for 66 hr by which time all of the green color had been lost. The solution was concentrated and the residue was chromatographed over silica gel using hexane containing a trace of benzene. The yellow fraction gave a yellow solid which, after recrystallization from aqueous methanol, yielded 60 mg (88%) of yellow crystals: mp 110–111°; uv $\lambda_{max}^{cyclohexane}$ 252 mμ (sh, ε 22,000), 260 (23,500), 272 (15,200), 298 (3720), 311 (4500), 325 (3550), 388 (4680), and 404 (sh, 3350); nmr (CCl_4) multiplet at τ 2.9–3.2 (3 H, Ar*H*), a multiplet at 3.5–4.5 (7 H, -C*H*=C*H*-), and a complex multiplet from 7.6 to 9.5 (14 H, $-CH_2CH_2CH_3$); mass spectrum m^+/e 288 with major fragmentation peaks at 245 and 202. The mass spectrum of **18c** is virtually superimposable with that of **1c**. The aromatic and vinyl hydrogen region in the nmr spectrum of **18c** is quite analogous to that observed for 13,15-dimethyldihydropyrene (**18a**).[2]

Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.54; H, 8.49.

Syntheses of [2.2]Metacyclophan-1-enes. An Alternate Route to *trans*-15,16-Dialkyldihydropyrenes[1-4]

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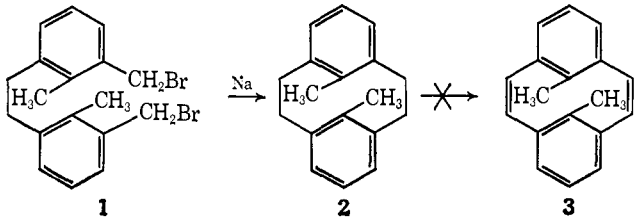
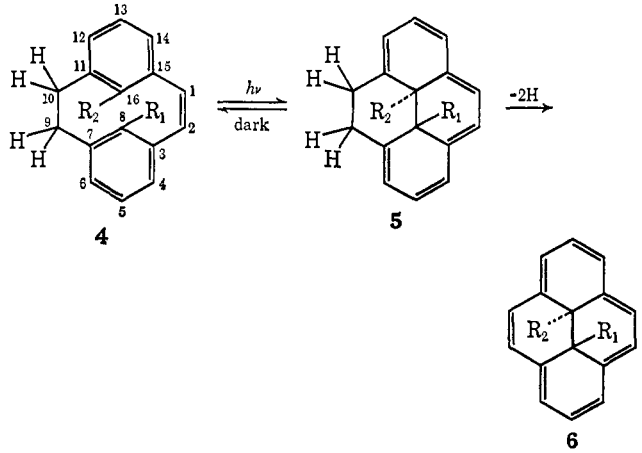
Abstract: It is shown that the cyclization of suitably substituted *cis*-stilbenes (**15, 23,** and **24**) yields [2.2]metacyclophan-1-enes (**4**). Dehydrogenation of 8,16-dimethyl[2.2]metacyclophan-1-ene (**4**, $R_1 = R_2 = -CH_3$) readily yields *trans*-15,16-dimethyldihydropyrene (**6**, $R_1 = R_2 = -CH_3$).

The methods presently available for the synthesis of *trans*-15,16-dialkyldihydropyrenes are lengthy and difficult.[4] For a variety of reasons it would be desirable to have alternate routes that would be more flexible and, hopefully, simpler for the preparation of examples of this interesting class of compounds. In our initial publication in this series,[5] we described the Wurtz cyclization of 1,2-diphenylethane derivatives such as **1** to give 8,16-dimethyl[2.2]metacyclophanes (**2**).[6] However, attempts to introduce unsaturation into the bridging ethano groups were unsuccessful and it was not possible to obtain the corresponding [2.2]metacyclophane-1,9-diene (**3**), the valence tautomer of *trans*-15,16-dimethyldihydropyrene.



1 **2** **3**

The photoisomerization of *cis*-stilbenes to 4a,4b-dihydrophenanthrenes is a well-studied reaction.[7] Thus it would be expected that a *cis*-stilbene such as **4** would undergo photoisomerization to the corresponding tetrahydropyrene derivative **5**. Since aromatization of **5** to give the corresponding 15,16-dihydropyrene derivative **6** only requires the loss of two hydrogen atoms, it would be anticipated that this would be a feasible, if not facile, reaction and would thus provide a new route to *trans*-15,16-dialkyldihydropyrenes.



4 **5** **6**

To test this hypothesis it was necessary to find a method of synthesis for [2.2]metacyclophan-1-enes (**4**). Since the Wurtz procedure is probably the most generally applicable one for preparing [2.2]metacyclophanes,[8] we turned our attention to the possibility of carrying out a Wurtz cyclization with an appropriately substituted *cis*-stilbene such as **15**. Although the presence of the *cis* double bond increases the possibility of side reactions, it also provides a more rigid molecule with conformations favorable to ring closure.

Our first studies were directed toward the synthesis of **4** ($R_1 = R_2 = -H$). This was accomplished by the reaction sequence shown in Scheme I. The starting

(1) We thank the National Science Foundation and the Office of Naval Research (Contract Nonr-2771(OR), NR-055-468) for their support of this investigation.

(2) For a preliminary communication on this work, see H. Blaschke and V. Boekelheide, *J. Amer. Chem. Soc.*, **89**, 2747 (1967).

(3) Abstracted in part from the doctoral dissertation of C. E. Ramey, University of Oregon, 1968.

(4) This is paper XX in our series on "Aromatic Molecules Bearing Substituents within the Cavity of the π-Electron Cloud." For the preceding article, see V. Boekelheide and T. A. Hylton, *J. Amer. Chem. Soc.*, **92**, 3669 (1970).

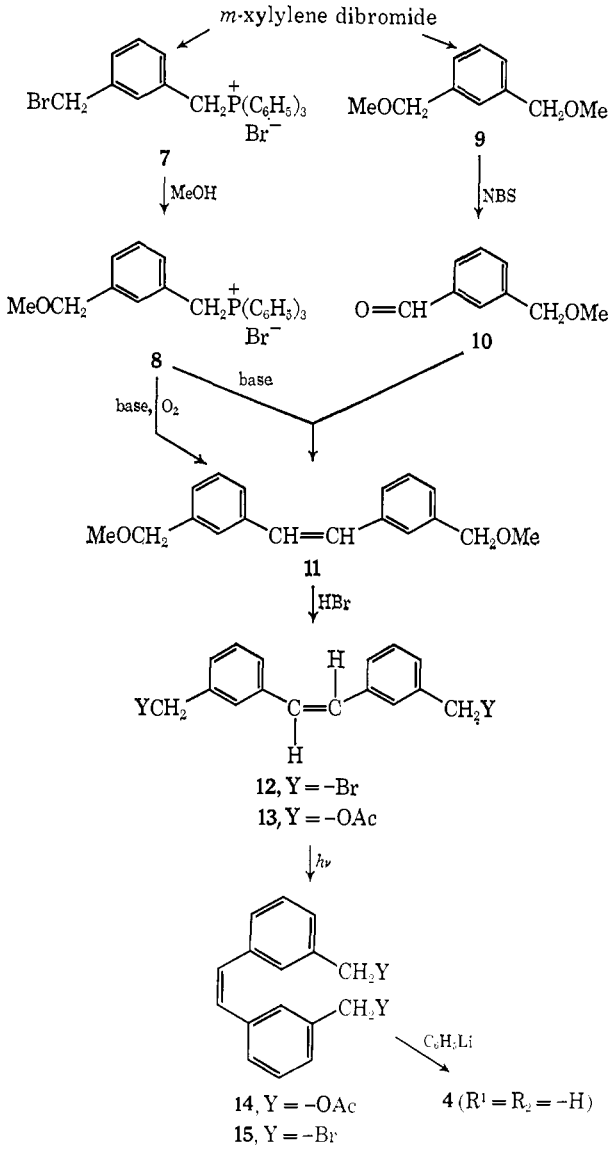
(5) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *ibid.*, **83**, 943 (1961).

(6) These were formerly named 4,12-dimethyl[2.2]metacyclophanes and have now been renamed to follow the nomenclature suggested by B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, N. Y., 1964, p 8.

(7) For a recent report on this reaction as well as earlier references, see K. A. Muszkat and E. Fischer, *J. Chem. Soc., B*, 662 (1967).

(8) See ref 6, p 88.

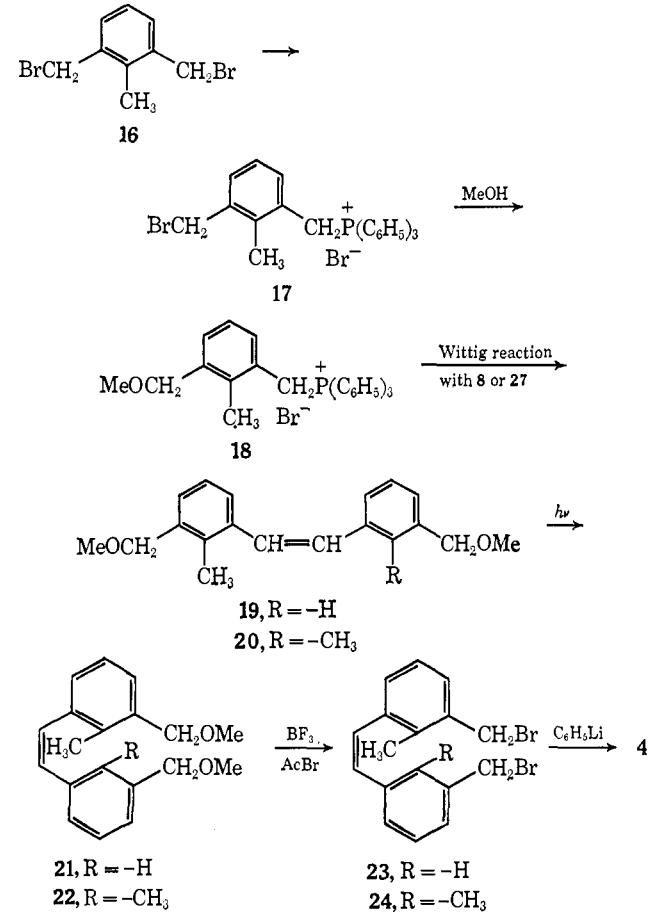
Scheme I



material was *m*-xylylene dibromide which by reaction with triphenylphosphine in benzene gave the monophosphonium salt **7**. Heating this in methanol then led to the methoxy derivative **8** in essentially a quantitative overall yield. On the other hand, treatment of *m*-xylylene dibromide with methanol gave the ether **9**, which by reaction with N-bromosuccinimide followed by hydrolysis led to 3-methoxymethylbenzaldehyde (**10**) in 71% yield.

The combination of **8** and **10** in a Wittig reaction gave **11** as a mixture of the *cis* and *trans* isomers in 85% yield. Alternatively, treatment of the ylide derived from **8** with oxygen, following the procedure devised by Bestmann,[9] yielded **11** directly in 40% yield. As determined by nmr analysis, the ratio of *cis* to *trans* isomers of **11** produced in the Wittig reaction is 3:2, whereas the ratio from the Bestmann procedure is 1:4. However, in both cases cleavage of the ether linkages with 48% hydrobromic acid gave the pure *trans*-dibromide **12**. Since the *cis*-dibromide **15** is needed for cyclization, the photoisomerization of **12** was investigated.[10] Unfortunately, the *trans*-dibromide **12** suffered photodecomposition. To avoid this difficulty the *trans*-dibromide **12** was converted to the corresponding *trans*-diacetate **13**. Photoisomerization of **13** then occurred smoothly to give a mixture of the *cis*- and *trans*-diacetates (**14**) in a ratio of 85:15. Hydrolysis of **14** followed by treatment of the diol with phosphorus tribromide regenerated the dibromide **15**. From nmr analysis this sample of dibromide consisted of a mixture of the *cis* and *trans* isomers in a ratio of 85:15. However, when this mixture was dissolved in chloroform, crystals of the *trans*-dibromide **12** deposited from solution leaving the mother liquor with essentially pure *cis*-dibromide **15**.

Scheme II



When the *cis*-dibromide **15** was treated with sodium and tetraphenylethylene, standard conditions for the Wurtz reaction,[5] 4,5-dihydropyrene (**28**) was formed in 52% yield. Apparently, cyclization to give **4** (R_1 = R_2 = -H), as desired, occurred smoothly enough, but in the presence of sodium **4** (R_1 = R_2 = -H) underwent further dehydrogenation and aromatization to give 4,5-dihydropyrene. The use of alkali metals for dehydrogenation–aromatization has been described before.[11] To avoid this the Wurtz reaction was then tried using phenyllithium, and [2.2]metacyclophan-1-ene (**4**, R_1 = R_2 = -H) was readily formed in 45% yield.

The preparation of 8-methyl[2.2]metacyclophan-1-ene (**4**, R_1 = -H; R_2 = $-CH_3$) was carried out following essentially the same route as outlined in Scheme I except that **18** was substituted for **8** in the Wittig reaction. Later, however, it was found that cleavage of the benzyl

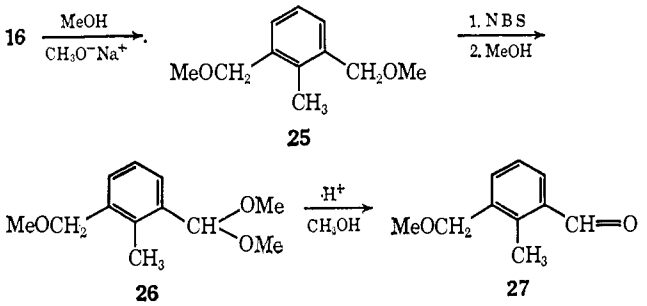
(9) H. J. Bestmann and O. Kratzer, *Chem. Ber.*, 96, 1899 (1963).

(10) For examples of the photoisomerization of sterically hindered stilbenes, see D. Gegiou, K. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, 90, 3907 (1968).

(11) L. Reggel, S. Friedman, and I. Wender, *J. Org. Chem.*, 23, 1136 (1958).

ether groups with a mixture of boron trifluoride etherate and acetyl bromide gave the corresponding benzyl bromide in high yield without isomerization of the stilbene double bond. This made it possible to shorten the overall synthesis very considerably as shown by Scheme II.

For the synthesis of 8,16-dimethyl[2.2]metacyclophan-1-ene (**4**, $R_1 = R_2 = -CH_3$) it was possible again to employ Scheme II. In this case, 3-methoxymethyl-2-methylbenzaldehyde (**27**) was substituted for **8** in the Wittig reaction and the subsequent steps were carried out as before. Although several routes to the synthesis of **27** were investigated, the one that proved most practical was that starting with 2,6-bis(bromomethyl)-toluene (**16**) and it is shown below.



The effect of the internal substituents on the Wurtz cyclization reaction is of interest. Whereas the unsubstituted dibromide **15** underwent cyclization to **4** ($R_1 = R_2 = -H$) in 45% yield, the presence of one internal methyl group, as in **23**, reduced the yield in the Wurtz reaction to 18%, and with two methyl groups, as in **24**, the yield of **4** ($R_1 = R_2 = -CH_3$) dropped to 10%.

The geometry of the [2.2]metacyclophanes has been shown by X-ray crystallographic analysis to have the two benzene rings in separate planes with the internal substituents at the 8 and 16 positions extending out over the face of the opposite benzene ring.[12,13] These substituents feel the diamagnetic ring current of the opposite ring and their proton signals in the nmr are characteristically shifted sharply to higher field.[14,15] Since the double bond in the ethylene bridge introduces new shielding and deshielding effects as well as altering the overall geometry of the [2.2]metacyclophane molecule, it is instructive to compare the nmr signals of the internal substituents of the [2.2]metacyclophanes with the corresponding [2.2]metacyclophan-1-enes. The data are assembled in Table I. The fact that the signal for hydrogen, as an internal substituent, is shifted to lower field by 1.18–1.45 ppm in the [2.2]metacyclophan-1-enes as compared to their saturated analogs would suggest that these internal hydrogens are in a strongly deshielding region of the bridging double bond. By contrast the signal for the hydrogens of the internal methyl groups are much less affected, the downfield shift for the methyl protons of the [2.2]metacyclophan-1-enes being shifted only 0.23–0.30 ppm as compared to their saturated analogs. However, when there is unsaturation in both bridging ethylenes, as in the case of 8,16-dimethyl[2.2]metacyclophane-1,9-diene, the valence tautomer of *trans*-15,16-dimethyldihydropyrene,[16] the signal for the protons of the internal methyl groups then appear at τ 8.48, a downfield shift of 0.96 ppm as compared to the case of 8,16-dimethyl[2.2]metacyclophane.

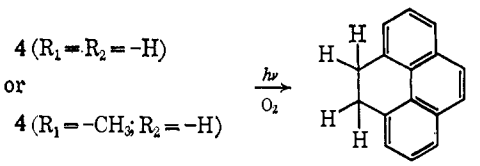
Table I. Proton Chemical Shifts of the Interior (8, 16) Substituents of [2.2]Metacyclophanes

Compound	Interior H, τ	Interior CH_3, τ
[2.2]Metacyclophane	5.83	
[2.2]Metacyclophan-1-ene	4.38	
8-Methyl[2.2]metacyclophane	6.28	9.52
8-Methyl[2.2]metacyclophan-1-ene	5.10	9.22
8,16-Dimethyl[2.2]metacyclophane		9.44
8,16-Dimethyl[2.2]metacyclophan-1-ene		9.21
8,16-Dimethyl[2.2]metacyclophane-1,9-diene		8.48

The chemical shifts of the internal substituents are highly sensitive to the overall geometry of the molecule and the introduction of internal methyl substituents clearly has a distorting effect. The effects of such twisting are also readily seen in the change of the AA′-BB′ pattern of the proton resonances of the ethano bridges. Thus, the chemical shift difference between the A and B protons in [2.2]metacyclophane is 1.00 ppm, whereas for 8,16-dimethyl[2.2]metacyclophane it is only 0.20 ppm.

As anticipated, all three of the [2.2]metacyclophan-1-enes (**4**) undergo photoisomerization to give the corresponding tetrahydropyrene derivatives (**5**) which, on standing in the dark, revert back to **4**. This photoisomerization and its reversal in the dark are the subjects of an accompanying paper.[17]

As might be expected, the photoisomerization of **4** ($R_1 = R_2 = -H$) is highly sensitive to the presence of oxygen and, unless oxygen is rigidly excluded, **5** ($R_1 = R_2 = -H$) is oxidized to 4,5-dihydropyrene (**28**). Surprisingly, though, the corresponding methyl derivative **4** ($R_1 = -CH_3$; $R_2 = -H$) is almost equally as sensitive to oxygen and gives **28** again as the major product.



28

On the other hand, 8,16-dimethyl[2.2]metacyclophan-1-ene (**4**, $R_1 = R_2 = -CH_3$) is not particularly sensitive to oxygen. Treatment of **4** ($R_1 = R_2 = -CH_3$) with either 2,3-dichloro-4,5-dicyanoquinone or with a palladium-on-charcoal catalyst readily effects a dehydrogenation–aromatization giving *trans*-15,16-dimethyldihydropyrene (**6**, $R_1 = R_2 = -CH_3$) in good yield. Thus, this route appears to be a useful, alternate pathway to *trans*-15,16-dimethyldihydropyrenes.[18] However, all attempts to effect such a dehydrogenation–

(12) C. J. Brown, *J. Chem. Soc.*, 3278 (1953).
(13) A. W. Hanson, *Acta Cryst.*, **15**, 956 (1952).
(14) D. J. Wilson, V. Boekelheide, and R. W. Griffin, Jr., *J. Amer. Chem. Soc.*, **82**, 6302 (1960).
(15) N. L. Allinger, B. J. Gorden, S.-E. Hu, and R. A. Ford, *J. Org. Chem.*, **32**, 2272 (1967).
(16) The description of 8,16-dimethyl[2.2]metacyclophane-1,9-diene will be presented in a paper on the photoisomerization of 15,16-dihydropyrenes to be published shortly.
(17) C. Ramey and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3681 (1970).
(18) For another example of the application of this method, see V. Boekelheide and W. Pepperdine, *ibid.*, **92**, 3684 (1970).

aromatization reaction with either [2.2]metacyclophan-1-ene (**4**, $R_1 = R_2 = -H$) or 8-methyl[2.2]metacyclophan-1-ene (**4**, $R_1 = -CH_3$; $R_2 = -H$) were unsuccessful. In these instances, the products were pyrene, 4,5-dihydropyrene, or 8-methyl[2.2]metacyclophane instead of the desired *trans*-15,16-dihydropyrene (**6**, $R_1 = R_2 = -H$) or *trans*-15-methyldihydropyrene (**6**, $R_1 = -CH_3$; $R_2 = -H$).

Experimental Section[19]

***m*-(Methoxymethyl)benzyltriphenylphosphonium Bromide (8).** A solution of 57.4 g of *m*-(bromomethyl)benzyltriphenylphosphonium bromide (**7**, Aldrich Chemical Co.) in 800 ml of dry methanol was boiled under reflux overnight. Concentration of the solution to a small volume followed by addition of ether caused the separation of 49.0 g (94%) of white crystals, mp 233–235°. A sample recrystallized from water gave white crystals, mp 234–235°.

Anal. Calcd for $C_{27}H_{26}OPBr$: C, 67.93; H, 5.49; P, 6.51. Found: C, 67.91; H, 5.70; P, 6.32.

3-Methoxymethylbenzaldehyde (10). To a solution of 29.0 g of 1,3-bis(methoxymethyl)benzene[20] in 250 ml of carbon tetrachloride there was added in portions 31.3 g of N-bromosuccinimide while irradiating the mixture with a 75-W Mazda lamp. When all of the N-bromosuccinimide had reacted, the solution was filtered to remove succinimide and the filtrate concentrated under reduced pressure. The residue was taken up in 250 ml of dry methanol containing 9 g of sodium methoxide and boiled under reflux for 4 hr. The solution was then concentrated, 200 ml of water was added, and the resulting mixture was extracted with methylene chloride. Concentration of the extract followed by distillation of the residue gave 6.68 g of a colorless oil, bp 97–99° (2.8 mm), whose nmr spectrum indicated it to be 3-methoxymethylbenzaldehyde dimethyl acetal contaminated with a small amount of starting material. This was dissolved in a mixture of 75 ml of methanol, 25 ml of water, and 10 ml of concentrated hydrochloric acid and boiled under reflux for 30 min. The solution was then poured into water and extracted with ether. Concentration of the dried ether extracts followed by distillation gave 5.87 g of a colorless oil: bp 65–70° (0.5 mm); nmr singlet at τ 0.05 (1 H, $-CH{=}O$), a multiplet at 2.25–2.63 (4 H, Ar*H*), a singlet at 5.58 (2 H, $ArCH_2-$), and a singlet at 6.67 (3 H, $-OCH_3$). A sample for analysis was collected by vapor phase chromatography using 20% SE-30 on a Chromosorb W column at 195° (retention time, 4 min).

Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.84; H, 6.71.

3,3′-Bis(methoxymethyl)stilbene (11). A. By the Wittig Reaction. A solution of sodium amide in liquid ammonia was prepared by dissolving 1.5 g of sodium in 300 ml of liquid ammonia containing 50 mg of ferric nitrate. To this was added 27.9 g of **8** with stirring. After all of the ammonia had evaporated, 300 ml of dry tetrahydrofuran was distilled directly into the flask. When the solution had been boiled under reflux for 15 min, all of the solids had dissolved and the solution was a deep orange. It was then cooled to room temperature and 8.32 g of 3-methoxymethylbenzaldehyde was added dropwise with stirring. Although the color disappeared as soon as the addition was complete, the solution was stirred an additional 15 min before concentrating under reduced pressure. The residue was taken up in a 9:1 petroleum ether (bp 30–60°)–benzene mixture and chromatographed over acidic alumina (Woelm, activity 1). The main eluate fraction gave an oil which, on distillation, yielded 12.5 g (85%) of a colorless oil, bp 100° (10^{-4} mm), whose nmr spectrum indicated it to be a 60:40 mixture of the *cis* to *trans* isomers of **11**.

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.23; H, 7.38.

The *cis* and *trans* isomers of **11** could be separated by vapor phase chromatography using 20% SE-30 on a firebrick column at 250°. Both were obtained as colorless oils whose spectral characteristics are as follows: *cis* isomer of **11**, nmr ($CDCl_3$) multiplet at τ 2.73–2.80 (8 H, Ar*H*), singlet at 3.39 (2 H, $-CH{=}CH-$), singlet at 5.65 (4 H, $ArCH_2-$), and a singlet at 6.68 (6 H, $-OCH_3$); *trans* isomer of **11**, ir $\nu_{max}^{CCl_4}$ 970 and 1640 cm^{-1} (*trans* $-CH{=}CH-$); nmr ($CDCl_3$) multiplet at τ 2.4–2.9 (10 H, Ar*H*, $CH{=}CH-$), singlet at 5.53 (4 H, $ArCH_2-$), and a singlet at 6.68 (6 H, $-OCH_3$).

B. By the Bestmann Procedure.[9] A solution of 2.3 g of sodium in 300 ml of liquid ammonia was prepared as in A and to this was added 47.7 g of **8** with stirring. After evaporation of the ammonia, 300 ml of xylene was added and the deep red solution was boiled under reflux while oxygen was being passed through. It required 12 hr before all of the red color was discharged. After concentration, the residue was taken up in a 19:1 petroleum ether–benzene mixture and chromatographed over basic alumina (Woelm, activity 1). The main eluate fraction gave 5.36 g (40%) of a colorless oil whose nmr spectrum showed it to be a mixture of the *cis* and *trans* isomers of **11** in a ratio of 1:4.

Irradiation of this mixture in a benzene solution using a 150-W, low-pressure Hanovia lamp gave, after isolation, an oil having the *cis* and *trans* isomers of **11** in a ratio of 3:1.

3,3′-Bis(bromomethyl)-*trans*-stilbene (12). A solution of 4.50 g of **11** (prepared either by procedure A or B) in 50 ml of an aqueous 48% hydrobromic acid solution was boiled under reflux. After the solution had cooled, the crystalline precipitate was collected and recrystallized from a chloroform–benzene mixture to give 5.9 g (96%) of white crystals: mp 161–162°; ir $\nu_{max}^{CHCl_3}$ 960 cm^{-1} (*trans* $-CH{=}CH-$); nmr ($CDCl_3$) multiplet at τ 2.4–3.0 (10 H, Ar*H* and $-CH{=}CH-$), and a singlet at 5.49 (4 H, $ArCH_2-$).

Anal. Calcd for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.86; Br, 43.66 Found: C, 52.63; H, 4.02; Br, 43.51.

3,3′-Bis(acetoxymethyl)-*trans*-stilbene (13). A solution of 3.3 g of **12** and 10 g of sodium acetate in 50 ml of acetic acid was heated on a steam bath for 14 hr. After concentration, the residue was triturated with a 10% aqueous solution of sodium bicarbonate. The resulting solid was recrystallized from chloroform to give 2.85 g (98%) of shiny white leaflets: mp 97–98°; ir $\nu_{max}^{CHCl_3}$ 1730 cm^{-1} ($-C{=}O$), 1610 (Ar C=C), and 962 (*trans* $-CH{=}CH-$); nmr (CCl_4) multiplet at τ 2.5–3.0 (10 H, Ar*H* and $-CH{=}CH-$), singlet at 4.96 ($ArCH_2-$), and a singlet at 7.96 (6 H, CH_3CO-).

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 73.77; H, 6.09.

Irradiation of 1.75–3.3% solutions of **13** in benzene using a 150-W, low-pressure Hanovia lamp gave a photoequilibrium steady-state mixture of the *cis* and *trans* isomers of **14** in the ratio of 85:15.

3,3′-Bis(hydroxymethyl)-*cis*-stilbene. A solution of 2.44 g of **14** (after irradiation) in 50 ml of a 50% aqueous ethanol solution containing 2.5 g of potassium hydroxide was allowed to stand at room temperature for 14 hr. It was then diluted with water and extracted with chloroform. Concentration of the dried chloroform extract gave an oily residue. This was purified by preparative thin layer chromatography over silica gel using a 9:1 mixture of chloroform–ethyl acetate. The colorless oil so isolated corresponded to the pure *cis* isomer as indicated by its spectra: ir $\nu_{max}^{CHCl_3}$ 3540 cm^{-1} (–OH) and 1640 ($-CH{=}CH-$); nmr ($CDCl_3$) multiplet at τ 2.7–2.8 (8 H, Ar*H*), singlet at 3.42 (2 H, $-CH{=}CH-$), singlet at 5.57 ($ArCH_2-$), and a singlet at 7.33 (2 H, $-OH$).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.34; H, 7.17.

3,3′-Bis(bromomethyl)-*cis*-stilbene (15). To a solution of 1.35 g of 3,3′-bis(hydroxymethyl)-*cis*-stilbene in 20 ml of chloroform there was added 4.5 g of phosphorus tribromide dropwise with stirring and cooling over a 15-min period. The solution was then poured onto ice and the aqueous solution was extracted with more chloroform. After the chloroform extract had been washed with water and dried, it was concentrated to give an oily residue. This was taken up in 19:1 petroleum ether–benzene mixture and chromatographed over silica gel. From the main eluate fraction there was isolated 834 mg of a pale yellow oil: nmr (CCl_4) multiplet at τ 2.6–2.9 (8 H, Ar*H*), a singlet at 3.47 (2 H, $-CH{=}CH-$), and a singlet at 5.72 (4 H, $ArCH_2-$).

Anal. Calcd for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.86. Found: C, 52.75; H, 4.05.

It was found later that **15** could be prepared more conveniently by treating **11** (after irradiation) with a threefold excess of boron trifluoride etherate and acetyl bromide. After work-up and chromatography as in the above experiment, the resulting oil still contained a small amount of the *trans* isomer **12**. However, when the oil was dissolved in a small quantity of chloroform and allowed to stand, the *trans* isomer **12** separated out as a crystalline precipitate and the mother liquor contained the *cis* isomer **15** essentially pure.

(19) Elemental analyses are by Microtech and by A. Bernhardt Microanalytical Laboratories. Ultraviolet and visible spectra were measured with Cary 14 or 15 spectrometers, infrared spectra with a Beckman I.R.-5 spectrometer, nmr spectra with a Varian A-60 or H.A.-100 MHz spectrometers, and mass spectra with a C.E.C.-110-21B double-focusing mass spectrometer. We thank the National Science Foundation for funds used toward the purchase of the Varian A-60, the C.E.C.-110-21B, and a Joy liquid nitrogen machine.

(20) F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 2819 (1954).

[2.2]Metacyclophan-1-ene (4, $R_1 = R_2 = -H$). To 1.45 g of **15** in 300 ml of ether there was added dropwise with stirring 60 ml of an ether solution containing 0.0043 mol of phenyllithium. The solution was then stirred for an additional 15 min at room temperature before being poured into ice water. The ether phase was separated, washed with water, dried, and concentrated. The oily residue was taken up in petroleum ether and chromatographed over silica gel using a 9:1 petroleum ether–benzene mixture for elution. The first two eluate fractions were combined and concentrated, and the residue was recrystallized from methanol. Sublimation at 100° at 15 mm then gave 371 mg (45%) of shiny white plates: mp 83.0–84.0°; uv λ_{max}^{EtOH} 350 mμ (ε 113), 300 (450), 250 (384), and 246 (2400); nmr (CCl_4) a multiplet at τ 2.68–3.20 (6 H, Ar*H*), a singlet at 3.43 (2 H, –C*H*=C*H*–), a singlet at 4.38 (2 H, internal Ar*H*), and an AA'BB' multiplet with major signals at 6.90, 6.93, 7.04, 7.05, 7.96, 7.97, 8.08, and 8.12 (4 H, $ArCH_2$–); mass spectrum, parent molecular ion, *m/e* 206 (intensity 100).

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.16; H, 6.98.

4,5-Dihydropyrene (28). To a solution of 1.0 g of sodium shot and 200 mg of tetraphenylethylene in 500 ml of dry tetrahydrofuran agitated with a high-speed stirrer in a Morton flask there was added a solution of 664 mg of the *cis*-dibromide **15** in 100 ml of tetrahydrofuran at a rate of 1 drop every 5 sec. When the addition was complete, the solution was decanted from the excess sodium, concentrated under reduced pressure, and poured into water. After extraction with chloroform, the organic layer was washed with water, dried, and concentrated. The residue was taken up in hexane and purified by preparative thin layer chromatography over silica gel. The fastest moving fraction consisted of 194 mg (52%) of white crystals, mp 131–132°. The melting point and spectral properties of these crystals are in complete agreement with those described for 4,5-dihydropyrene.[21]

Irradiation of **4** ($R_1 = R_2 = -H$) in the presence of oxygen also gave 4,5-dihydropyrene (**28**) in high yield. The properties of **28** formed in this way were identical in all respects with the sample prepared above.

3-Bromomethyl-2-methylbenzyltriphenylphosphonium Bromide (17). A solution of 2.57 g of 2,6-bis(bromomethyl)toluene[5] in 25 ml of ether was added to a solution of 2.42 g of triphenylphosphine in 50 ml of ether and allowed to stand for 3 days. There separated 4.01 g (80%) of a white crystalline powder: mp 219–221°; nmr ($CDCl_3$) multiplet at τ 2.0–3.0 (18 H, Ar*H*), a doublet at 4.55 (2 H, $ArCH_2P$), a doublet at 5.70 (2 H, $ArCH_2Br$), and a singlet at 8.30 (3 H, $ArCH_3$).

Anal. Calcd for $C_{27}H_{25}PBr_2$: C, 59.95; H, 4.65; Br, 29.59. Found: C, 59.91; H, 4.82; Br, 29.59.

3-Methoxymethyl-2-methylbenzyltriphenylphosphonium Bromide (18). A solution of 5.0 g of **17** in 250 ml of methanol was boiled under reflux for 24 hr. After concentration, the residual solid was taken up in acetonitrile and slow addition of ether caused the separation of 4.1 g (90%) of a white microcrystalline powder: mp 167–172°; nmr ($CDCl_3$) multiplet at τ 2.0–3.2 (18 H, Ar*H*), a doublet centered at 4.78 (2 H, *J* = 14 cps, $ArCH_2P$–), a singlet at 5.80 (2 H, $ArCH_2O$–), singlet at 6.70 (3 H, $-OCH_3$), and a singlet at 8.40 (3 H, $ArCH_3$).

Anal. Calcd for $C_{28}H_{28}POBr$: C, 68.43; H, 5.70. Found: C, 68.25; H, 5.55.

3,3'-Bis(methoxymethyl)-2-methylstilbene (19). A solution of sodium amide in liquid ammonia was prepared by dissolving 1.3 g of sodium in 400 ml of liquid ammonia in the presence of ferric chloride and to this was added 17.73 g of **18**. After the mixture had been stirred for 20 min, the ammonia was allowed to evaporate and 400 ml of dry tetrahydrofuran was introduced. To the resulting deep red solution held at room temperature there was added dropwise with stirring a solution of 4.50 g of **8** in 30 ml of dry tetrahydrofuran. When addition was complete (1 hr), the solution was stirred for 2 hr and filtered, and the filtrate concentrated. The residual solid was taken up in 500 ml of a 1:1 hexane–ether mixture, causing the separation of triphenylphosphine oxide. After filtration, the filtrate was concentrated and the residue was chromatographed over silica gel using a 3:7 benzene–hexane mixture. From the main eluate fraction there was isolated 8.1 g (95%) of a colorless oil corresponding to a 3:2 mixture of the *cis* and *trans* isomers of **19**. Separation of the two isomers was accomplished by vapor phase chromatography using 20% SE-30 on a Chromosorb W column at 270°; the *cis* isomer of **19** showed a retention time of 6.2 min, whereas the retention time of the *trans* isomer was 11.2 min.

The *cis* isomer of **19** was a colorless oil; nmr multiplet at τ 2.6–3.2 (7 H, Ar*H*), singlet at 3.41 (2 H, –CH=CH–), singlets at 5.61 and 5.82 (2 H each, $ArCH_2O$–), singlets at 6.71 and 6.85 (3 H each, $-OCH_3$), and a singlet at 7.81 (3 H, $ArCH_3$). The *trans* isomer of **19** was a colorless oil: nmr multiplet at τ 2.5–3.1 (9 H, Ar*H* and –CH=CH–), singlet at 5.61 (4 H, $ArCH_2O$–), singlet at 6.71 (6 H, $-OCH_3$), and a singlet at 7.68 (3 H, $ArCH_3$).

When the bulk of the 3:2 mixture of *cis* and *trans* isomers of **19** was irradiated as a 1% solution in benzene using a 200-W, low-pressure Hanovia lamp with a Corex filter, the stilbene mixture was reisolated after photoequilibrium and found by nmr analysis to be a 9:1 ratio of the *cis* and *trans* isomers of **19**.

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found (*trans* isomer of **19**): C, 80.12; H, 7.97. Found (*cis* isomer, **21**): C, 80.67; H, 7.80.

3,3'-Bis(bromomethyl)-2-methyl-*trans*-stilbene. A suspension of 650 mg of the 3:2 mixture of *cis* and *trans* isomers of **19** in 25 ml of an aqueous 48% hydrobromic acid solution was boiled under reflux for 2 hr. After the aqueous layer was decanted, the organic layer was taken up in a 1:1 hexane–benzene mixture and chromatographed over silica gel. The main eluate fraction was collected and recrystallized from hexane to give 490 mg (64%) of white needles: mp 130–131°; nmr (CCl_4) multiplet at τ 2.5–3.2 (9 H, Ar*H* and –C*H*=C*H*–), a singlet at 5.60 (4 H, $ArCH_2$–), and a singlet at 7.67 (3 H, $ArCH_3$).

Anal. Calcd for $C_{17}H_{16}Br_2$: C, 53.78; H, 4.25. Found: C, 53.58; H, 4.32.

3,3'-Bis(acetoxymethyl)-2-methyl-*trans*-stilbene. A solution of 900 mg of 3,3'-bis(bromomethyl)-2-methyl-*trans*-stilbene and 3.0 g of sodium acetate in 80 ml of glacial acetic acid was boiled under reflux for 2 hr. It was then poured into an excess of aqueous 5% sodium bicarbonate solution and extracted with ether. After the ether extract had been washed with water and dried, it was concentrated to give 790 mg (99%) of white crystals, mp 63–64°. A sample recrystallized from a methanol–water mixture gave fine white needles: mp 64.0–64.5°; nmr ($CDCl_3$) multiplet at τ 2.6–3.2 (9 H, Ar*H* and –C*H*=C*H*–), singlet at 5.00 (4 H, $ArCH_2$), a singlet at 7.69 (3 H, $ArCH_3$), and a singlet at 8.02 (6 H, CH_3CO–).

Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55. Found: C, 74.68; H, 6.62.

3,3'-Bis(acetoxymethyl)-2-methyl-*cis*-stilbene. A solution of 790 mg of 3,3'-bis(acetoxymethyl)-2-methyl-*trans*-stilbene in 100 ml of benzene was irradiated with a 200-W, low-pressure Hanovia lamp with a Corex filter and a nitrogen stream for agitation. After 3 hr the solution was concentrated under reduced pressure leaving a colorless oil. Analysis of this by nmr indicated it to be a 9:1 mixture of the *cis* and *trans* isomers. By vapor phase chromatography using a 20% SE-30 on a Chromosorb W column at 295°, a pure sample of the *cis* isomer (retention time, 7 min) was obtained as a colorless oil: nmr multiplet at τ 2.6–3.2 (7 H, Ar*H*), a broad singlet at 3.40 (2 H, –C*H*=C*H*–), a singlet at 4.95 (2 H, $ArCH_2O$–), a singlet at 5.18 (2 H, $ArCH_2O$–), a singlet at 7.80 (3 H, $ArCH_3$), and singlets at 8.02 and 8.11 (3 H each, CH_3CO–).

Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55. Found: C, 74.39; H, 6.35.

3,3'-Bis(bromomethyl)-2-methylstilbene (23). A. From 21. To a solution of 1.04 g of **19** (a 9:1 ratio of the *cis* to *trans* isomers after irradiation) in 80 ml of methylene chloride there was added a mixture of 4.20 g of boron trifluoride etherate and 3.62 g of acetyl bromide and the solution was boiled under reflux for 40 min. It was then cooled and poured into 100 ml of a 5% aqueous solution of sodium bicarbonate. After separation of the organic layer and a further extraction with methylene chloride, the combined methylene chloride extracts were washed with water, dried, and concentrated. The yellow residual oil was taken up in a 1:9 benzene–hexane mixture and chromatographed over silica gel. The main eluate fraction gave 540 mg (40%) of the *cis* isomer (**23**) as a pale yellow oil: nmr multiplet at τ 2.7–3.3 (7 H, Ar*H*), singlet at 3.40 (2 H, –CH=CH–), singlets at 5.57 and 5.83 (2 H each, $ArCH_2Br$), and a singlet at 7.75 (3 H, $ArCH_3$). Because **23** was somewhat unstable and difficult to handle, it was used directly in the Wurtz cyclization to prepare **4** ($R_1 = -H$, $R_2 = -CH_3$).

B. From 3,3'-Bis(acetoxymethyl)-2-methyl-*cis*-stilbene. A solution of 700 mg of 3,3'-bis(acetoxymethyl)-2-methyl-*cis*-stilbene in 20 ml of ether was added dropwise with stirring to a suspension of 1.0 g of lithium aluminum hydride in 30 ml of ether and the resulting mixture was boiled under reflux for 2 hr. A saturated aqueous solution of sodium sulfate was then added and the granular pre-

(21) C. W. Scherr, *J. Chem. Phys.*, 21, 1582 (1953).

cipitate was removed by filtration. Concentration of the filtrate gave 495 mg (94%) of a colorless oil whose nmr analysis indicated it to be a 9:1 mixture of the *cis* and *trans* isomers of 3,3′-bis(hydroxymethyl)-2-methylstilbene. Since the mixture showed no tendency to crystallize and chromatography had no beneficial effects in separating the isomers, the mixture was directly converted into the dibromide **23** by dissolving it in 10 ml of benzene, adding 0.5 ml of phosphorus tribromide, and boiling the mixture under reflux for 3 hr. After the cooled mixture had been poured onto ice, the benzene layer was separated and concentrated to give 510 mg (71%) of a pale yellow oil having the same spectral properties as that obtained in A.

8-Methyl[2.2]metacyclophan-1-ene (4, R_1 = -H; R_2 = $-CH_3$). To a solution of 1.7 g of **23** in 1.5 l. of boiling ether there was added dropwise over a 10-min period 10 ml of a 0.88 *M* solution of phenyllithium in ether. After the solution had been filtered through glass wool and concentrated, the residue was taken up in hexane and chromatographed over neutral alumina (Woelm, activity 1). From the first eluate fraction there was isolated 180 mg (18%) of colorless plates: mp 37–39°; uv $\lambda_{max}^{C_6H_{12}}$ 295 mμ (ε 1580), 248 (20,600), and 206 (42,900); nmr (CCl_4) multiplet at τ 2.85–3.35 (6 H, Ar*H*), an AB pattern centered at 3.50 (2 H, -CH=CH-, *J* = 15.2 cps), a broad singlet at 5.10 (1 H, Ar*H*), a multiplet at 6.75–8.22 (4 H, ArCH_2–), and a singlet at 9.22 (3 H, ArCH_3); mass spectrum, parent molecular ion, *m/e* at 220, with major fragmentation peaks at $M^+ - 15$, $M^+ - 16$, and $M^+ - 18$.

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.53; H, 7.27.

2,6-Bis(methoxymethyl)toluene (25). A solution of 50 g of 2,6-bis(bromomethyl)toluene (**16**) and 23 g of sodium methoxide in 500 ml of methanol was boiled under reflux for 36 hr. After concentration, the residue was treated with water and extracted with ether. After the ether extract had been washed with water, dried, and concentrated, the residual oil was distilled to give 26.7 g (82%) of a colorless oil: bp 118–120° (10 mm); nmr (CCl_4) multiplet at τ 2.7–3.2 (3 H, Ar*H*), and singlets at 5.70 (4 H, ArCH_2–), 6.80 (6 H, -OCH_3), and 7.9 (3 H, ArCH_3).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.19; H, 8.85.

3-Methoxymethyl-2-methylbenzaldehyde Dimethyl Acetal (26). To a solution of 29.5 g of bis(methoxymethyl)toluene (**25**) in 600 ml of boiling carbon tetrachloride there was added portionwise 15 g of N-bromosuccinimide over a period of 1 hr. After the mixture had been filtered and the filtrate concentrated, the residual oil was dissolved in 200 ml of anhydrous methanol and boiled under reflux for 12 hr. Concentration of the solution followed by distillation of the residue gave 20 g of 2,6-bis(methoxymethyl)toluene, bp 116–125° (10 mm), and then 9 g (88%, based on recovered starting material) of a colorless oil: nmr (CCl_4) multiplet at τ 2.5–3.0 (3 H, Ar*H*), and singlets at 4.60 (1 H, Ar$CH(O)_2$–), 5.62 (2 H, ArCH_2O), 6.71 (3 H, -OCH_3), 6.80 (6 H, -OCH_3), and 7.75 (3 H, ArCH_3). A sample for analysis was prepared by vapor phase chromatography using 20% SE-30 on a Chromosorb W column at 150°.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.39; H, 8.44.

3-Methoxymethyl-2-methylbenzaldehyde (27). A solution of 8.0 g of **26** and 75 ml of a 20% aqueous hydrochloric acid solution in 75 ml of methanol was boiled under reflux for 1.5 hr. After the solution was concentrated to one-half volume, it was extracted with ether. The ether extract was washed with water, dried, and concentrated to give 6.0 g (89%) of a colorless oil: bp 125–128° (4 mm); nmr (CCl_4) singlet at τ −0.17 (1 H, -C*H*=O), a multiplet at 2.2–3.0 (3 H, Ar*H*), and singlets at 5.65 (2 H, ArCH_2O–), 6.59 (3 H, -OCH_3), and 7.50 (3 H, ArCH_3).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.25; H, 5.55.

The **2,4-dinitrophenylhydrazone** of **27** was obtained after recrystallization from a chloroform–ether mixture as red crystals, mp 207–208°.

Anal. Calcd for $C_{16}H_{16}N_4O_5$: C, 55.81; H, 4.68; N, 16.27. Found: C, 55.75; H, 4.55; N, 16.25.

3,3′-Bis(methoxymethyl)-2,2′-dimethylstilbene (20). The Wittig reaction between **18** and **27** was carried out as described for the preparation of **19**. From 4.5 g of **27** and 15.0 g of **18** there was obtained 7.5 g (91%) of a mixture of the *cis* and *trans* isomers of **20**. Treatment of a sample of this oil with hexane effected a separation of the *trans* isomer of **20** as white needles: mp 91–92°; nmr ($CDCl_3$) multiplet at τ 2.3–2.9 (8 H, Ar*H* and -CH=C*H*-), and singlets at 5.55 (4 H, ArCH_2O–), 6.63 (6 H, -OCH_3), and 7.66 (6 H, ArCH_3).

Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.07; H, 8.30.

By preparative vapor phase chromatography using 20% SE-30 on a Chromosorb W column at 150°, a sample of the pure *cis* isomer of **20** was obtained as a colorless oil: nmr ($CDCl_3$) multiplet at τ 2.8–3.3 (8 H, Ar*H* and -C*H*=C*H*-), and singlets at 5.61 (4 H, ArCH_2O–), 6.68 (6 H, -OCH_3), and 7.79 (6 H, ArCH_3).

Anal. Calcd for $C_{20}H_{24}O_4$: C, 81.04; H, 8.16. Found: C, 80.86; H, 8.10.

Irradiation of the mixture of *cis* and *trans* isomers of **20** from the Wittig reaction as a 1% solution in benzene using a 200-W, low-pressure Hanovia lamp with a Corex filter gave an oil whose nmr spectrum indicated the ratio of *cis* to *trans* isomers of **20** was 85:15.

3,3′-Bis(bromomethyl)-2,2′-dimethylstilbene (24). A 2.0-g sample of the 85:15 mixture of the *cis* and *trans* isomers of **20** (after irradiation) was treated with boron trifluoride etherate and acetyl bromide as described under procedure A for the preparation of **23**. This gave 2.3 g (85%) of a 90:10 mixture (by nmr analysis) of the *cis* and *trans* isomers of **24** as a pale yellow oil. Treatment of this with hexane caused the separation of white needles, mp 204–205°, corresponding to the *trans* isomer of **24**.

Anal. Calcd for $C_{18}H_{18}Br_2$: C, 54.86; H, 4.60. Found: C, 55.07; H, 4.60.

The mother liquors of the hexane solution from which the *trans* isomer of **20** had been crystallized were concentrated. This gave a colorless oil whose nmr spectrum in carbon tetrachloride (multiplet at τ 2.8–3.5 (8 H, Ar*H* and -C*H*=C*H*-), and singlets at 5.60 (4 H, ArCH_2Br) and 7.71 (6 H, ArCH_3)) showed it to be essentially pure *cis* isomer of **24**. This was used directly in the Wurtz cyclization without further purification.

8,16-Dimethyl[2.2]metacyclophan-1-ene (4, R_1 = R_2 = $-CH_3$). A solution of 1.5 g of the *cis* isomer **24**, prepared as described in the preceding experiment, in 1.3 l. of dry ether was boiled under reflux while 10 ml of a 0.88 *M* solution of phenyllithium in ether was added over a 10-min period. After the solution had been filtered through glass wool and the filtrate concentrated, the residue was taken up in hexane and chromatographed over neutral alumina (Woelm, activity 1). The first eluate fraction gave 89 mg (10%) of white crystals, mp 149–150°. Recrystallization from methanol yielded colorless needles: mp 151–152°; $\lambda_{max}^{C_6H_{12}}$ 295 mμ (ε 1500), 256 (21,600), and 213 (40,000); nmr (CCl_4) multiplet at τ 2.8–3.3 (6 H, Ar*H*), a singlet at 3.40 (2 H, -C*H*=C*H*-), an AA′BB′ multiplet with major peaks at 7.01, 7.15, 7.25, 7.31, 7.41, and 7.56 (4 H, ArCH_2–), and a singlet at 9.21 (6 H, ArCH_3); mass spectrum, parent molecular ion, *m/e* 234, with major fragmentation peaks at $M^+ - 15$, $M^+ - 30$, and $M^+ - 32$.

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.09; H, 7.84.

***trans*-15,16-Dimethyldihydropyrene (6, R_1 = R_2 = $-CH_3$). A. By Catalytic Dehydrogenation.** To a solution of 9.6 mg of **4** (R_1 = R_2 = $-CH_3$) in 10 ml of benzene there was added 7.2 mg of a 30% palladium-on-charcoal catalyst and the mixture was boiled under reflux for 12 hr. After removal of the catalyst and solvent, the residue was taken up in a 19:1 mixture of hexane–ether and chromatographed over neutral alumina (Woelm, activity 1). The deep green eluate gave 6.5 mg (68%) of green plates, mp 118–120° (lit.[22] mp 119–120°), whose spectral properties agreed in all respects with those of an authentic specimen of **6** (R_1 = R_2 = $-CH_3$).[22]

B. Reaction of 4 (R_1 = R_2 = $-CH_3$) with DDQ. A solution of 20 mg of **4** (R_1 = R_2 = $-CH_3$) and 50 mg of 2,3-dichloro-5,6-dicyanoquinone (DDQ) in 30 ml of toluene was boiled under reflux overnight. After concentration, the residue was taken up in hexane and chromatographed over Florisil. Concentration of the deep green eluate gave 12.0 mg (60%) of green crystals, mp 118–120°, whose properties in all respects were in agreement with those of an authentic specimen of **6** (R_1 = R_2 = $-CH_3$).[22]

8-Methyl[2.2]metacyclophane. To a solution of 55 mg of **4** (R_1 = $-CH_3$; R_2 = -H) in 20 ml of cyclohexene there was added 20 mg of a 30% palladium-on-charcoal catalyst and the mixture was boiled under reflux overnight. After removal of the catalyst and solvent, the residue was taken up in hexane and chromatographed over silica gel. From the eluate there was isolated 17 mg (31%) of white crystals, mp 89–90°.

When 25 mg of **4** (R_1 = $-CH_3$; R_2 = -H) in 20 ml of ethanol was subjected to catalytic hydrogenation over a 5% palladium-on-charcoal catalyst, 1 molar equiv of hydrogen was absorbed and the crystals isolated, after work-up, were identical in all respects with

(22) V. Boekelheide and J. B. Phillips, *J. Amer. Chem. Soc.*, **89**, 1695 (1967).

those isolated above. Recrystallization from methanol gave 22 mg (90%) of white plates: mp 91.0–91.5°; nmr ($CDCl_3$) multiplet at τ 2.8–3.2 (6 H, Ar*H*), a singlet at 6.28 (1 H, Ar*H*), a multiplet at 6.8–8.2 (8 H, ArCH_2–), and a singlet at 9.52 (3 H, ArCH_3).

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.64; H, 8.19.

Reaction of 8-Methyl[2.2]metacyclophan-1-ene with N-Bromosuccinimide. A solution of 110 mg of **4** (R_1 = $-CH_3$; R_2 = –H) and 115 mg of N-bromosuccinimide in 30 ml of carbon tetrachloride containing 5 mg of azobisisobutyronitrile was boiled under reflux for 2 hr. After removal of the succinimide and concentration of the filtrate, the residue was taken up in hexane and chromatographed over neutral alumina (Woelm, activity 1). No green absorption bands were evident. From the eluate two main fractions were isolated. The first contained 45 mg of recovered **4** (R_1 = $-CH_3$; R_2 = –H). The second contained 40 mg of white crystals, mp 154–156°, identical in all respects with an authentic specimen of pyrene.

Reaction of 8-Methyl[2.2]metacyclophan-1-ene with DDQ. A solution of 55 mg of **4** (R_1 = $-CH_3$; R_2 = –H) and 115 mg of 2,3-dichloro-5,6-dicyanoquinone (DDQ) in 20 ml of toluene was boiled under reflux for 2 hr. After concentration the residue was taken up in hexane and chromatographed over neutral alumina (Woelm, activity 1). The first eluate fraction contained 20 mg of recovered **4** (R_1 = $-CH_3$; R_2 = –H). The second eluate fraction contained 20 mg of a mixture of pyrene and 1-methylpyrene. This mixture could be separated by vapor phase chromatography using SE-30 on a Chromosorb W column at 255°. Under these conditions, pyrene had a retention time of 9 min and 1-methylpyrene, 13.5 min. The identity of the two samples was confirmed by spectral comparison with authentic specimens. Furthermore, the sample of 1-methylpyrene was converted to the corresponding picrate, obtained as yellow crystals, mp 209–210° (lit.[23] mp 211–212°).

Other attempts at dehydrogenation of **4** (R_1 = $-CH_3$; R_2 = –H) using tetrachloro-*p*-benzoquinone or tetrachloro-*o*-benzoquinone gave similar mixtures of pyrene and 1-methylpyrene. Furthermore, irradiation of either **4** (R_1 = $-CH_3$; R = –H) or **4** (R_1 = R_2 = –H) in hexane solution in the presence of oxygen gave in good yield 4,5-dihydropyrene (**28**), identical in all respects with the authentic specimen described previously.

(23) H. Vollmann, H. Becker, M. Corell, and H. Streeck, *Ann.*, 531, 112 (1937).

Photochromism of [2.2]Metacyclophan-1-enes and the Thermal Isomerization of 4,5,15,16-Tetrahydropyrenes[1-3]

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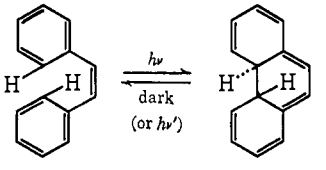
Abstract: Irradiation of [2.2]metacyclophan-1-enes (**3**, **4**, and **5**) with light in the region of 300 mμ gives photostationary equilibria in which the colored photoisomers, the 4,5,15,16-tetrahydropyrenes (**6**, **7**, and **8**), predominate. Such solutions of 4,5,15,16-tetrahydropyrenes are, in turn, bleached by light in the region of 500 mμ to give back the [2.2]metacyclophan-1-enes. The isomerization of 4,5,15,16-tetrahydropyrenes to their corresponding[2.2]-metacyclophan-1-enes also occurs thermally in the dark, and the kinetics of this thermal isomerization are discussed.

In 1940, Lewis, Magel, and Lipkin observed the formation of an unstable yellow intermediate during the low-temperature, ultraviolet irradiation of *cis*-stilbene (**1**) solutions.[4] Subsequent investigations have shown the unstable intermediate to be 4a,5a-dihydrophenanthrene (**2**),[5] and the easy oxidation of 4a,4b-dihydrophenanthrenes has made this an attractive synthetic route to phenanthrene derivatives.[6] More recently, Muszkat and Fischer have reported a detailed study of the photoisomerization of various *cis*-stilbenes to 4a,-4b-dihydrophenanthrenes as well as the reversal of this reaction either by light or thermally in the dark.[7] In an accompanying paper,[3] we have described the preparation of three [2.2]metacyclophan-1-enes (**3**, **4**, and **5**), which contain rigidly constrained *cis*-stilbene moieties. In view of the extensive and detailed studies by Muszkat and Fischer with the simple *cis*-stilbenes, it seemed appropriate to make a comparative study of the photoisomerization of our more rigid molecules as well as to examine the kinetics of the reverse, thermal, dark reaction.



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In each case irradiation of solutions of the [2.2]-metacyclophan-1-enes (**3**, **4**, and **5**) led to a photostationary state in which the [2.2]metacyclophan-1-ene was in equilibrium with the corresponding 4,5,15,16-tetrahydropyrene (**6**, **7**, and **8**). As expected, the photoisomer **6** is extremely sensitive to oxygen, being readily oxidized to 4,5-dihydropyrene (**9**). This sensitivity of 4a,4b-dihydrophenanthrenes to oxygen has been well documented previously.[5-7] However, when the 4a and 4b positions are occupied by methyl rather than hy-

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(2) Abstracted from the doctoral dissertation of C. E. Ramey, University of Oregon, 1968.

(3) This is paper XXI in our series on "Aromatic Molecules Bearing Substituents within the Cavity of the π-Electron Cloud." For the preceding article, see H. Blaschke, C. E. Ramey, I. Calder, and V. Boekelheide, *J. Amer. Chem. Soc.*, 92, 3675 (1970).

(4) G. N. Lewis, T. T. Magel, and D. Lipkin, *ibid.*, 62, 2973 (1940).

(5) W. M. Moore, D. D. Morgan, and F. R. Stermitz, *ibid.*, 85, 829 (1963).

(6) F. B. Mallory, J. T. Gordon, and C. S. Wood, *ibid.*, 85, 828 (1963).

(7) K. A. Muszkat and E. Fischer, *J. Chem. Soc., B*, 662 (1967).