

BORON PHOTOCHEMISTRY

IV. A STABLE TRIARYLBORANE FROM THE PHOTOLYSIS OF POTASSIUM DIMESITYLDIPHENYLBORATE

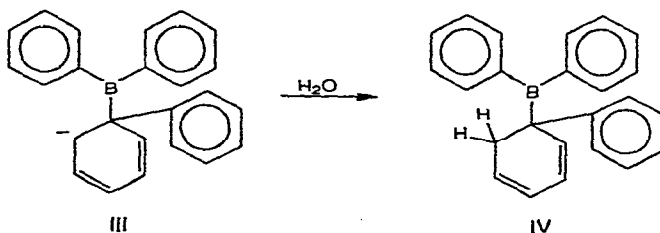
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SUMMARY

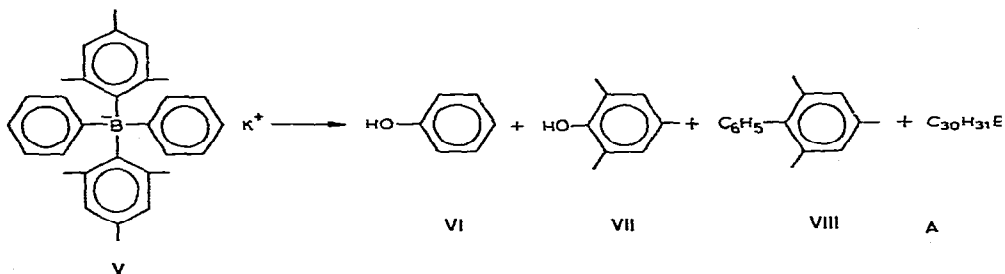
We have photolyzed potassium dimesityldiphenylborate in 1,2-dimethoxy ethane/water solution with light in the region of 2537 Å in the presence of air. The products were phenol (VI), 2-hydroxymesitylene (VII), 2,4,6-trimethylbiphenyl (VIII), and (2,4,6-trimethyl-3-biphenyl)mesitylphenylborane (XI). The structure of XI was determined from spectroscopic data, chemical degradation, and synthesis. We believe the presence of XI as a photoproduct is evidence for the original generation of a phenyl radical and a dimesitylphenylborane radical anion by photolysis of the borate salt. We have proposed reaction sequences to account for the reaction products, based on an intramolecular attack by radical species.

In previous publications¹⁻³ we have discussed the photochemistry of "ate" complexes of boron. These included the charged tetraarylborate salts Ar_4B^- and the neutral complexes Ar_3BX formed from triarylboranes and species X containing lone pairs of electrons capable of donating to the empty orbital on boron. The photochemistry which we have described occurs only with such tetrahedral complexes in protic solvents. For example, trimesitylborane (I), which is a highly hindered molecule, cannot interact with molecules having lone pairs of electrons⁴, and is resistant to photolysis under the conditions which we employed². In the possible reaction mechanisms for the photolysis of sodium tetraphenylborate (II), we have postulated very compact hindered intermediates III and IV.

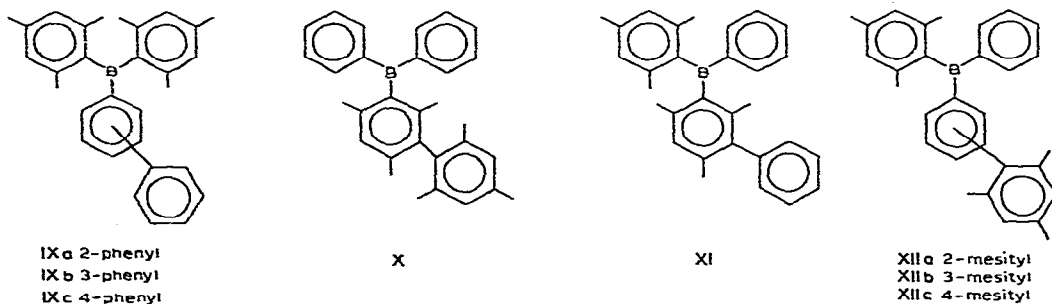


Alternative analogous radical intermediates were also proposed. In this way we account for the intramolecularity of the reaction, and the unique coupling of the phenyl rings in the positions which were originally bonded to boron, to produce biphenyl

and phenylcyclohexadienes¹. By selecting highly hindered tetraarylborates for study in the photolysis reaction, we hoped to stabilize intermediates, and to provide data to enable us to elucidate the mechanism. We have, therefore, synthesized potassium dimesityldiphenylborate (V) and studied its photolysis in 1,2-dimethoxyethane/water solution, with light in the region of 2537 Å, in the presence of oxygen. The products which were isolated as zones collected by preparative GLC were phenol (VI), 2-hydroxymesitylene (VII), 2,4,6-trimethylbiphenyl (VIII), and a boron-containing compound A.

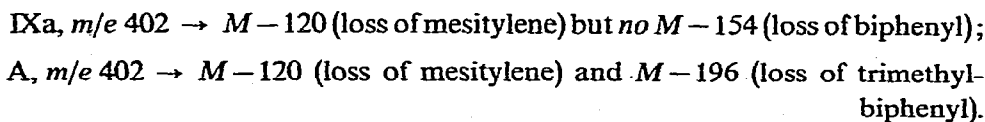


hydroxymesitylene (VII), 2,4,6-trimethylbiphenyl (VIII), and a boron-containing compound A. The unknown A was also isolated by crystallization. Compounds VI–VIII were identified by comparison of their ultraviolet and mass spectra, and GLC retention times with those of authentic samples. Compound A had an elemental analysis corresponding to $C_{30}H_{31}B$, and the parent ion in its mass spectrum had m/e 402. Its NMR spectrum showed absorption corresponding to a ratio of six methyl groups to thirteen aromatic protons. These data alone suggested that A had one of the following structures.



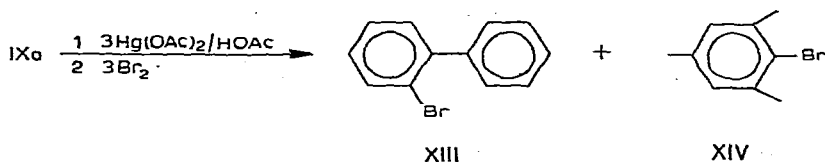
The unusual stability of A toward oxygen suggested a highly hindered triaryl compound. Structures IX, XI, and XIIa best fulfilled these requirements. The NMR spectrum of A showed that the methyl groups were not equivalent, but the proton resonances appeared as four peaks corresponding to methyl groups in the ratio 1:4:1. In such rigid molecules as IX to XII, it is uncertain which methyl groups would be equivalent. We therefore synthesized a sample of IXa as a model compound.

Compound IXa proved to be stable and showed protons corresponding to two types of methyl groups in its NMR spectrum. A schematic representation of the fragmentations observed in the mass spectra of IXa and the unknown A is shown below:

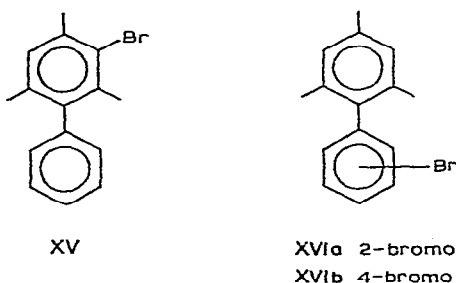


The appearance of a fragment ion peak at $M - 196$ in the spectrum of A, but the absence of a fragment ion peak at $M - 154$ in the spectrum of IXa, strongly suggests that the boron atom in A is attached to the biphenyl nucleus via the ring bearing the methyl substituents. The fact that a fragment ion $M - 120$ is observed in the spectrum of A indicates the presence of a mesityl group attached to boron. We decided that XI was the most probable structure for A.

Additional proof of structure of A came from chemical degradation studies. The model compound IXa was used to establish the reliability of the method, and was degraded according to the following scheme:



The aryl bromides XIII and XIV were separated by preparative GLC as zones which were identified by mass spectra, and by comparison with authentic samples. Although this procedure is not quantitative, it has enabled us to determine the point of attachment of the boron atom to the aryl groups. When this procedure was applied to A, five bromides were isolated: bromobenzene, bromomesitylene, dibromomesitylene, bromotrimethylbiphenyl and dibromotrimethylbiphenyl. Comparison of the isolated bromotrimethylbiphenyl with authentic samples of isomers XV and XVI enabled us to establish the structure of A to be XI.



We then converted XV to the corresponding lithio derivative, which was allowed to react with butoxymesitylphenylborane (XVII) to yield XI, which was identical in every respect with the unknown A.

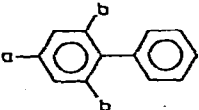
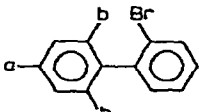
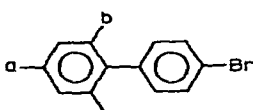
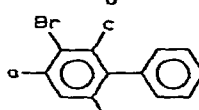
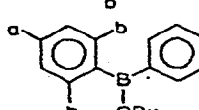
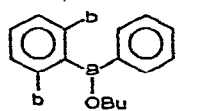
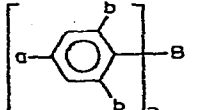
Data for the methyl absorptions from the NMR spectra of the compounds referred to in this paper are recorded in Table 1. Methyl protons *para* to the point of attachment to either boron or another aromatic ring occur at the lowest field region (130–145 Hz) in a given spectrum; those *ortho* to the point of attachment occur in the mid-region (115–130 Hz). This is evident from those compounds in the table whose structures are unequivocal. In compound XV, the shift to a lower field of the methyl designated c can be explained as a manifestation of the steric compression shift⁵ by the adjacent bromine atom. In compounds XI and XIX, the methyls designated c fall at significantly higher field than the generalization just given would predict. This shift is of the magnitude and direction found for analogous methyls in 1,4-dimethyl-tetraphenylbenzenes⁶, and is explained as a result of the "ring current" anisotropy

and the steric compression shifts by the adjacent pendent phenyl group. The adjacent phenyl is turned perpendicular to the plane of the mesitylene ring and is positioned so that the methyl falls in its shielding zone. The sum of this shift and the steric compression shift is the observed value of approximately 0.2 ppm.

Possible schemes to account for the reaction products are shown in Chart 1, page 68.

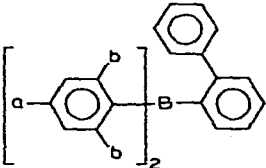
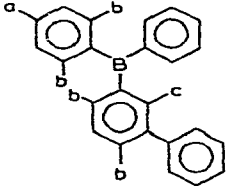
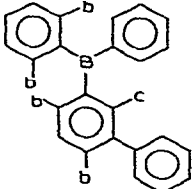
Several points should be noted. (A) In our previous studies, all of the multiaryl products isolated were shown to be derived by intramolecular routes. This appears to be the case in the present study. (B) We favor the formation and conversion of the anion biradicals XX and XXIII to anions XXI and XXIV, respectively, because we have no evidence in any of our studies for any hydrogen abstraction reactions, whereas we do have evidence for proton and deutron addition*. (C) In an earlier

TABLE 1
SHIFTS FOR THE METHYL PROTON RESONANCES FOR THE COMPOUNDS LISTED
(in Hz downfield from TMS, in deuteriochloroform)

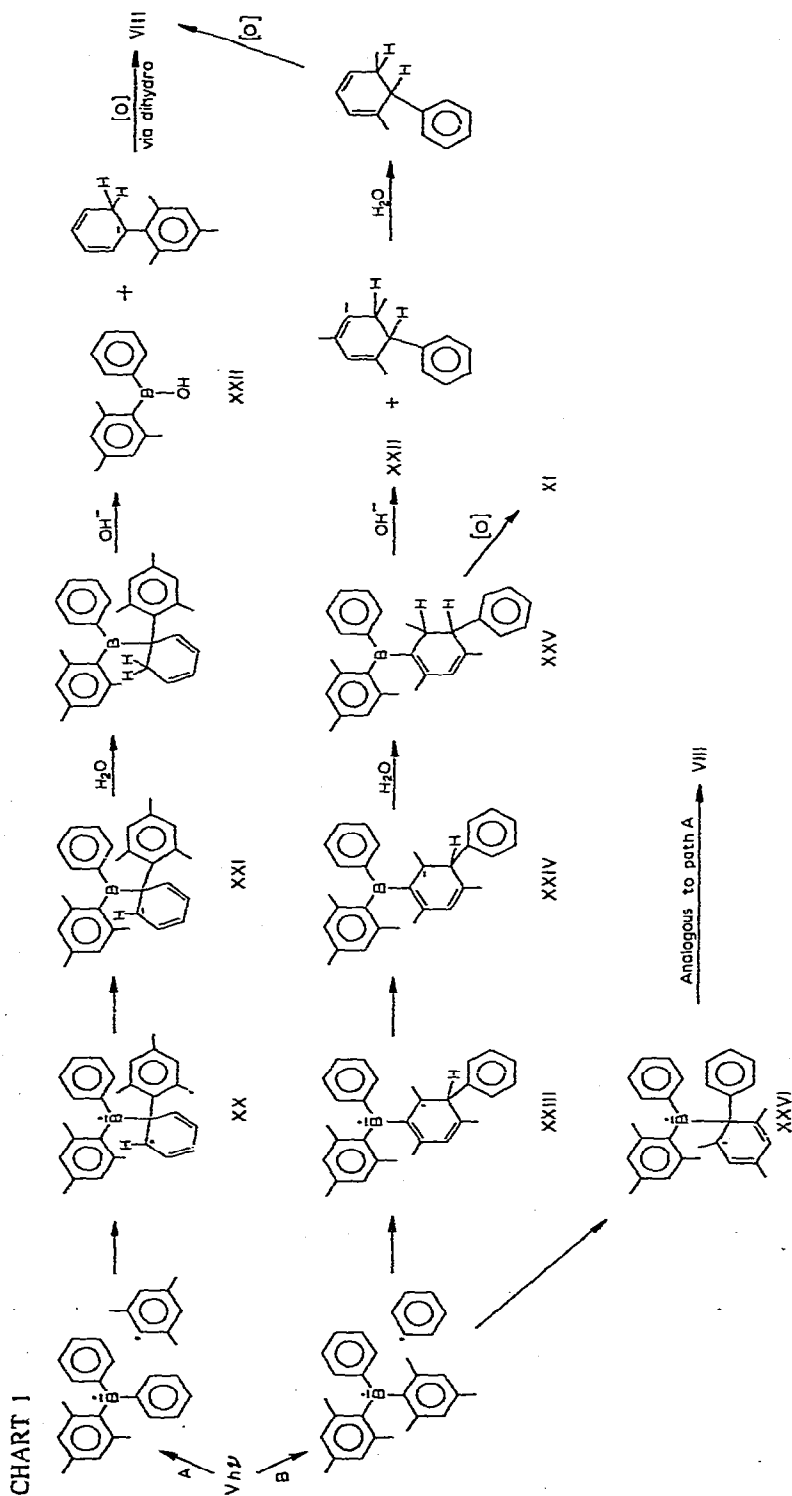
Compound	Number	CH ₃ ^a (No.)	CH ₃ ^b (No.)	CH ₃ ^c (No.)
	VIII	137(1)	119(2)	
	XVIa	138(1)	117(2)	
	XVIb	138(1)	119(2)	
	XV	146(1)	116(1)	128(1)
	XVII	139(1)	129(2)	
	XVIII		131(2)	
	I	134(3)	117(6)	

*In photolyses of sodium tetraphenylborate in enriched isopropyl alcohol-*O-d*, we have observed incorporation of deuterium in the products, rather than incorporation of hydrogen by abstraction of the α -hydrogen atom from the isopropyl alcohol.

TABLE 1 (Continued)

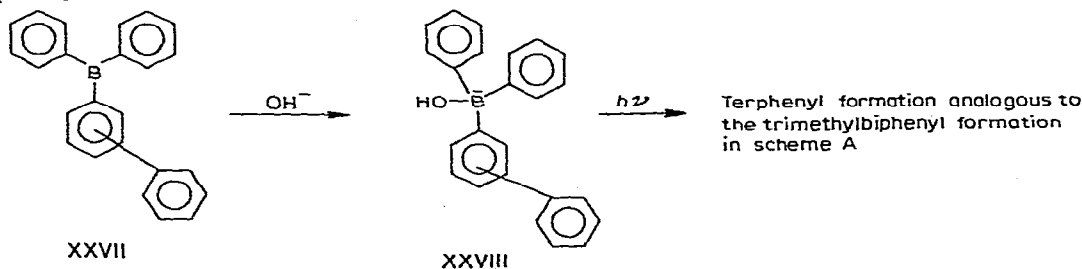
Compound	Number	CH ₃ ^a (No.)	CH ₃ ^b (No.)	CH ₃ ^c (No.)
	IXa	129(2)	117(4)	
	XI	138(1)	123(4)	103(1)
	XIX		125(4)	104(1)

publication⁷, we have discussed the oxidative breakdown of diaryl borinic acids to yield phenols. In this case, XXII would be expected to yield phenol (VI) and 2-hydroxymesitylene (VII). (D) No detectable amounts of biphenyl or hexamethylbiphenyl (< 1% of the trimethylbiphenyl yield) were produced in the photoreaction. Scheme A is essentially that proposed earlier, and accounts only for the production of trimethylbiphenyl. It is in line with the mass spectral data for the facile cleavage of a mesityl group, and accounts for the fact that no biphenyl is formed. Steric effects would prevent the formation of hexamethylbiphenyl via a pathway similar to that shown for the formation of trimethylbiphenyl (VIII). Trimethylbiphenyl (VIII) could also result from the sequence of reactions shown in Scheme B, via the immediate precursor XXV of the final triarylborane XI. The existence of XI as a photoproduct necessitates the cleavage of a phenyl species from V, and specific attack on the more hindered mesityl nucleus. This behavior is more characteristic of a phenyl radical than of a phenyl carbanion. A phenyl carbanion would be expected to attack a second phenyl group in preference to the electron-rich mesityl ring, but the data for radical phenylation show that attack on mesitylene is at least four times faster than that of benzene⁸. For these reasons, the *initial* formation of radical species from V seems most likely. Yet another route to trimethylbiphenyl (VIII) would be via XXVI, an intermediate formed by attack of the phenyl radical on the 1-position of the mesityl ring. A sequence of reactions analogous to that shown under path A would yield VIII. This route to VIII would be more in keeping with our previous observations that the aryl groups are bonded in the biaryl, by the ring atoms that were originally bonded to boron in the "ate" complexes^{1,3,8}. With the available data we are not able to rule out dual mechanisms A and B for the formation of VIII. In fact, if one considers the ultraviolet



spectral data one might expect dual mechanisms. In tetrahedral complexes there should be very little interaction between the π -electron systems of the aryl groups, and the intensity of the low-energy $\pi \rightarrow \pi^*$ absorptions should be comparable to those in uncomplexed molecules. At 2537 Å, the absorptions of bromomesitylene and bromobenzene are essentially identical. One would therefore expect both the phenyl and the mesityl groups to be excited in the complex, and expect both a phenyl and a mesityl species to leave boron.

We believe the data and the discussion are evidence for an initial radical mechanism for this reaction. In our studies on the photolysis of sodium tetraphenylborate under oxygen³, we demonstrated intramolecular formation of terphenyls. Intermediates XXVII analogous to XI could easily lead to the terphenyls via the "ate" complexes XXVIII.



The ideas proposed here form the basis for further experiments. Modification of the aryl groups in hindered tetraarylborates, and photolyses in labeled solvents should enable us to test some of these proposals. Such work is in progress and will be reported later.

EXPERIMENTAL

All melting points are corrected. Various spectra were determined on Cary Model 15 (UV), Perkin-Elmer Infracord (IR), and Varian A-60 (NMR) instruments. Mass spectra were determined with a CEC 21-110B instrument equipped with a heated inlet system*. GLC analyses and separations were run on a Model 5750 F and M gas chromatograph, equipped with a 1/4-in. stainless-steel column, 10 ft long, packed with 5% SE 30 on AWD MCS Chromosorb G. The column temperature was usually programmed from 150° to 350° at 10°/min.

Photolyses

A solution of 1 g of potassium dimesityldiphenylborate in a mixture of 100 ml of 1,2-dimethoxyethane and 100 ml of water was placed in a double-walled, water-cooled quartz tube. A small Teflon[®]-covered stirring bar was placed in the bottom of the tube and driven magnetically. The tube was placed in the center of a Rayonet reactor equipped with 2537-Å tubes. A stream of air was bubbled through the solution while the irradiation was conducted for 16 h. The dark brown solution was evaporated to dryness, then treated with 50 ml of water and 50 ml of benzene. The benzene layer was separated and dried, and examined by preparative GLC. The products were

* The system is described by V. J. Caldecourt⁹, but was constructed of glass.

phenol (*m/e* 94), 2-hydroxymesitylene (*m/e* 136), 2,4,6-trimethylbiphenyl (*m/e* 196) and the unknown boron compound A (*m/e* 402). The identification of the known compounds was confirmed by comparisons of UV or IR spectra with those of authentic samples. The phenolic materials which we were unable to measure quantitatively because of oxidation were removed by washing the benzene solution with 15% sodium hydroxide solution. The benzene layer was washed with water, dried, and evaporated to yield 0.4 g of residue. UV spectral analysis at 318 m μ and GLC analysis showed this to contain 0.22 g of A and 0.09 g of trimethylbiphenyl. This mixture was then treated with 2 ml of warm methanol and 3 drops of ether and chilled overnight. The solid so obtained was filtered off, m.p. 147–149°, 0.16 g. Crystallization from acetonitrile chloroform failed to improve the m.p. Compound A proved to be (2,4,6-trimethyl-3-biphenyl)mesitylphenylborane (XI). UV λ_{\max} in cyclohexane 259, 318 m μ ; ϵ 14,000, 12,000. (Found: C, 89.3; H, 7.7; B, 2.6; mol.wt. mass spectrum, 402. C₃₀H₃₁B calcd.: C, 89.6; H, 7.7; B, 2.7%; mol.wt. 402.3.)

Degradation experiments

The unknown photoproduct A and authentic isomeric 2-biphenyldimesitylborane IXa were submitted to the degradation described below. The triarylborane (0.5 mmole) was added to a solution of mercuric acetate (1.5 mmoles) in acetic acid (10 ml). The solution was boiled for 20 min and then treated with bromine (1.5 mmoles). The color disappeared immediately. The solution was poured into ice and water, and extracted with 1 ml of dichloromethane. The dichloromethane layer was separated and washed with dilute sodium hydroxide solution. The organic layer was dried and subjected to preparative GLC analysis. By this method, IXa yielded 2-bromomesitylene and 2-bromobiphenyl, whose retention times and UV spectra were identical with those of authentic samples. Similarly, A yielded bromobenzene, 2-bromomesitylene, 2,4-dibromomesitylene (*m/e* 276), 3-bromo-2,4,6-trimethylbiphenyl (*m/e* 274) and a dibromotrimethylbiphenyl (*m/e* 352). The monobromo compounds had retention times and UV spectra identical with those of authentic samples, the syntheses of which are described below.

Materials

All operations involving lithium and Grignard reagents were conducted under a nitrogen atmosphere. Fluorodimesitylborane and trimesitylborane were prepared by the methods of Brown and Dodson⁴. Potassium dimesityldiphenylborate was prepared via the lithium salt by the general method described by Wittig and Herwig¹⁰, from 2 moles of phenyllithium and 1 mole of fluorodimesitylborane.

4-Bromo-2',4',6'-trimethylbiphenyl (XVIIb)

A solution of *p*-bromoaniline (86.0 g, 0.5 mole) in 160 ml of concentrated hydrochloric acid and 90 ml of water was diazotized at 0–5° with a solution of sodium nitrite (35 g) in 90 ml of water. This solution of the diazonium salt was filtered and added to 500 ml of mesitylene at 0–5°. The vigorously stirred cold suspension was treated over 3 h with a solution of 80 g of sodium hydroxide in 500 ml of water. The stirring was continued overnight while the suspension was allowed to warm to room temperature. The mesitylene layer was separated and washed with water. The mesitylene was evaporated under a vacuum and the residue extracted with 1000 ml

of hexane. The hexane solution was poured through a 10-cm-diameter and 8-cm-high column of alumina (Woelm, neutral, activity grade 1). More hexane was used to elute the material and a total of 1000 ml was collected. The eluant was evaporated to yield the crude product. It crystallized from methanol in white plates, 20.5 g, 14.7%, m.p. 72–73°. (Found: C, 65.6; H, 5.7; Br, 29.0. $C_{15}H_{15}Br$ calcd.: C, 65.5; H, 5.5; Br, 29.1%.)

2-Bromo-2',4',6'-trimethylbiphenyl (XVIa) and 3-bromo-2,4,6-trimethylbiphenyl (XV)

These isomers were prepared as described for XVIb. Compound XVIa was prepared in 12.7% yield by reaction of 2-bromobenzenediazonium hydroxide with mesitylene. It had b.p. 120–124°/0.6 mm. Compound XV was prepared in 5.8% yield by reaction of benzenediazonium hydroxide with 2-bromomesitylene. It had b.p. 124–126°/0.4 mm. Both isomers were homogeneous to GLC analysis. (Found, isomer XVIa: C, 65.5; H, 5.5; Br, 29.5; isomer XV: C, 65.4; H, 5.7; Br, 28.8. $C_{15}H_{15}Br$ calcd.: C, 65.5; H, 5.5; Br, 29.1%.)

2,4,6-Trimethylbiphenyl (VIII)

A solution of 5.5 g (0.02 mole) of 4-bromo-2',4',6'-trimethylbiphenyl (XVIb) in 20 ml of dry ether was treated under a nitrogen atmosphere with 10.5 ml of 2 M n-butyllithium solution (Alfa Inorganics). After 10 min, the solution was poured into water and the ether layer was washed, dried, and evaporated to yield the pure trimethylbiphenyl as a colorless oil. It was homogeneous to GLC analysis. (Found: C, 91.6; H, 8.1; mol.wt. mass spectrum, 196. $C_{15}H_{16}$ calcd.: C, 91.7; H, 8.2%; mol.wt. 196.3.)

n-Butoxymesitylphenylborane (XVII)

A 0.2 mole Grignard reagent solution, prepared from 40 g of 2-bromomesitylene and 5.0 g of magnesium turnings in dry ether, was added to a solution of 47 g (0.2 mole) of di-n-butoxyphenylborane, with vigorous stirring at –70° over 2 h. The resulting suspension was allowed to warm overnight to room temperature, then washed with 10% aqueous hydrochloric acid. The ether was separated, washed with water, dried, and evaporated to yield the crude product. This was treated with 10 ml of dry n-butanol and fractionated. The fraction distilling at 120–125°/0.3 mm was collected, yielding 18.7 g, 33.5% of the pure borane. (Found: C, 81.1; H, 9.3; B, 3.8. $C_{19}H_{25}BO$ calcd.: C, 81.3; H, 9.0; B, 3.9%.)

n-Butoxy(2,6-dimethylphenyl)phenylborane (XVIII)

This compound was prepared as just described for the n-butoxymesitylphenylborane, from the Grignard reagent from 2,6-dimethylbromobenzene and di-n-butoxyphenylborane. Yield: 57%, b.p. 111–114°/0.4 mm. (Found: C, 81.3; H, 8.8; B, 4.0. $C_{18}H_{23}BO$ calcd.: C, 81.1; H, 8.7; B, 4.1%.)

o-Biphenyldimesitylborane (IXa)

A solution of 2-biphenyllithium, prepared from 8.4 g (0.03 mole) of 2-iodobiphenyl and 15 ml of 2 M n-butyllithium solution (Alfa Inorganics) in 30 ml of dry ether, was added to 8.1 g (0.03 mole) of fluorodimesitylborane in 30 ml of dry ether. The resulting solution was heated under reflux for 2 h. The suspension was then

treated with 50 ml of methanol and the white precipitate of the triarylborane filtered off and dried. Yield: 7.2 g, 60%, m.p. 154–155°. (Found: C, 89.2; H, 7.5; B, 2.9. $C_{30}H_{31}B$ calcd.: C, 89.5; H, 7.8; B, 2.7%.)

(2,4,6-Trimethyl-3-biphenyl)mesitylphenylborane (XI)

A solution of 2.74 g (0.01 mole) of 3-bromo-2,4,6-trimethylbiphenyl in 20 ml of dry ether was treated with 5 ml of 2 M n-butyllithium solution (Alfa Inorganics). The mixture was allowed to stand for 10 min and then added to a solution of 2.8 g (0.01 mole) of n-butoxymesitylphenylborane in dry ether. The mixture was heated under reflux for 2 h, by which time the Gilman test¹¹ for unused lithium reagent was negative. The solution was poured into water, and the ether layer was separated, washed with 1% aqueous hydrochloric acid, dried, and evaporated to yield an oil. This oil was stirred with methanol and a few drops of ether and allowed to stand overnight when it became solid. The solid which was filtered off and dried had m.p. 147–149°. Yield: 1.82 g, 45.5%. The mixed m.p. and IR and UV spectra were identical with those of the photoproduct A. (Found: C, 89.2; H, 7.4; B, 2.9. $C_{20}H_{31}B$ calcd.: C, 89.6; H, 7.7; B, 2.7%.)

(2,4,6-Trimethyl-3-biphenyl)(2,6-dimethylphenyl)phenylborane (XIX)

This borane was prepared exactly as described for XI from bromotrimethylbiphenyl and n-butoxy(2,6-dimethylphenyl)phenylborane. It was obtained in 12% yield and had m.p. 140–141°. (Found: C, 90.0; H, 7.8; B, 2.9. $C_{29}H_{29}B$ calcd.: C, 89.7; H, 7.5; B, 2.8%.)

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