, and $d_{calcd} = 1.228$ g cm^{-3} for $Z = 8$ ($C_{30}H_{35}N_3O_2$, $M_r = 469.62$). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). A crystal measuring approximately $0.10 \times 0.20 \times 0.25$ mm was used for the data collection. A total of 3842 reflections were measured for $\theta < 57°$, of which 2528 were considered to be observed [$I > 2.5\ \sigma(I)$]. The structure was solved by multiple solution procedure[29] and was refined by block-diagonal least-squares methods in which the matrix was partitioned into two blocks. In the final refinement anisotropic thermal parameters were used for the nonhydrogen atoms, and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are $R = 0.075$ and $R_w = 0.073$ for the remaining 2528 observed reflections. The final difference map has no peaks greater than ±0.4 eA^{-3}.

X-ray Crystal Structure Analysis of (+)-20. The crystals of (+)-**20** were monoclinic, space group $P2_1$, with $a = 15.670\ (3)$ Å, $b = 7.408\ (2)$ Å, $c = 12.693\ (2)$ Å, $\beta = 97.63\ (1)°$, and $d_{calcd} = 1.311$ g cm^{-3} for $Z = 2$ ($C_{32}H_{33}N_3O_2{\cdot}CH_2Cl_2$, $M_r = 576.56$). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). A crystal measuring approximately $0.10 \times 0.30 \times 0.55$ mm was used for data collection; the data were collected for absorption ($\mu = 22.8$ cm^{-1}). A total of 2144 reflections were measured for $\theta < 57°$, of which 1874 were considered to be observed [$I < 2.5\ \sigma(I)$]. The structure was solved by a multiple solution procedure[29] and was refined by full-matrix least-squares methods. In the final refinement anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are $R = 0.062$ and $R_w = 0.068$ for the 1874 observed reflections. The final difference map has no peaks greater than ±0.4 eA^{-3}.

(29) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

Acknowledgment. The research carried out at The Ohio State University was made possible by grants from the National Cancer Institute (CA-12115) and the National Science Foundation (CHE 790033). The 300-MHz FT NMR spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant CHE-7910019) with the help of Drs. A. G. Marshall and C. E. Cottrell.

Registry No. **1a**, 37845-14-0; **1b**, 24018-47-1; (±)-**2a**, 78624-48-3; (±)-**2b**, 78624-49-4; (±)-**3a**, 78624-50-7; (±)-**3b**, 78624-51-8; (±)-**4a**, 78624-52-9; **4a** α-chlorosulfide 1, 78638-30-9; **4a** α-chlorosulfide 2, 78638-31-0; **4a** α-chlorosulfone 1, 78624-53-0; **4a** α-chlorosulfone 2, 78624-54-1; (±)-**4b**, 78638-32-1; **4b** α-chlorosulfide 1, 78638-33-2; **4b** α-chlorosulfide 2, 78638-34-3; **4b** α-chlorosulfone 1, 78638-35-4; **4b** α-chlorosulfone 2, 78624-55-2; (±)-**5a**, 78624-56-3; **5a** dibromide, 78624-57-4; (±)-**5b**, 78624-58-5; **5b** dibromide, 78624-59-6; (±)-**6a**, 78624-60-9; (-)-**6a**, 78683-86-0; (±)-**6b**, 78624-61-0; (+)-**6b**, 78683-87-1; (±)-**7a**, 78683-88-2; (±)-**7b**, 78624-62-1; (+)-**8a**, 78624-63-2; (+)-**8b**, 78624-64-3; (-)-**9a**, 78684-33-0; (-)-**9b**, 78683-89-3; (-)-**12**, 78683-90-6; **13**, 7512-19-8; (±)-**14**, 78624-65-4; (±)-**15**, 78624-66-5; (±)-**16**, 78638-36-5; **16** α-chlorosulfide 1, 78624-67-6; **16** α-chlorosulfide 2, 78624-68-7; **16** α-chlorosulfone 1, 78624-69-8; **16** α-chlorosulfone 2, 78624-70-1; (±)-**17**, 78624-71-2; (±)-**18**, 78624-72-3; **18** dibromide, 78624-73-4; (±)-**19**, 78624-74-5; (+)-**19**, 78683-91-7; (-)-**19**, 78683-92-8; (+)-**20**, 78624-75-6; (-)-**21**, 78683-93-9; butadiene, 106-99-0; (±)-1,4,9,10-tetrahydro-4a,10a-phenanthrenedimethanol, 78624-76-7; methanesulfonyl chloride, 124-63-0; *N*-methyltriazolinedione, 13274-43-6; (-)-*endo*-bornyl-1,2,4-triazoline-3,5-dione, 73462-83-6; diethyl oxalate, 95-92-1; ethyl γ-(2,5-dimethylphenyl)butyrate, 24018-46-0; (±)-5,8-dimethyl-1,4,9,10-tetrahydro-4a,10a-phenanthrenedimethanol, 78624-77-8; (±)-1,4,9,10-tetrahydro-5,6-benzo-4a,10a-phenanthrenedimethanol, 78624-78-9; (±)-1,4,9,10-tetrahydro-5,6-benzo-4a,10a-(methanooxomethano)-phenanthrene, 78624-79-0.

Supplementary Material Available: Tables of the final atomic parameters, final anisotropic thermal parameters, bond lengths, and bond angles for **12**, (+)-**8**, and (+)-**20** (19 pages). Ordering information is given on any current masthead page.

Silyl Phosphites. 16.[1] Mechanism of the Perkow Reaction and the Kukhtin-Ramirez Reaction. Elucidation by means of a New Type of Phosphoryl Rearrangements Utilizing Silyl Phosphites

Mitsuo Sekine, Masashi Nakajima, and Tsujiaki Hata*

Department of Life Chemistry, Tokyo Institute of Technology, Nagatsuta, Midoriku, Yokohama 227, Japan

Received April 28, 1981

Reactions of α-lithiated diethyl α-[(trimethylsilyl)oxy]benzylphosphonate (**4**) with benzoyl chloride and chloroiodomethane afforded benzoylated and chloromethylated products (**1** and **2**) corresponding to the 1:1 carbonyl adducts of diethyl trimethylsilyl phosphite with benzil and phenacyl chloride which were not obtained by the reactions between the phosphite and benzil or phenacyl chloride. Pyrolysis of **1** and **2** afforded 1,3,2-dioxaphosphole (**6**) and enol phosphate (**8**). On the other hand, treatment of **1** and **2** with tetrabutylammonium fluoride afforded benzoin phosphate (**7**) and 1,2-epoxy phosphonate (**14**), respectively, as the main products. These results are also discussed in connection with the mechanism of the Perkow reaction and the Kukhtin–Ramirez reaction.

The Perkow reaction, represented by the reaction of trialkyl phosphites with α-halo carbonyl compounds, is one of the most valuable reactions in organophosphorus chemistry and numerous examples have appeared in the

0022-3263/81/1946-4030$01.25/0 © 1981 American Chemical Society