3 H), 2.17 (dd, J = 15, 12 Hz, 1 H), 2.38 (d, J = 15 Hz, 1 H), 2.43 (dd, J = 15, 5 Hz, 1 H), 4.93 (s, 2 H), 5.93 (d, J = 2.6 Hz, 1 H), 6.53 (d, J = 2.6 Hz, 1 H), 6.95 (br d, J = 7 Hz, 2 H), 7.26 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 12.0, 18.7, 21.2, 22.5, 22.8, 23.9, 24.3, 28.0, 28.3, 29.3, 29.7, 31.9, 35.8, 36.2, 36.6, 39.6, 40.1, 42.5, 42.8, 49.9, 54.0, 56.4, 105.9, 116.2, 119.6, 126.4, 127.1, 127.7, 128.5, 138.8; IR ($CHCl_3$) 1445, 1380, 1370, 1355, 1320 cm^{-1}; exact mass calcd for $C_{36}H_{53}N$ 499.4178, found 499.4182.

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Registry No. **2**, 73770-26-0; **5**, 73770-27-1; **7**, 73770-28-2; **12**, 73770-29-3; **13**, 63608-54-8; **14**, 27335-83-7; **15a**, 73770-30-6; **15b**, 73770-31-7; **16**, 73789-31-8; **17**, 73770-32-8; **18**, 5011-78-9; **19a**, 73770-33-9; **19b**, 73770-34-0; **20**, 73770-35-1; **21**, 73789-32-9; vinyl bromide, 593-60-2; biacetyl, 431-03-8; benzil, 134-81-6; 3-hydroxy-3,4-diphenylbut-1-en-4-one, 30935-15-0; cyclohexane-1,2-dione, 765-87-7; 2-acetoxy-2-vinylcyclohexanone, 73770-36-2; 1-phenyl-2-acetoxy-3-buten-1-one, 73770-37-3; α,α-dichloroacetophenone, 2648-61-5; 2,2-dimethoxyphenylacetaldehyde, 19159-39-8; 1,1-dimethoxy-1-phenyl-2-hydroxy-3-butene, 73770-38-4; 1,1-dimethoxy-1-phenyl-2-acetoxy-3-butene, 73770-39-5; α,α-dimethoxyacetophenone, 6956-56-5; 1,1-dimethoxy-2-hydroxy-2-phenyl-3-butene, 73770-40-8; 2-hydroxy-3-phenyl-3-butenal, 73770-41-9; benzylamine, 100-46-9; tetrakis(triphenylphosphine)palladium, 14221-01-3; 1-benzyl-2,3-diphenylpyrrole, 53646-89-2; deoxybenzoin, 614-29-9; 1-benzyl-4,5,6,7-tetrahydroindole, 27866-39-3.

Syntheses of Dihydropyrenes with Functionality in the Cavity of the π-Electron Cloud

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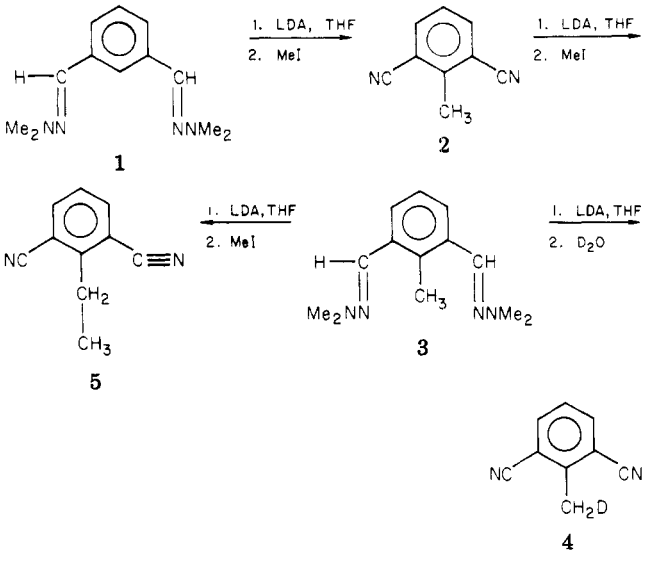
The cyano group is shown to be a good group for directing ortho lithiation and, with 2,6-dicyanotoluene as starting material, ortho lithiation provides easy access to a variety of 1,2,3-trisubstituted benzene derivatives. The use of such derivatives in the standard thiacyclophane synthesis of dihydropyrenes has provided in good yield *trans*-15-(4'-butenyl)-16-methyldihydropyrene (**14a**) and *trans*-15-(methoxyethyl)-16-methyldihydropyrene (**14b**), the first examples of dihydropyrenes having functionality within the cavity of the aromatic π-electron cloud.

Of the substituted dihydropyrenes prepared thus far, the internal substituents have been either hydrogen or saturated alkyl groups.[1] Although it has long been of interest to examine the properties of molecules having functionality within the cavity of an aromatic π-electron cloud, the attainment of this objective has been thwarted by certain practical difficulties. The reaction conditions employed in the standard thiacyclophane syntheses of dihydropyrenes are such that only certain types of functionality will survive these conditions unchanged. Secondly, the 1,2,3-trisubstitution pattern needed for such thiacyclophane precursors is an awkward one to provide synthetically, particularly if functionality is to be preserved. We now describe a convenient method for preparing 1,2,3-trisubstituted benzene derivatives and the employment of these precursors for syntheses of dihydropyrenes with internal substituents having vinyl and ether functional groups.

Recently, we reported a synthesis of *trans*-15-*n*-butyl-16-methyldihydropyrene in which a bis(oxazoline) derived from isophthalic acid was used to provide the 1,2,3-trisubstitution pattern through ortho lithiation.[2] Unfortunately, the removal of the oxazoline rings after alkylation requires a rather vigorous acidic hydrolysis, and under these conditions vinyl groups underwent undesired hydration and/or lactonization. To circumvent this, we examined other groups that have been used to direct ortho lithiation.

Corey and Enders have used *N,N*-dimethylhydrazones as protecting and directing groups for α-lithiation of aliphatic carbonyl derivatives.[3] When the bis(*N,N*-dimethylhydrazone) of isophthalaldehyde (**1**) was treated with lithium diisopropylamide (LDA) in tetrahydrofuran (THF) and the resulting anion was alkylated with methyl iodide, 2,6-dicyanotoluene (**2**) was isolated in 54% yield (Scheme I). It seemed likely that the conversion of the *N,N*-dimethylhydrazone group to a cyano group was simply a base-catalyzed elimination of dimethylamine. In support of this it was found that treatment of the bis(*N,N*-dimethylhydrazone) of 2-methylisophthalaldehyde (**3**) with LDA followed by addition of deuterium oxide gave in high yield 2,6-dicyano-α-deuteriotoluene (**4**). On the other hand, treatment of the anion of **3** with methyl iodide gave 2,6-dicyanoethylbenzene (**5**) in 81% yield. That the *N,N*-dimethylhydrazone group served no useful purpose,

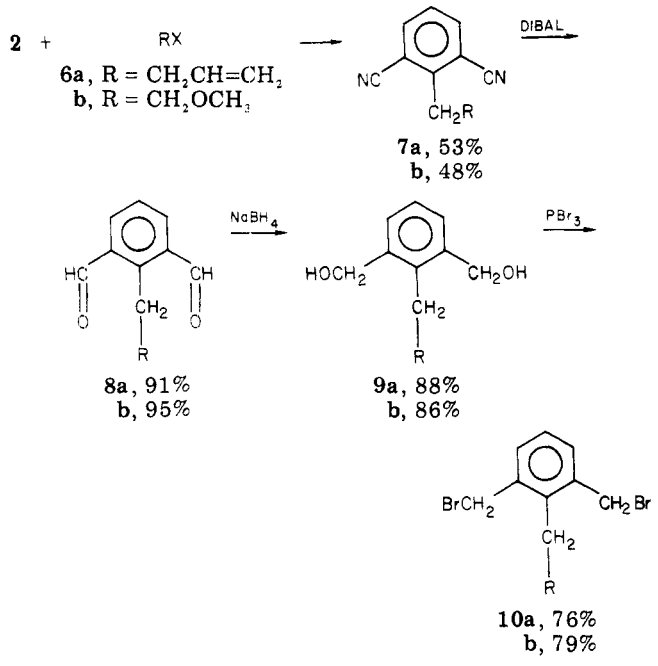
Scheme I



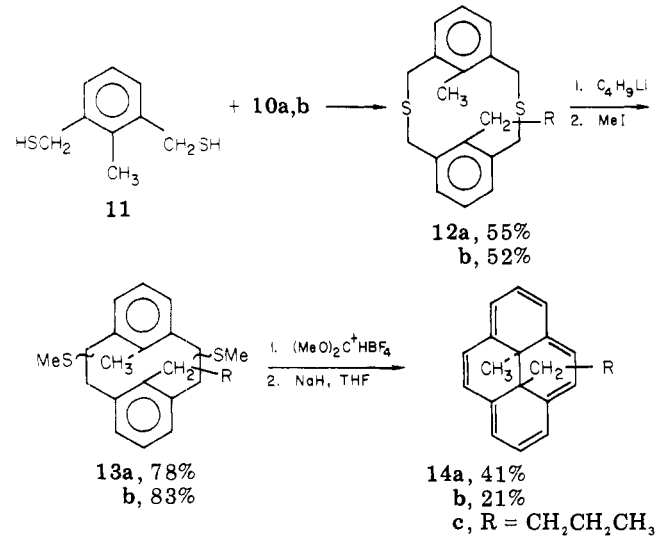
(1) Boekelheide, V. *Top. Nonbenzenoid Aromat. Chem.* **1973**, *1*, 47.
(2) Harris, T. D.; Neuschwander, B.; Boekelheide, V. *J. Org. Chem.* **1978**, *43*, 727.
(3) Corey, E. J.; Enders, D. *Tetrahedron Lett.* **1976**, 3.

0022-3263/80/1945-2746$01.00/0

Scheme II



Scheme III



other than being a precursor to the cyano group, was then shown by direct alkylation of 2,6-dicyanotoluene (**2**) with methyl iodide to give 2,6-dicyanoethylbenzene (**5**) in 84% yield.

These results establish 2,6-dicyanotoluene as an attractive precursor for syntheses of 1,2,3-trisubstituted benzene derivatives. As shown in Scheme II, alkylation of 2,6-dicyanotoluene (**2**) with allyl bromide (**6a**) or with chloromethyl methyl ether (**6b**) readily gave the desired products **7a** and **7b** in good yield. Reduction of cyano groups with diisobutylaluminum hydride (DIBAL) is a convenient, high-yield method of preparing aldehydes and readily converted **7a** and **7b** to the dialdehydes **8a** and **8b**. Subsequent reduction of **8a** and **8b** with sodium borohydride followed by treatment of the resulting alcohols, **9a** and **9b**, with phosphorus tribromide smoothly gave the dibromides **10a** and **10b**.

The coupling of the dibromides **10a** and **10b** with 2,6-bis(mercaptomethyl)toluene (**11**) proceeded smoothly in the usual fashion to give the dithiacyclophanes **12a** and **12b** (Scheme III). A Wittig rearrangement of the dithiacyclophanes gave the ring-contracted cyclophanes **13a** and **13b** which, by a Hofmann elimination reaction, then gave the desired dihydropyrenes, **14a** and **14b**.

Table I. Comparison of the Chemical Shifts of the Internal Protons of Dihydropyrenes 14a-c with Respect to the Type and Position of the Proton Relative to Standard Reference Values for That Type of Proton in the Absence of a Ring Current

distance from center	obsd chemical shift,[a] δ	ref value, δ	upfield shift due to ring current, ppm
One Atom Removed			
14a, $CH_2CH_2CH{=}CH_2$	−4.14	1.33[6]	5.47
CH_3	−4.25	0.91[6]	5.15
b, $CH_2CH_2OCH_3$	−3.52	1.33	4.85
CH_3	−4.30	0.91	5.21
c, $CH_2CH_2CH_2CH_3$	−4.02	1.33	5.35
CH_3	−4.30	0.91	5.21
Two Atoms Removed			
14a, $CH_2CH_2CH{=}CH_2$	0.36	2.00[6]	1.70
b, $CH_2CH_2OCH_3$	0.51	3.40[6]	2.89
c, $CH_2CH_2CH_2CH_3$	−1.71	1.33	3.04
Three Atoms Removed			
14a, $CH_2CH_2CH{=}CH_2$	3.86	5.72[6]	1.86
c, $CH_2CH_2CH_2CH_3$	−0.41	1.33	1.74
Four Atoms Removed			
14a, $CH_2CH_2CH{=}CH_2$	3.50	5.28[6]	1.78
b, $CH_2CH_2OCH_3$	2.40	3.30[6]	0.90
c, $CH_2CH_2CH_2CH_3$	−0.10	0.91	1.01

[a] Midpoint values of multiplets.

The dihydropyrenes **14a** and **14b** are low-melting, dark green needles, whose ultraviolet and visible spectra are quite analogous to that of *trans*-15-*n*-butyl-16-methyldihydropyrene (**14c**).[2] Also, similar to the case of **14c**, the mass spectra of **14a** and **14b** show low-intensity parent molecular ions with a fragmentation pattern of predominantly ejecting first the bulky internal substituent and second the internal methyl group to give a very strong signal for the pyrene ion.

It is of interest that the proton chemical shift for the internal methyl group has essentially the same value for all three dihydropyrenes, **14a–c**, as well as for *trans*-15,16-dimethyldihydropyrene itself.[4] This clearly shows that the extent of the ring current in all four of these dihydropyrenes is essentially the same and suggests that there is little, if any, interaction between the peripheral π-electron cloud and the π electrons of the vinyl group in **14a** or the p electrons of the ether group in **14b**. Examining the ring-current effects on the proton chemical shifts of the internal 4′-butenyl and methoxyethyl groups provides an extended mapping of the magnetic field due to ring current in these molecules. For a precise evaluation of the ring-current effect, the exact time-averaged position in space of each proton being compared should be used.[5] However, since those data are not known to us, we have instead made a comparison in Table I of the ring-current effects of the various internal protons in **14a–c**, correlating them as being one, two, three, or four atoms removed from the center of the molecule. This is not exact, of course, because of differing bond lengths and bond angles, but it does provide a rough comparison and leads to the con-

(4) Phillips, J. B.; Boekelheide, V. *J. Am. Chem. Soc.* **1967**, *89*, 1695.
(5) Otsubo, T.; Gray, R.; Boekelheide, V. *J. Am. Chem. Soc.* **1978**, *100*, 2449.
(6) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon: New York, 1969; Part 3, Chapters 1–3.

clusion that the absolute magnitude of the ring-current effect is approximately the same within each category and pretty much independent of the type of functionality adjacent to the proton being considered.

Experimental Section[7]

Bis(dimethylhydrazones) 1 and 3. These were prepared by following the procedure of Newkome and Fishel.[8] From the reaction of 13.4 g (0.1 mol) of isophthalaldehyde with 23.7 g (0.4 mol) of anhydrous *N,N*-dimethylhydrazine there was isolated 20.0 g (92%) of **1** as a pale yellow oil: bp 134–135 °C (0.15 mm); ^{1}H NMR δ 3.00 (12 H, s, $N(CH_3)_2$), 7.28 (2 H, s, ArCH=N), 7.34–7.56 (3 H, A_2B, J_{AB} = 8 Hz, J_{AC} = 2 Hz, Ar H), 7.72 (1 H, d, J_{AC} = 2 Hz, Ar H); mass spectrum, *m/e* 218, 203, 188, 170, 155, 143. Anal. Calcd for $C_{12}H_{18}N_4$: C, 66.06; H, 8.26. Found: C, 66.12; H, 8.21.

From the reaction of 14.8 g (0.1 mol) of 2-methylisophthalaldehyde and 23.7 g (0.4 mol) of anhydrous *N,N*-dimethylhydrazine there was isolated 20.8 g (90%) of **3** as a pale yellow oil: bp 142–143 °C (0.018 mm); ^{1}H NMR δ 2.50 (3 H, s, $ArCH_3$), 3.02 (12 H, s, $N(CH_3)_2$), 7.10–7.77 (3 H, A_2B, J_{AB} = 9 Hz, Ar H), 7.57 (2 H, s, ArCH=N). Anal. Mol wt Calcd for $C_{13}H_{20}N_4$: 232.169. Found (high-resolution mass spectrum): 232.168.

Methylation of 1 To Give 2,6-Dicyanotoluene (2). To a solution of 6.6 mmol of lithium diisopropylamide in 25 mL of THF there was added dropwise with stirring a solution of 436 mg of **1** in 10 mL of THF. After the mixture had been stirred for 1 h, the red solution was quenched with excess methyl iodide. Water was then added, and the organic layer was extracted with four 50-mL portions of ether. The ether extract was washed successively with aqueous acid and water, dried, and concentrated. The residual brown oil was chromatographed over silica gel by using dichloromethane for elution to give 2,6-dicyanotoluene in 54% yield as white crystals [mp 136–137 °C (lit.[9] mp 135–136 °C)] identical in all respects with an authentic specimen.

Conversion of 3 to 2,6-Dicyanoethylbenzene (5) and to 2,6-Dicyano-α-deuteriotoluene (4). To a solution of 13.2 mmol of lithium diisopropylamide in 50 mL of THF there was added dropwise with stirring a solution of 928 mg of **3** in 20 mL of THF. After the deep red solution had been stirred under an atmosphere of argon at −78 °C for 1 h, it was divided into two equal parts. To the first part was added an excess of methyl iodide with stirring. Water was then added, and the organic layer was extracted with four 50-mL portions of ether. The ether extract was washed successively with aqueous acid and water, dried, and concentrated. The residual oil was chromatographed over silica gel by using dichloromethane for elution to give 231 mg (81%) of pale yellow crystals: mp 116–118 °C (lit.[10] mp 118 °C); ^{1}H NMR δ 2.38 (3 H, t, J_{AX} = 8 Hz, CH_3), 3.14 (2 H, q, J_{XA} = 8 Hz, $ArCH_2CH_3$), 7.46 (1 H, t, A_2B, J_{BA} = 6 Hz, Ar H), 7.84 (2 H, d, A_2B, J_{AB} = 6 Hz, Ar H); IR (Nujol) 2350 cm^{-1} (C≡N), no absorption present for ArCH=N.

To the second half of the solution of the anion of **3** there was added an excess of deuterium oxide. After the reaction mixture had been worked up as described for the first half of the solution, **4** was isolated as white crystals [mp 135–136 °C (lit.[9] mp 135–136 °C)] whose ^{1}H NMR spectrum showed the substitution of approximately one deuterium at the benzylic position.

Alkylation of 2,6-Dicyanotoluene (2) To Give 5 and 7a,b. To a solution of 3 mmol of lithium diisopropylamide in 50 mL of THF there was added dropwise with stirring at −78 °C a mixture of 142 mg (1 mmol) of 2,6-dicyanotoluene (**2**) and 3 mmol of tetramethylethylenediamine in 15 mL of THF. After the resulting deep blue solution had been stirred at −78 °C for 2 h, an excess (10 mmol) of methyl iodide was added, and the resulting mixture was stirred for an additional 2 h. Ice (25 g) was then added with vigorous stirring, and the organic layer was extracted with ether. The ether extract was washed successively with aqueous acid and water, dried, and concentrated. The residual oil was chromatographed over silica gel by using dichloromethane for elution to give 131 mg (84%) of **5** as pale yellow crystals [mp 116–118 °C] identical in all respects with an authentic sample of 2,6-dicyanoethylbenzene.[10]

When the above experiment was repeated with allyl bromide (**6a**) in place of methyl iodide, workup as described before gave 96 mg (53%) of **7a** as an oil: ^{1}H NMR δ 2.56 (2 H, q, J = 7 Hz, $CH_2CH_2CH=CH_2$), 3.22 (2 H, t, J = 7 Hz, $ArCH_2$), 5.06 (2 H, m, $CH=CH_2$), 5.72–6.10 (1 H, m, $CH_2CH=CH_2$), 7.52 (1 H, t, J = 8 Hz, Ar H), 7.90 (2 H, d, J = 8 Hz, Ar H); mass spectrum, *m/e* 182, 168, 143, 116. Anal. Mol wt Calcd for $C_{12}H_{10}N_2$: 182.085. Found (high-resolution mass spectrum): 182.085.

When the above experiment was repeated with chloromethyl methyl ether (**6b**) in place of methyl iodide, workup as described before gave 89 mg (48%) of **7b** as a colorless oil: ^{1}H NMR δ 3.21 (3 H, s, CH_3), 3.23 (2 H, t, J_{AX} = 5 Hz, $ArCH_2$), 3.66 (2 H, t, J_{XA} = 6 Hz, $CH_2CH_2OCH_3$), 7.48 (1 H, A_2B, J = 8 Hz, Ar H), 7.82 (2 H, d, J = 8 Hz, Ar H); mass spectrum, *m/e* 186, 171, 156, 155, 141, 128. Anal. Mol wt Calcd for $C_{11}H_{10}ON_2$: 186.077. Found (high-resolution mass spectrum): 186.078.

DIBAL Reduction of 7a,b To Give 8a,b. To a solution of 309 mg of **7a** in 20 mL of benzene there was added dropwise with stirring under a nitrogen atmosphere 29 mL of a 20% solution of DIBAL in benzene. After the addition was complete, the orange solution was stirred an additional hour at room temperature, and then it was decomposed by successive additions with stirring of methanol, a 1:1 aqueous methanol solution, and a 3.6 N aqueous solution of hydrochloric acid. The organic layer was extracted with ether; the ether extract was washed with water, dried, and concentrated. The residual oil was chromatographed over silica gel by using dichloromethane for elution to give 291 mg (91%) of **8a** as a colorless oil: ^{1}H NMR δ 2.30 (2 H, q, J = 8 Hz, $CH_2CH_2CH=CH_2$), 3.48 (2 H, t, J = 8 Hz, $ArCH_2CH_2$), 4.82–5.01 (2 H, m, $CH=CH_2$), 5.60–6.08 (1 H, m, $CH_2CH=CH_2$), 7.42 (1 H, A_2B, J = 7 Hz, Ar H), 7.95 (2 H, d, J = 7 Hz, Ar H), 10.28 (2 H, s, CH=O); mass spectrum, *m/e* 188, 173, 170, 160, 147, 141. Anal. Mol wt Calcd for $C_{12}H_{12}O_2$: 188.084. Found (high-resolution mass spectrum): 188.083.

When the above experiment was repeated with 316 mg of **7b** instead of **7a**, there was isolated 310 mg (95%) of **8b** as a colorless oil: ^{1}H NMR δ 3.10 (3 H, s, OCH_3), 3.32–3.64 (4 H, m, $ArCH_2CH_2O$), 7.40 (1 H, t, J = 9 Hz, Ar H), 7.92 (2 H, d, J = 9 Hz, Ar H), 10.18 (2 H, s, ArCH=O); mass spectrum, *m/e* 192, 177, 165, 160, 147, 132. Anal. Mol wt Calcd for $C_{11}H_{12}O_3$: 192.079. Found (high-resolution mass spectrum): 192.081.

Sodium Borohydride Reduction of 8a,b To Give 9a,b. A solution of 188 mg (1 mmol) of **8a** in 5 mL of THF was added to a mixture of 250 mg of sodium borohydride in 4 mL of THF. After the mixture had been stirred at room temperature overnight, it was decomposed by addition of 3 N aqueous hydrochloric acid, and the organic layer was extracted with ether. The ether extract was washed with water, dried, and concentrated. The residual oil was chromatographed over silica gel by using dichloromethane for elution to give 169 mg (88%) of **9a** as a colorless oil: ^{1}H NMR δ 2.22 (2 H, q, J = 6 Hz, CH_2CH_2), 2.79 (2 H, br s, OH), 2.66–2.82 (2 H, t, J = 6 Hz, $ArCH_2$), 4.64 (4 H, s, $ArCH_2$), 4.96–5.17 (2 H, m, $CH=CH_2$), 5.72–6.10 (1 H, m, $CH=CH_2$), 7.11–7.38 (3 H, m, Ar H); mass spectrum, *m/e* 192, 175, 162, 157, 152, 142, 129, 122, 95, 91. Anal. Mol wt Calcd for $C_{12}H_{16}O_2$: 192.241. Found (high-resolution mass spectrum): 192.239.

When the above experiment was repeated with 192 mg of **8b** instead of **8a**, there was isolated 169 mg of **9b** as a colorless oil: ^{1}H NMR δ 1.6 (2 H, s, OH), 2.81 (2 H, t, J = 6 Hz, CH_2O), 2.96 (2 H, t, J = 6 Hz, $ArCH_2$), 3.22 (3 H, s, OCH_3), 4.55 (4 H, s, $ArCH_2$), 7.16–7.38 (3 H, m, Ar H); mass spectrum, *m/e* 196, 179, 164, 162, 158, 144, 117, 91. Anal. Mol wt Calcd for $C_{11}H_{16}O_3$: 196.110. Found (high-resolution mass spectrum): 196.109.

Reaction of 9a,b with Phosphorus Tribromide To Give 10a,b. A solution of 0.5 mL of phosphorus tribromide in 4 mL of benzene was added dropwise with stirring to a solution of 192 mg (1 mmol) of **9a** in 5 mL of benzene. The resulting solution

(7) Mass spectra (taken at 70 eV) and elemental analyses are by Dr. R. Wielesek of the University of Oregon Microanalytical Laboratories. Ultraviolet and visible spectra were measured with a Cary 15 spectrometer. NMR spectra were measured with deuteriochloroform as solvent and tetramethylsilane as an internal standard on a Varian XL-100 instrument. Melting points were taken with a Mel-Temp apparatus and are uncorrected.

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(9) Lindsay, W. S.; Stokes, P.; Humber, L. G.; Boekelheide, V. *J. Am. Chem. Soc.* **1961**, *83*, 943.

(10) Tsai, C. H. Ph.D. Thesis, University of Oregon, 1975.

was then boiled under reflux for 0.5 h and cooled, and ice was added with stirring. The organic layer was extracted with ether, washed with water, dried, and concentrated. The residual oil was chromatographed over silica gel by using dichloromethane for elution to give 240 mg (76%) of **10a** as a pale yellow oil: ^{1}H NMR δ 2.44 (2 H, q, J = 9 Hz, $CH_2CH{=}CH_2$), 3.00 (2 H, t, J = 9 Hz, $ArCH_2$), 4.56 (4 H, s, $ArCH_2$), 5.18 (2 H, m, $CH{=}CH_2$), 5.78–6.18 (1 H, m, $CH{=}CH_2$), 7.10–7.40 (3 H, m, Ar H); mass spectrum, m/e 320, 318, 316, 279, 277, 275, 240, 239, 238, 237, 236. Anal. Mol wt Calcd for $C_{12}H_{14}Br_2$: 315.944. Found (high-resolution mass spectrum): 315.945.

When the above experiment was repeated with substitution of 196 mg (1 mmol) of **9b** for **9a**, there was isolated 252 mg (79%) of **10b** as a pale yellow oil: ^{1}H NMR δ 2.90 (2 H, t, CH_2O), 3.12 (2 H, t, $ArCH_2$), 3.36 (3 H, s, OCH_3), 4.40 (4 H, s, $ArCH_2$), 7.08–7.38 (3 H, m, Ar H); mass spectrum, m/e 324, 322, 320, 243, 241, 223, 221, 219, 198, 196, 160. Anal. Mol wt Calcd for $C_{11}H_{14}OBr_2$: 319.961. Found (high-resolution mass spectrum): 319.960.

Coupling Reactions of 2,6-Bis(mercaptomethyl)toluene (11) with 10a,b To Give 12a,b. A solution of 184 mg (1 mmol) of 2,6-bis(mercaptomethyl)toluene (**11**)[11] and 316 mg (1 mmol) of **10a** in 50 mL of dry, degassed benzene was placed in a 50-mL, gas-tight syringe, and this in turn was placed in a syringe pump. This solution was then added, under syringe pump control, at the rate of 2 mL/h with stirring to a solution of 125 mg (2.2 mmol) of potassium hydroxide in 2.5 L of degassed ethanol. When the addition was complete, the mixture was stirred for another 24 h and then concentrated. The residue was taken up in chloroform and the mixture washed with water, dried, and concentrated. The resulting solid was chromatographed over silica gel by using benzene for elution to give 185 mg (55%) of a mixture of the syn and anti isomers of **12a** as white crystals: mp 189–194 °C; ^{1}H NMR δ 1.32 and 1.76 (3 H, s, syn and anti $ArCH_3$), 3.62–3.92 (8 H, m, CH_2S), 4.76–4.92 (2 H, m, $CH{=}CH_2$), 5.38–5.74 (1 H, m, $CH{=}CH_2$), 7.10–7.30 (6 H, m, Ar H); mass spectrum, m/e 340, 300, 265, 189, 146. Anal. Mol wt Calcd for $C_{21}H_{24}S_2$: 340.132. Found (high-resolution mass spectrum): 340.136.

When the above experiment was repeated with 320 mg (1 mmol) of **10b** instead of **10a**, there was isolated 182 mg (53%) of a mixture of the syn and anti isomers of **12b** as white crystals: mp 176–179 °C; ^{1}H NMR δ 1.24 and 1.36 (3 H, s, $ArCH_3$), 2.04 (2 H, t, J = 8 Hz, $ArCH_2$), 2.96 (2 H, m, J = 8 Hz, CH_2OCH_3), 3.14 (3 H, s, OCH_3), 3.72 (8 H, m, CH_2S), 7.04–7.38 (6 H, m, Ar H); mass spectrum, m/e 344, 312, 265, 193, 161, 149, 147, 118. Anal. Mol wt Calcd for $C_{20}H_{24}OS_2$: 344.124. Found (high-resolution mass spectrum): 344.128.

Wittig Rearrangements of 12a,b To Give 13a,b. To a solution of 170 mg (0.5 mmol) of **12a** in 10 mL of THF there was added 1.5 mmol of n-butyllithium in hexane at 0 °C. After the mixture had been stirred for 4 min, it was quenched by addition of 1 mL of methyl iodide and stirred an additional 10 min. The mixture was then taken up in dichloromethane, washed with water, dried, and concentrated. The residual oil was chromatographed over silica gel by using a 1:1 mixture of ether–benzene for elution. From the main fraction of eluate there was obtained 144 mg (78%) of a mixture of isomers corresponding to **13a** as a pale yellow oil: ^{1}H NMR δ 1.38 (3 H, s, $ArCH_3$), 1.40–1.84 (4 H, m, CH_2CH_2), 2.20 (6 H, s, SCH_3), 3.58–4.05 (6 H, m, CH_2CHS), 4.78–4.82 (2 H, m, $CH{=}CH_2$), 5.42–5.82 (1 H, m, $CH{=}CH_2$), 7.03–7.65 (6 H, m, Ar H); mass spectrum, m/e 368, 343, 328, 314, 305, 280, 265, 229, 205, 202, 175, 158, 139, 119. Anal. Mol wt Calcd for $C_{23}H_{28}S_2$: 368.347. Found (high-resolution mass spectrum): 368.351.

When the above experiment was repeated with 172 mg (0.5 mmol) of **12b** instead of **12a**, there was isolated 154 mg (83%) of a mixture of isomers corresponding to **13b** as a colorless oil: ^{1}H NMR δ 1.38 (3 H, s, $ArCH_3$), 2.02 (2 H, t, J = 7 Hz, $ArCH_2$), 2.20 (6 H, s, SCH_3), 2.97 (2 H, t, J = 7 Hz, CH_2CH_2O), 3.12 (3 H, s, OCH_3), 3.50–3.92 (6 H, m, CH_2CHS), 7.06–7.39 (6 H, m, Ar H); mass spectrum, m/e 372, 357, 342, 328, 315, 285, 271, 239, 179, 123. Anal. Mol wt Calcd for $C_{22}H_{28}OS_2$: 372.342. Found (high-resolution mass spectrum): 372.340.

***trans*-15-(β-Methoxyethyl)-16-methyldihydropyrene (14b).** A solution of 37 mg (0.1 mmol) of **13b** in 5 mL of dry dichloromethane was added dropwise with stirring to a suspension of 110 mg of dimethoxycarbonium fluoroborate[12] in 3 mL of dichloromethane held at −30 °C under a nitrogen atmosphere. The mixture was stirred for 6 h, the supernatant liquid was decanted, and the residue was stirred with ethyl acetate. Again, the supernatant liquid was decanted, and the residue was stirred with fresh ethyl acetate. The bis(dimethylsulfonium) salt of **13b** was collected by filtration and dried. It was then dissolved in 10 mL of THF, and to this, under a nitrogen atmosphere, there was added portionwise with stirring over a period of 2 h a suspension of 150 mg of sodium hydride in 15 mL of THF. After the resulting mixture had been stirred an additional 6 h, the dark green solution was then decomposed by successive additions with stirring of 10 mL of benzene, 2 mL of water, and 3 mL of a 3 N aqueous solution of hydrochloric acid. The organic layer was then extracted with benzene, washed with water, dried, and concentrated. The resulting residue was chromatographed over silica gel by using a 1:1 mixture of hexane–benzene for elution. From the main fraction of eluate there was obtained 12 mg (43%) of **14b** as dark green needles: mp 50–51 °C; ^{1}H NMR δ −4.30 (3 H, s, CH_3), −3.43 to −3.63 (2 H, t, J = 8 Hz, CH_2CH_2), −0.40 to −0.61 (2 H, t, J = 8 Hz, CH_2CH_2O), 2.40 (3 H, s, OCH_3), 7.98–8.26 (2 H, m, Ar H), 8.58–8.82 (8 H, m, Ar H); UV (cyclohexane) 275 nm (ϵ 770), 324 (31 000), 337 (67 000), 346 (98 000), 357 (25 000), 380 (38 000), 430 (4100), 481 (5700), 533 (610), 569 (320), 583 (240), 635 (690), 651 (570); mass spectrum, m/e (relative intensity) 276 (6), 217 (48), 202 (100), 189 (32). Anal. Mol wt Calcd for $C_{20}H_{20}O$: 276.151. Found (high-resolution mass spectrum): 276.152.

***trans*-15-(4′-Butenyl)-16-methyldihydropyrene (14a).** The conversion of **13a** to **14a** was carried out just as described for the preparation of **14b**. From 37 mg (0.1 mmol) of **13a** there was obtained 11 mg (41%) of **14a** as dark green needles: mp 42–43 °C; ^{1}H NMR δ −4.25 (3 H, s, CH_3), −4.21 to −4.10 (2 H, t, $CH_2CH_2CH{=}CH_2$), 0.29–0.42 (2 H, m, $CH_2CH{=}CH_2$), 3.39–3.61 (3 H, m, $CH{=}CH_2$), 7.98–8.26 (2 H, m, Ar H), 8.58–8.82 (8 H, m, Ar H); UV (cyclohexane) 237 nm (ϵ 5700), 275 (680), 320 (37 500), 341 (96 300), 345 (10 500), 358 (33 000), 380 (41 000), 384 (49 000), 415 (4200), 439 (3800), 450 (5900), 475 (6100), 483 (5700), 534 (600), 574 (570), 590 (620), 605 (1300), 617 (1500), 634 (1850), 651 (2000); mass spectrum, m/e (relative intensity) 272 (3), 257 (5), 217 (60), 202 (100), 189 (32), 174 (16), 102 (42). Anal. Mol wt Calcd for $C_{21}H_{20}$: 272.157. Found (high-resolution mass spectrum): 272.157.

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Registry No. 1, 73712-54-6; **2**, 2317-22-8; **3**, 73712-55-7; **4**, 73712-56-8; **5**, 41052-95-3; **6a**, 106-95-6; **6b**, 107-30-2; **7a**, 73712-57-9; **7b**, 73712-58-0; **8a**, 73712-59-1; **8b**, 73712-60-4; **9a**, 73728-28-6; **9b**, 73712-61-5; **10a**, 73712-62-6; **10b**, 73712-63-7; **11**, 41563-67-1; *syn*-**12a**, 73712-64-8; *anti*-**12a**, 73745-82-1; *syn*-**12b**, 73712-65-9; *anti*-**12b**, 73745-83-2; **13a**, 73712-36-4; **13b**, 73712-37-5; **14a**, 73712-66-0; **14b**, 73712-67-1; **14c**, 64682-47-9; isophthalaldehyde, 626-19-7; *N,N*-dimethylhydrazine, 57-14-7; 2-methylisophthalaldehyde, 51689-50-0.

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