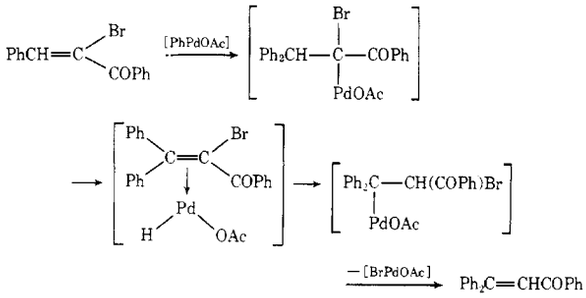
IIIf: mp 122 °C; IR (KBr) 1643, 1595, 1522, 1445, 1344, 780, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.90–7.08 (m, 15 H, phenyl). Found: C, 76.70; H, 4.58; N, 4.20.

IIIg: mp 116 °C; IR (KBr) 1731, 1645, 1449, 1233, 1107, 778, 700 cm^{-1}; NMR ($CDCl_3$) δ 7.95–7.10 (m, 15 H, phenyl), 4.03 (q, 2 H, methylene, J = 7 Hz), 0.93 (t, 3 H, methyl). Found: C, 80.95; H, 5.60.

Registry No.—IIe, 60999-93-1; IIf, 60999-95-3; IIg, 60999-96-4; IIh, 606-86-0; IIIe, 60999-94-2; IIIf, 60999-97-5; IIIg, 61024-39-3; V, 64235-45-6; benzene, 71-43-2; $Pd(OAc)_2$, 3375-31-3.

References and Notes

(1) (a) I. Moritani and Y. Fujiwara, *Tetrahedron Lett.*, 1119 (1967); (b) Y. Fujiwara, R. Asano, I. Moritani, and S. Teranishi, *J. Org. Chem.*, **41**, 1681 (1976), and references therein.
(2) (a) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5518 (1968); (b) H. A. Dieck and R. F. Heck, *ibid.*, **96**, 1133 (1974), and references therein.
(3) K. Yamamura and S. Watarai, *Bull. Chem. Soc. Jpn.*, **48**, 3757 (1975).
(4) K. Yamamura, *J. Chem. Soc., Perkin Trans. 1*, 988 (1975).
(5)



(6) Attempted isolation of IV by hydrolysis of IIg was unsuccessful and IIh was produced directly from IIg.
(7) T. Sakakibara, S. Nishimura, K. Kimura, I. Minato, and Y. Odaira, *J. Org. Chem.*, **35**, 3884 (1970).
(8) The structures of II'e was determined by its NMR spectrum; the spectrum of IIe shows the methine proton signals at δ 6.34 and 5.33 (doublet). II'e shows no peak in the δ 6.34 region from a methine proton on the carbon bearing two benzoyl groups and the signal at δ 5.34 changes to a triplet.
(9) R. F. Heck, *J. Am. Chem. Soc.*, **91**, 6707 (1969).
(10) It seems that this carbanion is stabilized by the two powerful electronwithdrawing groups on the same carbon atom bearing the negative charge.
(11) Formed by the oxidative coupling of benzene.
(12) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. 1, Academic Press, New York, N.Y., 1971, p 66.
(13) Ph.D. Thesis of K. Yamamura, Osaka University, 1975 (in Japanese).
(14) According to this mechanism (vida infra), the yield of the saturated compounds should be lower than those of the olefinic compounds.

$$RCH_2CH_2M \rightarrow RCH{=}CH_2 + [M\text{-}H]$$

$$RCH_2CH_2M + [M\text{-}H] \rightarrow RCH_2CH_3 + 2M$$

(15) H. Horino, M. Arai, and N. Inoue, *Bull. Chem. Soc. Jpn.*, **47**, 1683 (1974).
(16) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).
(17) W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **75**, 5990 (1953).
(18) T. Yokoyama and F. Nohara, *Bull. Chem. Soc. Jpn.*, **38**, 1498 (1965).
(19) R. E. Lutz, D. F. Hinkey, and R. H. Jordan, *J. Am. Chem. Soc.*, **73**, 4647 (1951).
(20) E. F. Pratt and E. Werble, *J. Am. Chem. Soc.*, **72**, 4638 (1950).
(21) K. Yamamura, S. Watarai, and T. Kinugasa, *Bull. Chem. Soc. Jpn.*, **44**, 2440 (1971).
(22) G. S. Cruiskshanks, *J. Prakt. Chem.* (*2*), **89**, 194 (1914).

A Synthesis of *trans*-15-*n*-Butyl-16-methyldihydropyrene. Synthetic Access to 1,2,3-Trisubstituted Benzene Derivatives via Direct Alkylation of 1,3-Bis(4',4'-dimethyl-2'-oxazolinyl)benzene

Thomas D. Harris, Brent Neuschwander, and Virgil Boekelheide*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Received July 18, 1977

A convenient general synthesis of 15,16-dihydropyrenes requires easy access to 1,2,3-trisubstituted benzene derivatives having appropriate functionality. It is now shown that isophthalic acid on conversion to 1,3-bis(4',4'-dimethyl-2'-oxazolinyl)benzene (**1**), followed by alkylation of the corresponding anion, gives the 2-alkyl derivatives **3** and **4** in high yield. Similarly, alkylation of the anion of 2,6-bis(4',4'-dimethyl-2'-oxazolinyl)toluene (**3**) occurs smoothly to give 2-substituted 1,3-bis(4',4'-dimethyl-2'-oxazolinyl)benzene derivatives (**8** or **9**). The hydrolysis of 2-*n*-butyl-1,3-bis(4',4'-dimethyl-2'-oxazolinyl)benzene (**8**) to 2-*n*-butylisophthalic acid and its subsequent conversion to dithiacyclophane **13** followed by a Wittig rearrangement and a Hofmann elimination to give *trans*-15-*n*-butyl-16-methyldihydropyrene (**15**) are described.

The route involving synthesis of dithiacyclophanes,[1-4] followed by elimination of sulfur to give cyclophanes,[5-9] cyclophanedienes,[10-12] and dihydropyrenes,[1] has proved to be an extremely useful method. The general application of this method, though, requires the availability of 1,2,3-trisubstituted benzene derivatives with appropriate functionality as starting materials. For the important case requiring 2,6-bis(bromomethyl)toluene, this starting compound can be made in a reasonable fashion from commercial chemicals. However, for other examples, where the internal substituents of the target dihydropyrenes are varied, the synthesis of the requisite starting materials is a tedious chore.[13] We now describe a method of alkylating aromatic rings which provides 1,2,3-trisubstituted benzene derivatives conveniently and in high yield.

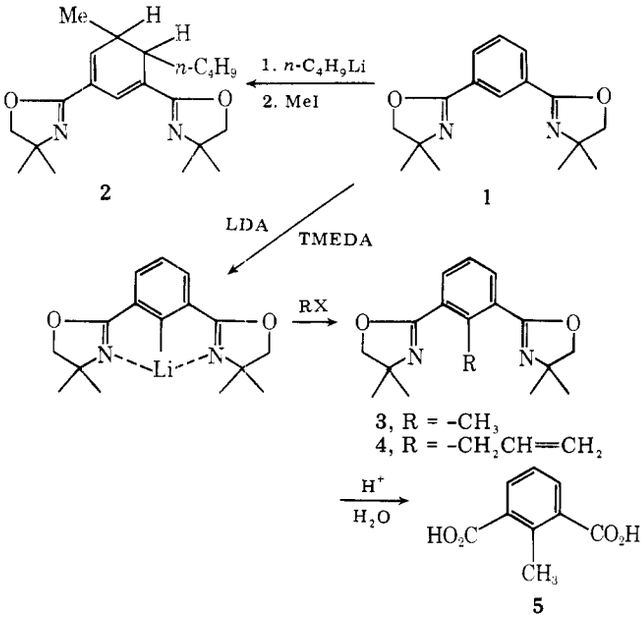
Metalation of anisoles followed by reaction with an electrophile has been a useful synthetic procedure and recent developments of this method have been summarized in a series of papers by Slocum.[14] The extensive studies of Meyers on aryloxazolines led to the discovery that the reaction of *o*-methoxyaryloxazolines with Grignaid reagents and organolithium compounds results in the displacement of the methoxyl by alkyl or aryl substituents.[15] Gschwend and Hamdan showed that the reaction of simple aryloxazolines with alkyllithium reagents followed by treatment with an electrophile leads to introduction of the electrophilic substituent ortho to the oxazoline group.[16] Furthermore, *o*-methylaryloxazolines on reaction with *n*-butyllithium followed by reaction with an electrophile generates a product in which the electrophilic substituent is attached to the methyl group. Subsequently, Gschwend et al. extended this method to show that *N,N*-dimethylbenzamides can be readily converted to ortho-substituted aryl ketones.[17]

It appeared to us that the oxazoline ring served two func-

0022-3263/78/1943-0727$01.00/0

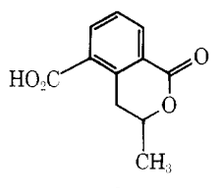
tions: (1) it increased the acidity of the aromatic protons; and (2) by providing the imino nitrogen for coordination with the lithium it directed substitution ortho to the oxazoline ring. Thus, it seemed likely that 1,3-bis(4′,4′-dimethyl-2′-oxazolinyl)benzene (**1**), which is readily prepared from commercial isophthalic acid, would undergo reaction with *n*-butyllithium to yield the 2-lithio derivative. However, when **1** was treated with *n*-butyllithium followed by addition of methyl iodide, the product isolated was a mixture of isomers having the spectral properties and composition for the various dihydrobenzenes such as **2** to be expected from addition of *n*-butyllithium to the aromatic ring followed by methylation. Apparently, with two oxazoline substituents addition of *n*-butyllithium to the aromatic ring becomes favored over the simple acid–base reaction. Substitution of *sec*-butyllithium or phenyllithium for *n*-butyllithium did not change the course of the reaction.

However, when a benzene solution of **1** was treated with 3 equiv of lithium diisopropylamide (LDA) and 3 equiv of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), a deep purple solution of the anion resulted which, on reaction with methyl iodide, gave 2,6-bis(4′,4′-dimethyl-2′-oxazolinyl)toluene (**3**) in 98% yield. Hydrolysis of **3** by heating in aqueous 3 N hydrochloric acid for 20 h gave a crystalline dicarboxylic acid, identical in all respects with the known 2-methylisophthalic acid (**5**).[1]



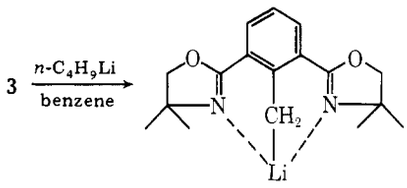
2 **1** **5**

Similarly, treatment of the lithio derivative of **1** with allyl bromide gave the allyl derivative **4**. Hydrolysis of **4** with aqueous hydrochloric acid was accompanied by lactonization to give compound **6**.

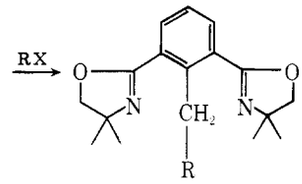


6

Analogous to Gschwend's observation, the methyl derivative **3** was easily converted to the corresponding lithio derivative **7**, which readily underwent alkylation to give compounds **8** and **9**. It is noteworthy that reaction of **3** with *n*-butyllithium in benzene proceeded smoothly to give the corresponding lithio derivative **7** in quantitative yield without any evidence of nucleophilic addition to the ring as had occurred with **1**.



7



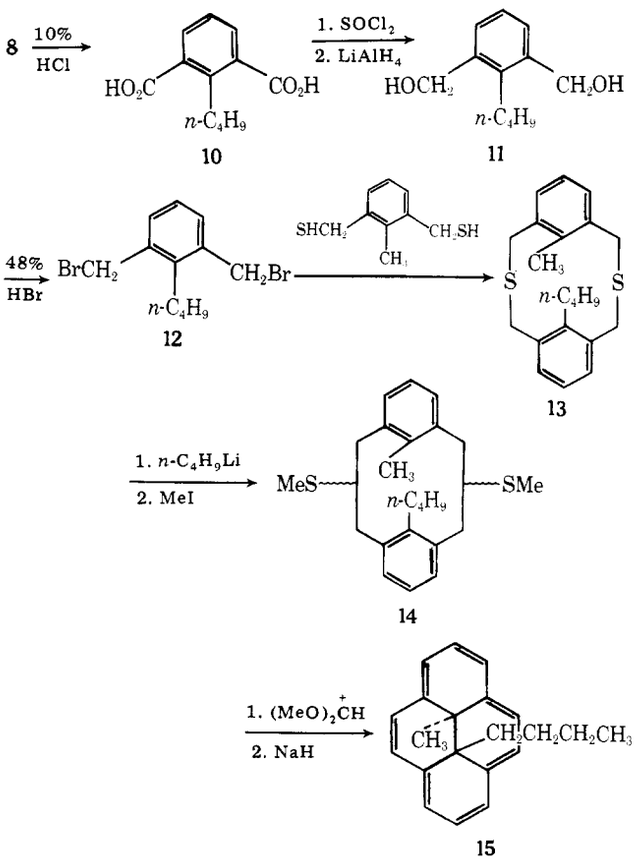
8, R = -$CH_2CH_2CH_3$
9, R = -$CH_2C{\equiv}CH$

Apparently, the benzylic protons of **3** are sufficiently acidic that the acid–basic exchange completely dominates.

Alkylation of **7** using *n*-propyl bromide gave the corresponding *n*-butyl derivative **8** in 84% yield. Similarly, alkylation of **7** with propargyl bromide occurred smoothly to give **9**.

To examine the usefulness of this synthetic method the *n*-butyl derivative **8** was carried through to give *trans*-15-*n*-butyl-16-methyldihydropyrene (**15**), as shown in Scheme I. Hydrolysis of **8** with 10% hydrochloric acid gave 2-*n*-butylisophthalic acid (**10**) in 91% yield. Conversion of **10** to the corresponding acid chloride followed by reduction with lithium aluminum hydride produced the 2,6-bis(hydroxymethyl)-*n*-butylbenzene (**11**) in 84% yield. Heating a solution of **11** in aqueous 48% hydrobromic acid led in 96% yield to 2,6-bis(bromomethyl)-*n*-butylbenzene (**12**). A coupling reaction of **12** with 2,6-bis(mercaptomethyl)toluene, under the usual conditions,[10] gave the *anti*-9-*n*-butyl-18-methyl-

Scheme I



10 **11** **12** **13** **14** **15**

2,11-dithia[3.3]metacyclophane (**13**) in 80% yield with no evidence for the syn isomer. A Wittig rearrangement of the dithiacyclophane **13** followed by reaction with methyl iodide gave the ring contracted product **14** as a mixture of isomers in 80% yield. This was subjected to the Hofmann elimination procedure[1] and gave *trans*-15-*n*-butyl-16-methyldihydropyrene (**15**) in 68% yield.

trans-15-*n*-Butyl-16-methyldihydropyrene is the first dihydropyrene to be synthesized having different internal substituents at the 15 and 16 positions. It forms deep green crystals, mp 54.0–54.5 °C. Although the ultraviolet–visible spectrum of *trans*-15-*n*-butyl-16-methyldihydropyrene (**15**) is quite similar to that of the parent compound, *trans*-15,16-dimethyldihydropyrene,[18] **15** shows considerably more fine structure and its extinction coefficients in the region of 580–650 nm are in the range of 950–2100, whereas the extinction coefficients for *trans*-15,16-dimethyldihydropyrene in this region are only in the range of 110–330. The ^{1}H NMR spectrum of **15** is pretty much as expected, but provides an extended mapping of the magnetic field due to ring current. Thus, the protons of the internal methyl group appear at τ 14.30, and the butyl group shows four multiplets: the α-methylene protons at τ 13.90–14.14, the β-methylene at τ 11.51–11.91, the γ-methylene at τ 10.20–10.62, and the methyl protons as a triplet at τ 10.10.

The mass spectra of the dihydropyrenes are characterized by a small signal for the parent molecular ion, a somewhat larger signal for the fragment corresponding to loss of one internal alkyl group, and then a large signal for the pyrene molecular ion, corresponding to loss of both internal alkyl groups. In the case of **15**, in which the internal alkyl groups differ, it was of interest to see which would be more readily ejected. On a scale where the pyrene molecular ion is 100, the signal for the parent molecular ion was 2; that of the fragment for loss of the methyl group (M − 15) was 0.5; and that of the fragment for loss of the butyl group (M − 57) was 29. Thus, **15** on electron impact leads predominantly to ejection of the larger *n*-butyl group rather than the methyl group.

Experimental Section[19]

1,3-Bis(4′,4′-dimethyl-2′-oxazolinyl)benzene (1). This was prepared following the general procedure of Meyers et al.[20] To a solution of 35.60 g (0.4 mol) of 2-amino-2,2-dimethylethanol in 500 mL of anhydrous chloroform cooled to 0 °C there was added dropwise with stirring over a 3-h period a solution of 20.30 g (0.1 mol) of isophthaloyl chloride in 100 mL of anhydrous chloroform. The mixture was then allowed to warm to room temperature and was stirred an additional 24 h. The resulting mixture was washed with two 150-mL portions of water and the aqueous washings were extracted with chloroform. The combined chloroform solutions were dried and concentrated to give the expected bis(hydroxyamide) as a viscous oil. This was suspended in 250 mL of chloroform and 39 mL of thionyl chloride was added dropwise with stirring at a rate to maintain gentle boiling under reflux. After the addition was complete, the mixture was stirred at room temperature for an additional 3 h. Addition of 750 mL of ether then caused the separation of a white crystalline solid. This solid, the hydrochloride salt of **1**, was collected by filtration, washed with ether, and dried. A solution of this hydrochloride salt in 150 mL of water was brought to a pH of 10 by addition of a 10% aqueous solution of sodium hydroxide and the resulting oily suspension was extracted with chloroform. After the chloroform extract had been washed with water, it was dried and concentrated to give 23.2 g (85%) of faintly yellow crystals: mp 78–80 °C; NMR ($CDCl_3$) τ 1.53 (s, 1 H, ArH), 1.98 (d, 2 H, J = 7 Hz, ArH), 2.60 (t, 1 H, J = 7 Hz, ArH), 5.93 (s, 4 H, $-OCH_2-$), 8.67 (s, 12 H, $-CH_3$); IR ($CHCl_3$) 1650 cm^{-1} (−C=N−).

Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.60; H, 7.35; N, 10.05.

Alkylation of 1. General Method. To a solution of 2.72 g (0.01 mol) of 1,3-bis(4′,4′-dimethyl-2′-oxazolinyl)benzene (**1**) and 4.50 mL (0.03 mol) of TMEDA in 30 mL of benzene was added a benzene solution containing 0.03 mol of lithium diisopropylamide. The resulting deep purple solution was stirred at room temperature for 7 h and then was quenched by addition of 6.2 mL of methyl iodide. After the mixture had been diluted by addition of 75 mL of ethyl acetate, it was washed with water, dried, and concentrated to give a brown oil. This was taken up in ether and passed over a short silica gel column. Concentration of the eluate followed by recrystallization of the solid residue from hexane gave 2.80 g (98%) of **3** as white crystals: mp 80–82 °C; NMR ($CDCl_3$) τ 2.38 (d, 2 H, J = 7 Hz, ArH), 2.88 (t, 1 H, J = 7 Hz, ArH), 6.02 (s, 4 H, $-OCH_2-$), 7.46 (s, 3 H, $-CH_3$), 8.74 (s, 12 H, $-CH_3$); IR (KBr) 1645 cm^{-1} (−C=N−).

Anal. Calcd for $C_{17}H_{22}N_2O_2$: C, 71.30; H, 7.74; N, 9.78. Found: C, 71.27; H, 7.67; N, 9.46.

2-Methylisophthalic Acid. As proof of structure, a 2.80-g sample of **3** in 100 mL of 3 N hydrochloric acid was hydrolyzed by boiling under reflux for 20 h. The crystalline mass which separated was collected by filtration, washed with water, and dried to give 1.39 g (77%) of crystals, mp 232–235 °C (lit.[1] gives 228–229 °C), identical in all respects with an authentic sample of 2-methylisophthalic acid.

Lactone 6. When the experiment described above for the preparation of **3** was repeated, but substituting allyl bromide for methyl iodide, the corresponding allyl derivative **4** was isolated as a viscous oil in 41% yield. This was subjected directly to hydrolysis using 3 N hydrochloric acid as described for the preparation of **5**. In this case the product isolated had the composition and spectral properties to be expected for lactone **6** rather than the simple dicarboxylic acid. Lactone **6** was isolated, after recrystallization from benzene, as faintly yellow crystals: mp 165–168 °C; NMR ($CDCl_3$) a singlet at τ 0.60 (s, 1 H, ArH), 1.64 (d, 2 H, J = 3.5 Hz, ArH), 5.12–5.53, 6.20, and 6.49 (m, 3 H, ABC), 8.45 (d, 3 H, J = 3 Hz, CH_3-); IR (KBr) 1724 (−OC−), 1695 (>C=O).

Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 63.87; H, 4.78.

Alkylation of 3. General Method. To a solution of 5.38 g (0.18 mol) of 2,6-bis(4′,4′-dimethyl-2′-oxazolinyl)toluene (**3**) in 300 mL of benzene was added a solution of 0.0226 mol of *n*-butyllithium in hexane with vigorous stirring under a nitrogen atmosphere. After the resulting dark purple solution had been stirred at room temperature for an additional 30 min, 9 g of *n*-propyl bromide was added and the orange mixture was stirred for 24 h. Addition of 100 mL of water was followed by vigorous stirring and then 200 mL of diethyl ether. The organic layer was separated, washed twice with water, dried, and concentrated to give 6.21 g of **8** as a thick oil. This was taken up in ether and chromatographed over silica gel. Concentration of the main eluate fraction gave 5.20 g (84%) of white crystals: mp 67–68 °C; NMR ($CDCl_3$) τ 2.52 (d, 2 H, J = 7 Hz, ArH), 2.80 (t, 1 H, J = 7 Hz, ArH), 5.95 (s, 4 H, $-CH_2O-$), 6.85 (t, 2 H, J = 7 Hz, $ArCH_2-$), 8.2–8.8 (m, 4 H, $-CH_2-$) with a coincidental singlet at 8.63 (12 H, $-CH_3$), 9.11 (t, 3 H, J = 7 Hz, $-CH_3$); IR ($CHCl_3$) 1650 cm^{-1} (−N=C−); mass spectrum (70 eV) *m/e* (rel intensity) 328 (72), 313 (21), 299 (49), 285 (8), 273 (23), 256 (60), 243 (100), 230 (26), 214 (19), 202 (45); UV (cyclohexane) 275 nm (ϵ 1300).

Anal. Calcd for $C_{20}H_{28}N_2O_2$: c, 73.14; H, 8.59; N, 8.53. Found: C, 72.99; H, 8.76; N, 8.32.

2-(3-Butyn-1-yl)-1,3-bis(4′,4′-dimethyl-2′-oxazolinyl)benzene (9). When the experiment described above for the preparation of **8** was repeated, but substituting propargyl bromide for *n*-propyl bromide, the corresponding propargyl derivative **9** was formed. The viscous oil first isolated was chromatographed over silica gel using a 1:3 ether–chloroform solution for elution. The main eluate fraction gave in 26% yield a pale yellow oil: NMR ($CDCl_3$) a doublet at τ 2.29 (d, 2 H, J = 7 Hz, ArH), 2.75 (t, 1 H, J = 7 Hz, ArH), 5.95 (s, 4 H, $-OCH_2-$), 6.55 (t, 2 H, J = 8 Hz, $-CH_2-$), 7.50 (m, 2 H, A_2M_2X, J_{AM} = 8 Hz, J_{MX} = 2 Hz), 8.05 (t, 1 H, J = 2 Hz, −C≡CH), 8.63 (s, 12 H, CH_3-); IR (KBr) 3300 (≡CH) and 1650 cm^{-1} (−N=C−).

Anal. Mol wt calcd for $C_{20}H_{24}N_2O_2$: 324.184. Found (high-resolution mass spectrum): 324.183.

2-*n*-Butylisophthalic Acid (10). A solution of 1.3 g of 2-*n*-butyl-1,3-(4′,4′-dimethyl-2′-oxazolinyl)benzene (**8**) in 150 mL of a 10% aqueous solution of hydrochloric acid was boiled under reflux for 18 h. It was then allowed to stand in the refrigerator for 24 h and the crystalline precipitate which formed was collected by filtration. The aqueous filtrate was extracted with ethyl acetate and concentration of the ethyl acetate gave an additional amount of crystals. The combined solids were recrystallized from a water–methanol mixture to give 847 mg (91%) of colorless crystals: mp 208–209 °C; NMR ($CDCl_3$) τ 2.72 (d, 2 H, J = 7 Hz, ArH), 3.29 (t, 1 H, J = 7 Hz, ArH), 7.41 (t, 2 H, J = 8 Hz, $ArCH_2-$), 8.61 (m, 2 H, $-CO_2H$), 8.9–9.5 (m, 4 H, $-CH_2-$), 9.81 (t, 3 H, J = 6 Hz, $-CH_3$); mass spectrum (70 eV) (rel intensity) 222 (38), 205 (7), 193 (5), 189 (4), 180 (72), 175 (43), 161 (26), 147 (5), 134 (100); UV (EtOH) 281 nm (ϵ 1300).

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.79; H, 6.37.

2,6-Bis(hydroxymethyl)-*n*-butylbenzene (11). A solution of 1.62 g of 2-*n*-butylisophthalic acid (**10**) in 15 mL of thionyl chloride containing 2 drops of dimethylformamide was boiled under reflux for 30 min. The solution was then concentrated under vacuum and the residue was taken up in 25 mL of dry tetrahydrofuran. This was added dropwise to a stirred suspension of 1.19 g of lithium aluminum hydride in 75 mL of dry tetrahydrofuran. When the addition was complete, the mixture was boiled under reflux for 6 h and decomposed by the addition of 10 mL of a saturated sodium sulfate solution followed by 10 mL of aqueous 3 N hydrochloric acid. The mixture was then partitioned between 200 mL each of water and ether. The ether extract was separated, dried, and concentrated to give 1.41 g (100%) of a colorless solid. This was recrystallized from benzene to yield 1.19 g (84%) of colorless fibers: mp 63–64 °C; NMR ($CDCl_3$) τ 2.5–2.8 (m, 3 H, ArH), 5.26 (s, 4 H, $-CH_2O-$), 7.26 (t, 2 H, J = 8 Hz, $ArCH_2-$), 8.36 (s, 2 H, –OH), 8.2–8.7 (m, 4 H, $-CH_2-$), 9.03 (t, 3 H, J = 7 Hz, $-CH_3$); IR ($CHCl_3$) 3595 cm^{-1} (–OH); UV (EtOH) 213 (ϵ 11 000), 238 (70), 243 (100), 247 (160), 253 (230), 259 (270), 263 (270), 278 nm (190); mass spectrum (70 eV) (rel intensity) 194 (64), 178 (15), 161 (14), 158 (74), 151 (10), 147 (19), 137 (15), 133 (17), 129 (100).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.79; H, 9.15.

2,6-Bis(bromomethyl)-*n*-butylbenzene (12). A solution of 933 mg of 2,6-bis(hydroxymethyl)-*n*-butylbenzene (**11**) in 40 mL of a 48% aqueous solution of hydrobromic acid was stirred at 50 °C for 30 min. When the solution was allowed to stand overnight in the refrigerator, a crystalline mass separated. This was collected, washed successively with aqueous sodium bicarbonate and water, and dried to give 1.57 g of white crystals. These, on recrystallization from petroleum ether (30–60 °C), gave 1.36 g (90%) of colorless needles: mp 57–58 °C; NMR ($CDCl_3$) τ 2.62–3.00 (m, 3 H, ArH), 5.48 (s, 4 H, $-CH_2Br$), 7.09 (t, 2 H, J = 8 Hz, $ArCH_2-$), 8.2–8.6 (m, 4 H, $-CH_2-$), 9.00 (t, 3 H, J = 6 Hz, $-CH_3$); IR ($CHCl_3$) 550 cm^{-1} (–CBr); mass spectrum (70 eV) (rel intensity) 320 (36), 277 (46), 239 (19), 199 (62), 197 (63), 159 (100).

Anal. Calcd for $C_{12}H_{16}Br_2$: C, 45.03; H, 5.04. Found: C, 45.19; H, 5.13.

9-*n*-Butyl-18-methyl-2,11-dithia[3.3]metacyclophane (13). A solution of 539 mg of 2,6-bis(bromomethyl)-*n*-butylbenzene (**12**) and 384 mg of 2,6-bis(mercaptomethyl)toluene in 300 mL of benzene was added dropwise from a Hershberg funnel to a stirred solution of 200 mg of sodium hydroxide in 800 mL of 95% ethanol under nitrogen. The addition was complete in 24 h; the mixture was stirred an additional 24 h and then concentrated. The residue was dissolved in chloroform, washed with aqueous brine, dried, and concentrated. The resulting solid was taken up in benzene and chromatographed over silica gel. The crystalline solid from the main fraction of eluate was recrystallized from a benzene–petroleum ether (30–60 °C) mixture to give 464 mg (80%) of colorless needles: mp 98–100 °C; NMR ($CDCl_3$) τ 2.64–3.06 (m, 6 H, ArH), 6.28–6.38 (m, 8 H, $ArCH_2S-$), 8.36 (t, 2 H, J = 7 Hz, $ArCH_2-$), 8.70 (s, 3 H, $ArCH_3$), 8.9–9.2 (m, 4 H, $-CH_2-$), 9.22 (m, 3 H, J = 6 Hz, $-CH_3$); UV (EtOH) 285 nm (ϵ 360); mass spectrum (70 eV) (rel intensity) 342 (100), 308 (3), 299 (11), 265 (16), 191 (71), 159 (29), 149 (81).

Anal. Calcd for $C_{21}H_{26}S_2$: C, 73.63; H, 7.62. Found: C, 73.73; H, 7.71.

Wittig Rearrangement of 13 to Give 14. To a solution of 1.01 g of 9-*n*-butyl-18-methyl-2,11-dithia[3.3]metacyclophane (**13**) in 25 mL of dry tetrahydrofuran there was added a solution of 7.36 mmol of *n*-butyllithium in hexane at 0 °C. After the mixture had been stirred for 4 min, it was quenched by addition of 3 mL of methyl iodide and stirred a further 10 min. The mixture was then taken up in dichloromethane, washed with water, dried, and concentrated. The residue was chromatographed over silica gel using a 1:1 mixture of ether–benzene for elution. From the main fraction of eluate there was obtained 875 mg (80%) of a colorless oil: NMR ($CDCl_3$) τ 2.23–3.3 (m, 6 H, ArH), 5.94 (dd, 2 H, $-CH(SMe)CH_2-$), 6.80 (m, 4 H), 7.32 (m, 2 H), 7.89 (s, 6 H, $-SCH_3$), 8.4–9.6 (m, 4 H, $-CH_2-$), 9.39 (t, 3 H, J = 4 Hz, $-CH_3$); mass spectrum (70 eV) (rel intensity) 370 (59), 355 (19), 323 (16), 308 (34), 217 (31), 202 (80), 149 (91), 147 (100).

Anal. Calcd for $C_{23}H_{30}S_2$: C, 74.54; H, 8.16. Found: C, 74.54; H, 8.82.

***trans*-15-*n*-Butyl-16-methyldihydropyrene (15).** A solution of 470 mg of the Wittig product **14** in 15 mL of dichloromethane was added dropwise with stirring to a suspension of 601 mg of dimethoxycarbonium fluoroborate in 5 mL of dichloromethane held at −30 °C under nitrogen. The mixture was then allowed to warm to room temperature and was stirred for 6 h. After addition of 20 mL of ethyl acetate, the mixture was stirred and the liquid decanted. The solid residue of the bis(dimethylsulfonium) salt was washed again with ethyl acetate, decanted, and used directly without further purification. To a stirred solution of the bis(dimethylsulfonium) salt in 20 mL of dry tetrahydrofuran under nitrogen there was added a suspension of 1.10 g of sodium hydride in 30 mL of dry tetrahydrofuran. The resulting mixture was boiled under reflux for 7.5 h, cooled, and decomposed by successive additions of 10 mL of benzene, 10 mL of water, and 10 mL of aqueous 3 N hydrochloric acid. The organic layer was separated, washed with water, dried, and concentrated to give a dark green oil. Chromatography of this oil over silica gel using hexane for elution gave 236 mg (68%) of deep green crystals: mp 54.0–54.5 °C; NMR ($CDCl_3$) τ 1.45 (m, 8 H, ArH), 1.89–2.22 (m, 2 H, ArH), 10.10 (t, 3 H, J = 7 Hz, $-CH_2CH_2CH_2CH_3$), 10.20–10.62 (m, 2 H, $-CH_2CH_2CH_2CH_3$), 11.51–11.91 (m, 2 H, $-CH_2CH_2CH_2CH_3$), 13.90–14.14 (m, 2 H, $-CH_2CH_2CH_2CH_3$), 14.30 (s, 3 H, $-CH_3$); UV (cyclohexane) 238 (ϵ 6300), 273 (780), 324 (34 000), 340 (100 000), 343 (110 000), 358 (25 000), 379 (43 000), 383 (52 000), 420 (3100), 441 (4300), 463 (6200), 478 (6500), 485 (6300), 533 (640), 542 (590), 575 (430), 581 (570), 592 (950), 605 (1400), 618 (1800), 634 (1900), 647 (2100), 652 nm (2100); mass spectrum (70 eV) *m/e* (rel intensity) 274 (2), 269 (0.5), 217 (29), 215 (7), 202 (100), 189 (4).

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.81; H, 8.00.

Acknowledgment. We thank the National Science Foundation for their support of this work. T. D. Harris thanks the National Institute of Health for a postdoctoral fellowship award, 1732GM05326.

Registry No.—**1**, 64682-37-7; 1 HCl, 64682-38-8; **3**, 64682-39-9; **4**, 64682-40-2; **6**, 64682-41-3; **8**, 64682-42-4; **9**, 64682-43-5; **10**, 5293-56-1; **11**, 64682-44-6; **12**, 64682-45-7; **13**, 64682-46-8; **14**, 64682-34-4; **14** bis(dimethylsulfonium)tetrafluoroborate salt, 64682-36-6; **15**, 64682-47-9; 2-amino-2,2-dimethylethanol, 124-68-5; isophthaloyl chloride, 99-63-8; allyl bromide, 106-95-6; propyl bromide, 106-94-5; propargyl bromide, 106-96-7; 2,6-bis(mercaptomethyl)toluene, 41563-67-1.

References and Notes

(1) R. H. Mitchell and V. Boekelheide, *J. Am. Chem. Soc.*, **96**, 1547 (1974).
(2) F. Vogtle and L. Schunder, *Chem. Ber.*, **102**, 2677 (1969).
(3) M. Haenel and H. A. Staab, *Chem. Ber.*, **106**, 2203 (1973).
(4) T. Umemoto, T. Otsubo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 593 (1973).
(5) M. Haenel and H. A. Staab, *Tetrahedron Lett.*, 3585 (1970).
(6) F. Vögtle, *Angew. Chem.*, **81**, 258 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 274 (1969).
(7) S. A. Sherrod, R. L. DaCosta, R. A. Barnes, and V. Boekelheide, *J. Am. Chem. Soc.*, **96**, 1565 (1974).
(8) V. Boekelheide, I. D. Reingold, and M. Tuttle, *J. Chem. Soc., Chem. Commun.*, 406 (1973).
(9) J. Bruhin and W. Jenny, *Tetrahedron Lett.*, 1215 (1973).
(10) R. H. Mitchell, T. Otsubo, and V. Boekelheide, *Tetrahedron Lett.*, 219 (1975).
(11) R. B. DuVernet, T. Otsubo, J. A. Lawson, and V. Boekelheide, *J. Am. Chem. Soc.*, **97**, 1629 (1975).
(12) T. Otsubo and V. Boekelheide, *Tetrahedron Lett.*, 3881 (1975).
(13) See, for example, the syntheses of *trans*-15,16-diethyldihydropyrene and *trans*-15,16-di-*n*-propyldihydropyrene [V. Boekelheide and T. A. Hylton, *J. Am. Chem. Soc.*, **92**, 3669 (1970)].
(14) D. W. Slocum and C. A. Jennings, *J. Org. Chem.*, **41**, 3653 (1976); D. W. Slocum and B. P. Koonsvitsky, *ibid.*, **41**, 3664 (1976); D. W. Slocum and P. L. Gierer, *ibid.*, **41**, 3668 (1976).
(15) A. I. Meyers and E. D. Mihelich, *J. Am. Chem. Soc.*, **97**, 7383 (1975).
(16) H. W. Gschwend and A. Hamdan, *J. Org. Chem.*, **40**, 2008 (1975).
(17) L. Barsky, H. W. Gschwend, J. McKenna, and H. R. Rodriguez, *J. Org. Chem.*, **41**, 3651 (1976).
(18) V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **89**, 1695 (1967).
(19) Mass spectra 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 and NMR spectra were taken on a Varian HA-100 MHz spectrometer. Melting points are uncorrected.
(20) A. I. Meyers, D. L. Temple, D. Haidukewych, and E. D. Mihelich, *J. Org. Chem.*, **39**, 2787 (1974).