crystallized from methanol–ethyl acetate and dried over phosphorus pentoxide for 48 hours at 110° (0.07 mm.); yield 93 mg. (32%), m.p. 198° dec., $[\alpha]^{26}\text{D}$ −42.8 ± 3.3° (0.416% in methanol); λ_{max} in mμ ($\epsilon \times 10^{-3}$): *p*H 1, 254 (13.7), 299 (9.30); *p*H 7, 258 (11.0), 287 (8.75); *p*H 13, 257 (10.7), 288 (8.99); $\bar{\nu}$ in cm.$^{-1}$: 3350 and 3150 (broad, OH, NH); 1660 (NH); 1600, 1540 and 1510 (C=C, C=N); 1125, 1080 and 1055 (C–O–).

Anal. Calcd. for $C_{11}H_{16}N_6O_4$: C, 44.59; H, 5.44; N, 28.37. Found: C, 44.48; H, 5.73; N, 28.00.

6-Amino-2-hydrazino-9-β-D-ribofuranosylpurine (XII).—To 30 ml. of anhydrous hydrazine was added portionwise 602 mg. (2.00 mmoles) of 6-amino-2-chloro-9-β-D-ribofuranosylpurine. The reaction mixture was kept at room temperature for 16 hours in a nitrogen atmosphere, and then the volatile materials were removed *in vacuo* (bath 30°). The last traces of hydrazine were removed by evaporating the residue with isopropyl alcohol (3 × 15 ml.). The residue was crystallized from a mixture of water and ethanol; yield 225 mg. (38%), m.p. 143°, resolidified at 150–155° and melted with decomposition at 200°. A second crop (51 mg.) of material which had the same melting point, was obtained from the mother liquor. Two recrystallizations of the crude product from water and ethanol gave the pure material; m.p. 143°. Since this compound was sensitive to heat, it was dried at room temperature at 0.07 mm. for 24 hours before analysis, $[\alpha]^{26}\text{D}$ −33.0 ± 1.8° (0.763% in water); λ_{max} in mμ ($\epsilon \times 10^{-3}$): *p*H 1, 256 (9.48), 277 (10.2); *p*H 7, 257 (11.0), 278 (9.30); *p*H 13, 250 (10.2), 282 (9.05); $\bar{\nu}$ in cm.$^{-1}$: 3380 (broad OH, NH); 1645 (NH); 1605, 1600 and 1525 (C=N, C=C); 1130, 1080 and 1045 (C–O–).

Anal. Calcd. for $C_{10}H_{15}N_7O_4 \cdot {}^1/_2C_2H_5OH$: C, 41.30; H, 5.68; N, 30.70. Found: C, 41.21; H, 5.84; N, 31.27.

6-Amino-2-azido-9-β-D-ribofuranosylpurine (XIII).—To a solution of 297 mg. (1.00 mmole) of 6-amino-2-hydrazino-9-β-D-ribofuranosylpurine in 7 ml. of 5% aqueous acetic acid which was cooled in an ice-bath, was added a cooled solution of 83 mg. (1.20 mmoles) of sodium nitrite in 17 ml. of water. After ten minutes, crystals began to separate; the reaction mixture was kept cold for one hour, and the solid was collected by filtration; yield 218 mg. (71%), m.p. 157–160° dec. One recrystallization from water gave the pure material, which was dried at 100° (0.07 mm.) over phosphorus pentoxide for 48 hours before analysis; yield 142 mg. (46.3%), m.p. 159–160° dec., $[\alpha]^{26}\text{D}$ −27.6 ± 5.8° (0.232% in methanol); λ_{max} in mμ ($\epsilon \times 10^{-3}$): *p*H 1, 273 (14.6); *p*H 7, 230 (20.8), 271 (11.9), 309 (4.75); *p*H 13, 230 (16.2), 271 (12.7); $\bar{\nu}$ in cm.$^{-1}$: 3370 (OH, NH); 2155 ($-N_3$); 1645 (NH); 1605, 1600 and 1520 (C=N, C=C); 1140, 1080 and 1055 (C–O–).

Anal. Calcd. for $C_{10}H_{12}N_8O_4$: C, 38.96; H, 3.92; N, 36.35. Found: C, 39.20; H, 4.47; N, 36.27.

BIRMINGHAM, ALABAMA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

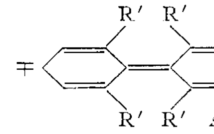
The Near Ultraviolet Absorption of Hindered Biphenyls[1]

BY ERICH MARCUS,[2] W. M. LAUER AND R. T. ARNOLD

RECEIVED FEBRUARY 8, 1958

Several biphenyls (Ar–Ar) with alkyl substituents in the four *o*-positions have been synthesized. A study of their spectra in the near ultraviolet region indicates that a comparison of the extinction coefficients of a biphenyl derivative with its monophenyl analog (Ar–H) at corresponding peaks, for the purpose of determining differences in steric effects is not unequivocal.

The broad, relatively intense absorption bands which characterize biphenyl derivatives in the 250–300 mμ region usually are attributed to resonance interactions involving the two benzenoid rings as shown in A.



A

It is now well established[3-5] that the position and intensity of these absorption bands are determined by the nature and size of the substituents present.

The insertion of *o*-substituents into biphenyl brings about dramatic changes in its spectrum. This effect is usually attributed[4] to non-bonded repulsions which inhibit coplanarity and thus reduce resonance interactions between the benzenoid rings. Although the characteristic "K-band" in these derivatives is shifted to shorter wave lengths and diminished in intensity,[5] its influence on the "B-band," which is the object of this study, is still quite evident.

The present investigation was initiated in the hope that an examination of the spectra of carefully selected biphenyl derivatives related to hydrindene and tetralin would permit a more quantitative evaluation of the difference in the steric effect of methylene groups in five- and six-membered rings. Such a difference has been observed repeatedly in earlier studies reported from this Laboratory.[6]

For this purpose, the following compounds (I–V) were prepared and their spectra in the near ultraviolet region examined.

It has been common practice[3,4,7] in studies of this kind to compare the spectra of symmetrical biphenyls (Ar–Ar) with their corresponding monophenyl analogs (Ar–H) and we, at first, followed this procedure (see Figs. 1 and 2).

Such comparisons seem to imply that it should be possible to "insulate" the two halves of a biphenyl molecule by rotating the two benzenoid rings sufficiently with respect to each other and thus reduce the resonance interaction to an insignificant value. If this were true, the spectrum of a

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[1] Taken from the Ph.D. Thesis of Erich Marcus, June, 1956.

[2] Parke–Davis Fellow, 1954–1955; National Science Foundation Fellow, 1955–1956.

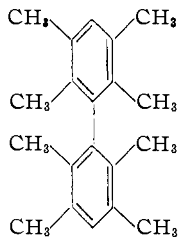
[3] M. Calvin, *J. Org. Chem.*, **4**, 256 (1939).

[4] B. Williamson and W. H. Rodebush, THIS JOURNAL, **63**, 3018 (1941).

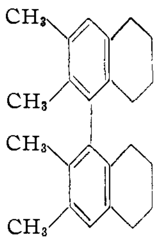
[5] E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 3776 (1955).

[6] S. W. Fenton, A. E. DeWald and R. T. Arnold, THIS JOURNAL, **77**, 979 (1955), and earlier papers.

[7] L. W. Pickett, G. F. Walter and H. France, *ibid.*, **58**, 2296 (1936).



I



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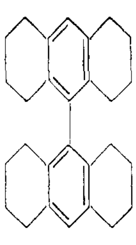

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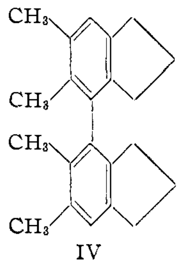
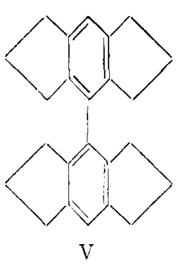


IV



V

highly hindered biphenyl might be expected to resemble that of its monophenyl analog (Ar–H) and the ratio of the extinction coefficients for corresponding peaks should approximate two (or one-half). The present study confirms earlier work[4,8] which proves the fallacy of this oversimplification. It becomes extremely difficult, therefore, to use the method as a general one for quantitative measurements of steric effects. Table I summarizes the ratios of extinction coefficients observed for the pertinent absorption band for compounds I–V and their corresponding monophenyl analogs.

TABLE I

Compound	$\lambda_{max.}$, mμ	$\epsilon_{max.}$	$\frac{\epsilon_{max.}\ Ar–Ar}{\epsilon_{max.}\ Ar–H}$
I	279	777	1.11
Durene	278	697	
II	281	1330	1.21
6,7-Dimethyltetralin	281	1100	
III	283	2080	1.07
Octahydroanthracene	285	1950	
IV	281	2740	1.30
5,6-Dimethylhydrindene	282	2100	
V	284	6000	1.56
Hydrindacene	287	3850	

Although they are of little quantitative significance, the higher ratios for the extinction coefficients found in Table I for the biphenyls derived from hydrindene (*i.e.*, IV and V) do indicate a smaller deviation from coplanarity in these molecules—with respect to I, II and III—and, therefore, support our earlier views pertaining to the relative smallness of methylene groups in five-membered rings.

Perhaps the most significant conclusion drawn from the present study arose from an attempt to account for the low ratios reported in Table I. Wepster[8] already has raised the question as to whether bimesityl should be compared with mesitylene or isodurene. Our own data seem to indicate that a comparison of Ar–Ar with Ar–CH_3 is qualitatively, at least, better than that of Ar–Ar with Ar–H. Theoretical support for this view is found in an earlier publication by Sklar[9] dealing with the spectra of alkylbenzenes. Any attempt at the moment, however, to use even these comparisons in a quantitative manner for the purpose of measuring steric effects, we believe, is subject to serious objections.

There is a striking similarity in the spectra for biduryl and pentamethylbenzene. This suggests, of course, that the electronic transitions in these two compounds are comparable. The low absorption of pentamethylbenzene[10]—compared to durene—could, therefore, account in large part for the low biduryl/durene value.

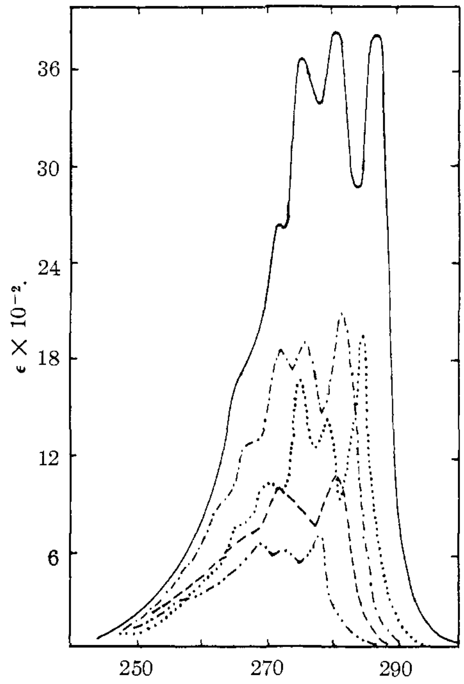


Fig. 1.—Hydrindacene, ———; 5,6-dimethylhydrindene, —·—·—; octahydroanthracene, ...; 6,7-dimethyltetralin, -------; durene, —··—··—.

Correspondingly, if one compares the ratio of intensities for the absorption bands of 2,2′,6,6′-tetramethylbiphenyl[11] at 263 and 269 mμ with those of the analogous Ar–H compound (*i.e.*, *m*-xylene) at 265 and 272 mμ, low values of 1.66 and 1.45, respectively, are found. It is suggested that these low values really are due to the close relationship of 2,2′,6,6′-tetramethylbiphenyl with 1,2,3-trimethylbenzene[12] which actually absorbs less strongly in this region than does *m*-xylene.

Interestingly enough, ratios of extinction coefficients, when one compares Ar–Ar with Ar–H, are not invariably low. For example: the ratios of intensities for the absorption bands of bimesityl at 267 and 272 mμ with mesitylene at 265 and 272 mμ are considerably in excess of two, namely, 2.64 and 2.42, respectively. The argument used above also

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[8] B. M. Wepster, *Rec. trav. chim.*, **71**, 1160 (1952).

[9] A. L. Sklar, *J. Chem. Phys.*, **10**, 135 (1942).

(10) American Petroleum Institute Project 44, Catalogue of Ultraviolet Spectra. Serial No. 393.

(11) We are indebted to Dr. R. B. Carlin, Carnegie Institute of Technology, for this sample.

(12) American Petroleum Institute Project 44, Catalogue of Ultraviolet Spectra, Serial No. 162.

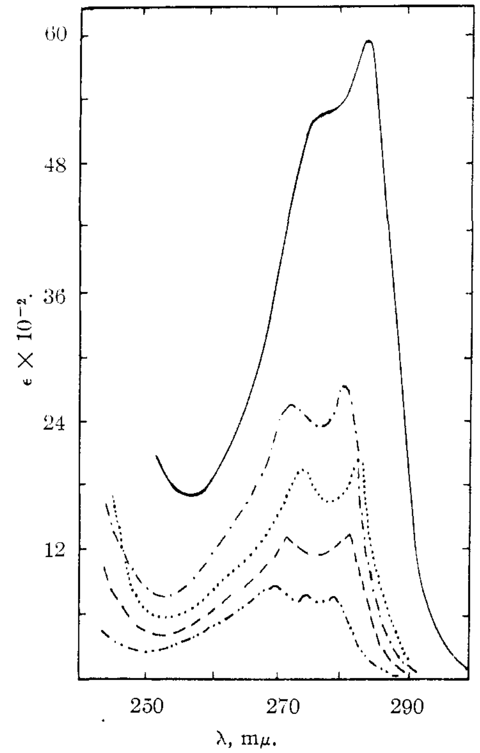


Fig. 2.—Bihydrindacyl (V), ———; 5,5′,6,6′-tetramethyl-4,4′-bihydrindyl (IV), –·–·–·; bioctahydroanthracyl (III), ...; 6,6′,7,7′-tetramethyl-5,5′-bitetralyl (II), --------; biduryl (I), –··–··–.

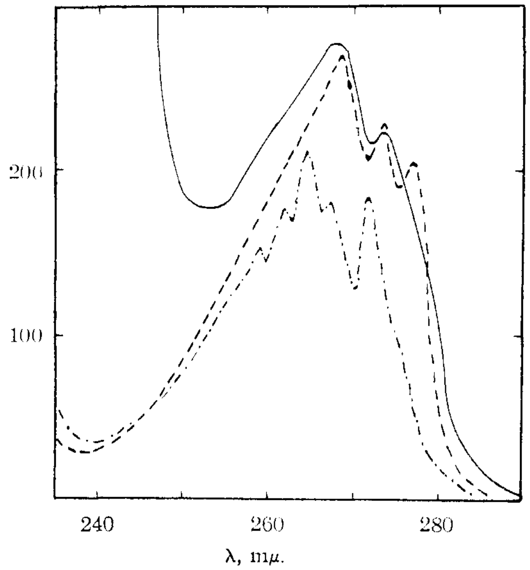


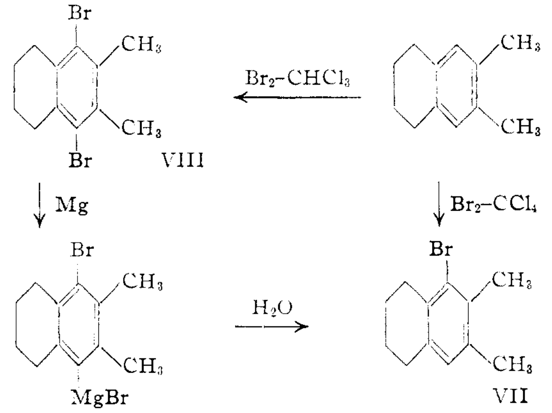
Fig. 3.—Bimesityl × $^1/_2$, ———; isodurene,[13] --------; mesitylene, –·–·–·–.

suffices to explain this case. Figure 3 shows clearly the unusual resemblance in the spectra for bimesityl and 1,2,3,5-tetramethylbenzene[13] (isodurene). Thus the high values for bimesityl/mesitylene are accountable for in terms of the higher absorption of isodurene with respect to mesitylene.

Synthetic Procedures.—The symmetrical biphenyl derivatives I–V were all prepared by coupling the appropriate organometallic compounds (VI) with cobaltous bromide.

$$\text{Ar-Br} \longrightarrow \underset{\text{VI, M = Li, MgBr}}{\text{Ar-M}} \xrightarrow{\text{CoBr}_2} \text{Ar-Ar}$$

Direct ring bromination of 1,2,4,5-tetraalkylbenzenes and their cyclic methylene analogs (*i.e.*, octahydroanthracene, etc.) to form monobromo derivatives is very sensitive to the nature of the solvent employed. In general, when carbon tetrachloride was used as solvent, the monobromo compound could be isolated readily by fractional distillation. Use of chloroform as a solvent in this reaction, however, often leads to excessive dibromination.[14] In particular, we have observed that solvent effects in the direct bromination of 6,7-methyltetralin are especially pronounced. An excellent yield (81%) of 5-bromo-6,7-dimethyltetralin (VII) was obtained using carbon tetrachloride as solvent. Use of chloroform led preferentially to 5,8-dibromo-6,7-dimethyltetralin (VIII). The latter, however, could be converted into VII by means of a Grignard intermediate.



Experimental

Spectra.—Except where otherwise indicated, all spectra reported here were recorded on a Cary spectrophotometer using ethanolic (95%) solutions. The instrument was calibrated[15] and the data were reproducible to ±1–2%.

2,2′,3,3′,5,5′,6,6′-Octamethylbiphenyl (I).—A Grignard solution prepared from bromodurene[16] (18.7 g.), magnesium (2.5 g.), a trace of iodine and ether (100 ml.) was cooled in an ice-bath, and anhydrous cobaltous bromide (19.2 g.) was added. The reaction appeared to be sluggish at low temperature. As the temperature rose gradually, the solution turned dark and finally boiled. With external heating, refluxing was continued for 19 hours. The solution was poured onto ice and hydrochloric acid, and the whole extracted with ether. After being dried, the ether layer was evaporated and the residue fractionally distilled. Durene (6 g.) was recovered from fraction 1, and fraction 2 (b.p. 80–160° (15 mm.)) was discarded. Fraction 3 (b.p. 140–155° (1 mm.)) consisted of an oil which partially solidified. Two recrystallizations of the latter from ethanol gave pure biduryl; yield 1.15 g. (10%). The melting point of this material was most unusual and indicated two crystalline modifications. A sharp melting point was observed repeatedly at 126–127° followed by resolidification and subsequent melting at 136–138°.

Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.13; H, 9.81.

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[13] *Ibid.*, Serial No. 391.

[14] G. Schroeter, *Ber.*, **60**, 2035 (1927).

[15] G. W. Haupt, *J. Research Natl. Bur. Standards*, **48**, 414 (1952).

[16] We are indebted to Dr. Lee I. Smith of the University of Minnesota for a generous supply of this material.

5-Bromo-6,7-Dimethyltetralin (Method A).—6,7-Dimethyltetralin (90.9 g.) and iodine (0.3 g.) were dissolved in carbon tetrachloride (100 ml.), cooled in a salt–ice-bath, and held at a temperature of −10 to −15° during the course of the reaction. A solution of bromine (93.6 g.) in carbon tetrachloride (100 ml.) was added dropwise with stirring during a period of 75 minutes. The solution was stirred for an additional three hours during which time the temperature of the reaction mixture rose to room temperature. The organic layer was washed with water, dilute sodium hydroxide, dilute sodium bisulfite and finally with water. Removal of the solvent gave an oil which, upon fractionation, gave 5-bromo-6,7-dimethyltetralin; yield 110 g. (81%), b.p. 105–110° (0.5 mm.), $n^{24.8}\text{D}$ 1.580.

Anal. Calcd. for $C_{12}H_{15}Br$: C, 60.26; H, 6.32. Found: C, 60.51; H, 6.49.

When chloroform was employed as solvent in the direct bromination of 6,7-dimethyltetralin (11.7 g.), there was obtained 5-bromo-6,7-dimethyltetralin (2.4 g., 14%) and 5,8-dibromo-6,7-dimethyltetralin (5.2 g., 22%) melting at 122–124°.

Anal. Calcd. for $C_{12}H_{14}Br_2$: C, 45.31; H, 4.44. Found: C, 45.41; H, 4.44.

5-Bromo-6,7-dimethyltetralin (Method B).—Magnesium turnings (0.8 g.) were added to a solution containing 5,8-dibromo-6,7-dimethyltetralin (9.5 g.), a few crystals of iodine and ether (30 ml.). The solution was boiled under nitrogen for three hours and then decomposed with a few drops of aqueous sulfuric acid (25%). Through ultimate fractionation of the ethereal solution, there was obtained pure 5-bromo-6,7-dimethyltetralin; yield 4.9 g. (68%), b.p. 109° (0.5 mm.), $n^{25}\text{D}$ 1.5785.

6,6′,7,7′-Tetramethyl-5,5′-bitetralyl (II).—Finely cut lithium wire (0.2 g.) was added under nitrogen to a solution of 5-bromo-6,7-dimethyltetralin (2.2 g.) in dry ether (15 ml.). The solution was stirred at its boiling point, and a white precipitate formed gradually. After five hours of refluxing, the solution was cooled and cobaltous bromide (2.1 g.) was added in portions. The solution boiled spontaneously and turned black. It was held under reflux with external heating for one hour, poured onto ice and hydrochloric acid, and the whole was extracted with ether. After drying the ethereal layer, the ether was evaporated to give a yellow solid (0.65 g.), m.p. 136–140°. The latter was purified by chromatographic adsorption using alumina (Alcoa, grade F-20) and petroleum ether (b.p. 30–60°). Final crystallization from absolute ethanol gave pure 6,6′,7,7′-tetramethyl-5,5′-bitetralyl; yield 0.52 g. (36%), m.p. 146–148°.

Anal. Calcd. for $C_{24}H_{30}$: C, 90.50; H, 9.50. Found: C, 90.79; H, 9.79.

9-Bromoöctahydroanthracene.—A solution prepared from octahydroanthracene (9.3 g.), carbon tetrachloride (50 ml.) and a few crystals of iodine, was cooled in an ice-bath. To this was added dropwise with stirring over a period of 40 minutes, a solution containing bromine (8.2 g.) and carbon tetrachloride (5 ml.). During another 4.5 hours of stirring, the solution was brought gradually to room temperature. It was then washed with water, dilute sodium hydroxide, dilute sodium bisulfite, and again with water. The solution was dried over calcium chloride and evaporated to give a colorless oil which solidified. This residue was distilled (b.p. 151–160° (1 mm.)), and the distillate was crystallized from ethanol to give pure 9-bromoöctahydroanthracene; yield 7.2 g. (54%), m.p. 75.5–76.5° (reported[14] 74–75°).

9,9′-Bi-octahydroanthracyl (III).—Finely cut lithium wire (0.4 g.) was added under nitrogen to a solution of 9-bromoöctahydroanthracene (5.3 g.) in dry ether (30 ml.). The solution was stirred under reflux for 16 hours. Anhydrous cobaltous bromide (4.4 g.) was added to the solution at room temperature. The mixture turned black immediately and spontaneous boiling resulted. After four hours at reflux temperature (under nitrogen), the mixture was poured onto ice and concentrated hydrochloric acid. The dried ethereal layer was evaporated to remove solvent, and the residue was distilled to remove components boiling below 165° (2 mm.). The brown residue (1.5 g.) was chromatographed over alumina (Alcoa, grade F-20) using petroleum ether (b.p. 30–60°) as eluent. The white solid (0.9 g.) so obtained was crystallized from glacial acetic acid and finally washed with methanol; yield 0.77 g. (21%), m.p. 214–218°.

Anal. Calcd. for $C_{28}H_{34}$: C, 90.75; H, 9.25. Found: C, 90.63; H, 9.75.

4-Bromo-5,6-dimethylhydrindene.—The bromination of 5,6-dimethylhydrindene (4.9 g.) was carried out in carbon tetrachloride (12 ml.) as described above for the corresponding tetralin derivatives. Fractional distillation of the crude product gave a light yellow oil which solidified at room temperature; yield 5.1 g. (68%), b.p. 94° (0.4 mm.). After recrystallization from ethanol white needles were obtained, m.p. 33.5–35°.

Anal. Calcd. for $C_{11}H_{13}Br$: C, 58.68; H, 5.82. Found: C, 58.88; H, 5.88.

5,5′,6,6′-Tetramethyl-4,4′-bihydrindyl (IV) was prepared as described above for analogous examples by coupling with cobaltous bromide (2.8 g.) the organolithium derivative prepared from 4-bromo-5,6-dimethylhydrindene (2.8 g.) and lithium (0.23 g.) in ether (20 ml.). The crude product was purified by chromatographing over activated alumina; yield 0.43 g. (23%), m.p. 101–102°.

Anal. Calcd. for $C_{22}H_{26}$: C, 90.97; H, 9.03. Found: C, 91.10; H, 8.90.

4-Bromo-*sym*-hydrindacene.—A solution of *sym*-hydrindacene (6.3 g.) in carbon tetrachloride (20 ml.) containing a trace of iodine was brominated as described above with bromine (6.6 g.). The product was obtained by fractionation of the residue after removal of the solvent. The fraction (b.p. 114–119° (0.8 mm.)) solidified and was recrystallized from methanol; yield 4.7 g. (50%), m.p. 38.5–39.5°.

Anal. Calcd. for $C_{12}H_{13}Br$: C, 60.77; H, 5.52. Found: C, 60.51; H, 5.69.

4,4′-*sym*-Bihydrindacyl (V).—Considerable difficulty was encountered in the preparation of this hydrocarbon probably due to the formation of insoluble coatings on the metal. Finely cut lithium wire (0.4 g.) was added under nitrogen to a solution of 4-bromo-*sym*-hydrindacene (4.3 g.) in dry ether (20 ml.). After 21 hours of stirring under reflux, only a gray coating had appeared on the lithium surface. Magnesium turnings (0.44 g.) and a trace of iodine were then added. The solution was stirred at its boiling point for an additional 24 hours. Still no sign of reaction was visible. Anhydrous cobaltous bromide (4 g.) was added. Stirring the solution at the boiling point for an additional day caused the slow precipitation of black cobalt. After decomposition with ice and hydrochloric acid and removal of the solvent, the residue was chromatographed on alumina with petroleum ether to give a colorless oil which crystallized. Recrystallization from absolute ethanol gave a white solid product; yield 0.5 g. (18%), m.p. 146–148°.

Anal. Calcd. for $C_{24}H_{26}$: C, 91.67; H, 8.33. Found: C, 91.33; H, 8.35.

MINNEAPOLIS, MINNESOTA