a solid (1.2 g, 69%) containing equal proportions of starting material and anthracene as estimated from nmr and tlc.

Acetyl Methanesulfonate (11) and 9,9-Dibenzyl-9,10-dihydroanthracene (15). A.—Acetyl methanesulfonate (11) (1.3 g. 9.4 mmol) was heated with the dibenzyldihydroanthracene (15) (500 mg, 1.4 mmol) at 130° for 2 hr. Work-up in the usual manner (but with chloroform as solvent) gave a dark solid whose nmr showed the presence of only starting material.

B.—Repeat of reaction A (2.6 g of mixed anhydride + 360 mg of reagent) in refluxing acetic acid (10 ml) for 30 min gave again only recovered starting material (280 mg).

Triphenylmethyl Fluoroborate and 9,9-Dibenzyl-9,10-dihydroanthracene (15).—The dihydroanthracene (15) (358 mg, 1.0 mmol) and triphenylmethyl fluoroborate (1.5 g, 3.8 mmol) were refluxed in acetic acid (10 ml) for 30 min when the color of the reaction mixture was observed to change to a deep red from the original yellow. Work-up in the usual manner gave an oil (1.65 g) whose nmr spectrum and tlc showed the absence of starting material and the probable presence of triphenylmethane and triphenylmethanol. The crude oil was placed on a silica column which was then eluted with pentane followed by 5% ether. The first fraction contained triphenylmethane which was recrystallized from hexane to give pure material, mp 92°, mmp 92°, yield 300 mg. Elution with 5% ether gave a glass which could not be crystallized but which was shown to contain 9,10-dibenzylanthracene (17). The glass was purified by precipitation from ether with pentane and sublimation at 300° under reduced pressure (0.01 mm). The resulting glass registered as a single spot on tlc (20% ether–pentane on silica): uv λ_{max} 270 mμ (ϵ 58,000) [lit.[12g] λ_{max} 266 mμ, (ϵ 84,000)]: nmr δ 4.70, 5.0 (m, CH_2Ar), and 7.2 (m, ArH); yield 242 mg (67%).

Diphenylmethane and Acetyl *p*-Toluenesulfonate (2).—Diphenylmethane (2.5 g, 15 mmol) was heated with acetyl *p*-toluenesulfonate (2) (10 g, 47 mmol) at 130° for 2 hr. Work-up in the usual manner gave an oil (2.2 g) whose composition, as judged from the nmr and tlc, was 90% diphenylmethane. The remaining 10% (seven distinct spots on tlc) appeared from the nmr (singlets at δ 2.0, 2.15) to contain some acetylated material.

Registry No.—1, 2216-69-5; 2, 26908-82-7; 4, 93-04-9; 6, 100-66-3; 10, 103-73-1; 11, 100-06-1; 13, 7509-23-1; mesitylene, 108-67-8; thiophene, 110-02-1; 14, 613-31-0; 15, 26908-83-8; triphenylmethyl fluoroborate, 341-02-6.

Boron Photochemistry. VI. The Possible Role of Bridged Intermediates in the Photolysis of Borate Complexes

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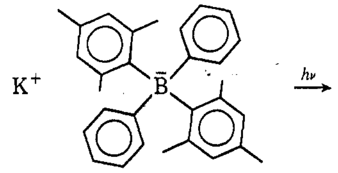
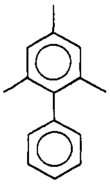
Received July 1, 1970

Several hindered tetraarylborate salts have been synthesized and photolyzed. The unexpected nature of some of the photolysis products has led us to reexamine the photolysis of potassium dimesityldiphenylborate labeled with a deuterium atom in each of the 4-position methyl groups. An examination of the products from the photolysis of this compound has demonstrated that an unusual and unanticipated rearrangement involving a 1,3 shift of a diarylbora group has taken place. A possible mechanism involving bridged intermediates has been proposed to account for this rearrangement.

In a previous publication[1] we discussed the photochemistry of the highly hindered potassium dimesityldiphenylborate (1) in the presence of oxygen to yield 2,4,6-trimethylbiphenyl (2) and (2,4,6-trimethyl-3-biphenylyl)mesitylphenylborane (3).

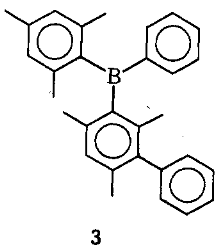


1



2

+



3

Three possible routes to 2 were discussed but at that time no attempt was made to distinguish between them. We have now conducted the photolysis of 1 in D_2O–1,2-dimethoxyethane in place of the H_2O–dimethoxyethane used earlier. Previously we considered two primary photochemical processes: (1) the generation of a phenyl radical (R·) by homolytic fission of a phenyl boron bond in the "ate" complex 1; (2) the generation of a mesityl radical by an analogous process. Path a based on process 1 is shown in Scheme I[2] and reveals that in D_2O the 2,4,6-trimethylbiphenyl (2) should contain zero or one D atom/molecule. The deuterium would be located in the mesityl ring since a phenyl radical has attacked the mesityl ring. A similar route, b (not shown), based on process 2, would predict 2,4,6-trimethylbiphenyl (2), which would have a maximum of two D atoms/molecule incorporated into the phenyl ring. A third route, c, which involves the radical pair, 4, of route a is shown in Scheme II. Route c leads to 2,4,6-trimethylbiphenyl (2) containing one deuterium atom per molecule, located on the mesityl ring. Therefore, by examining the position and content of deuterium in the isolated 2, we hoped to be able to determine the route followed by the rearrangement.

2,4,6-Trimethylbiphenyl (2) containing approximately 10% monodeuterated material was obtained experimentally. We were unable to determine the exact ring location of the deuterium label. However, the small extent of incorporation of deuterium is consistent when route a is considered as the major route to 2. Further examination of the proposed routes to 2 reveals a second distinction. Paths a and b yield 2,4,6-tri-

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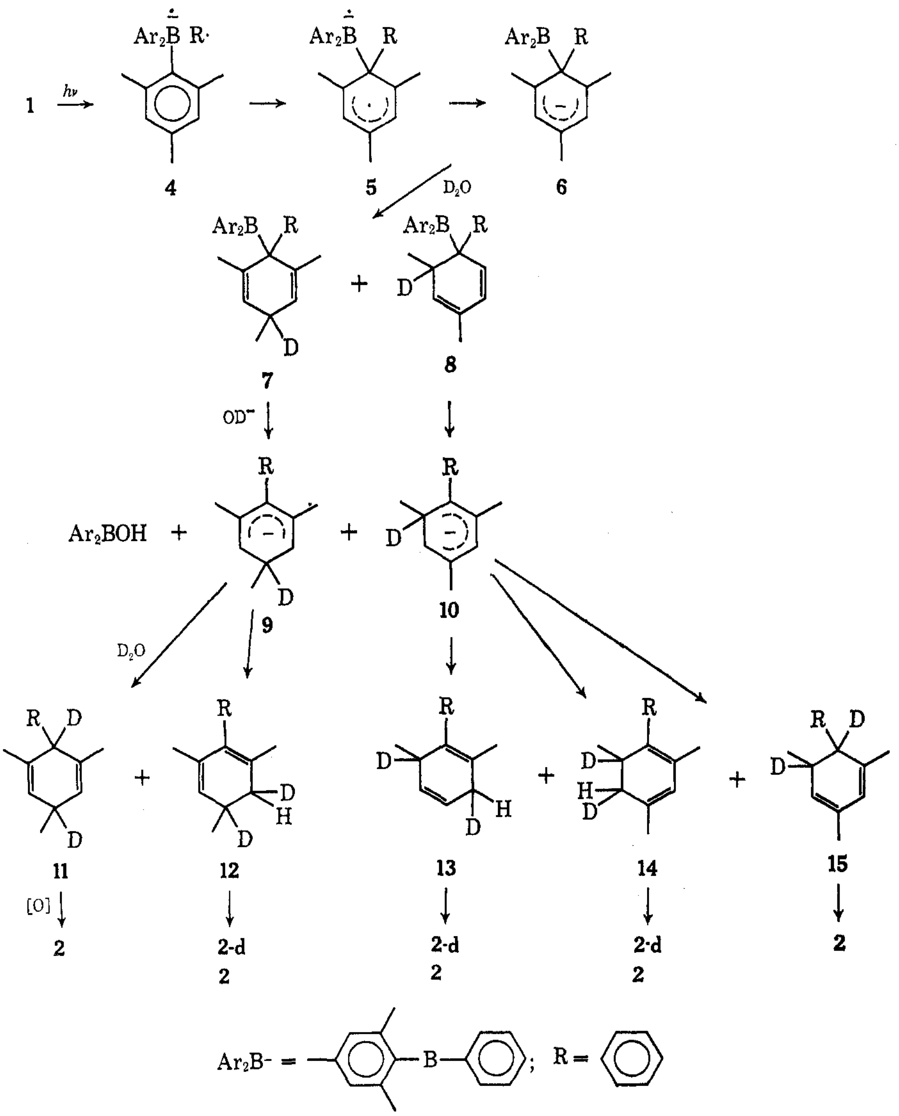
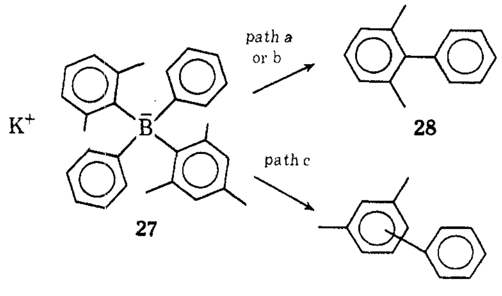
[1] P. J. Grisdale, B. E. Babb, J. C. Doty, T. H. Regan, D. P. Maier, and J. L. R. Williams, *J. Organometal. Chem.*, **14**, 63 (1968).

[2] The spin state of the biradical **5** is unknown. As a singlet **5** and **6** become canonical structures.

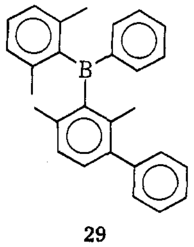
SCHEME I

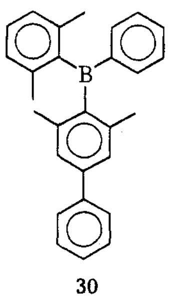


methylbiphenyl (**2**) with the phenyl attached to the mesityl residue at the position originally bonded to boron, whereas path c leads to compound **2** with the phenyl group attached to a position on the mesityl ring, which was *not* originally bonded to boron. We have, therefore, synthesized and studied the photolysis of potassium 2,6-dixylyldiphenylborate (**27**) and examined the hydrocarbon products. The biphenyl fraction consisted solely of the 2,6-dimethyl isomer **28**, which was isolated by preparative glc and identified by its spectral properties. This result is consistent with paths a or b. In addition to the biphenyl fraction, we had anticipated two isomeric triarylboranes, **29** and **30**, which would be formed from **27** *via* the intermediate produced by attack of a phenyl radical on a xylyl group. This rearrangement would be analogous to that shown in Scheme II for the production of **3** from **1** *via* **16** and **17**.



However, we were unable to detect any products in the photolysis mixture whose m/e values in the mass spectrum corresponded to those expected for **29** or **30**.

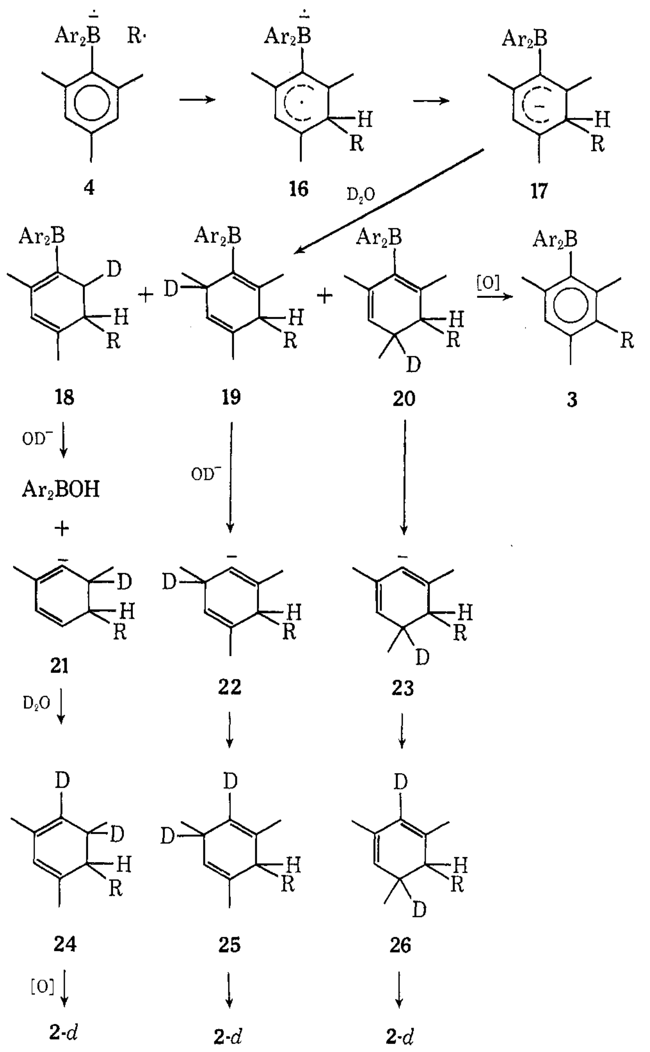

29


30

In the case of the photolysis of compound **1**, the triarylborane (**3**) is isolated as a stable product. The stability is due to the shielding of the B atom by the four *o*-methyl groups, which prevent the oxidative decomposition. Such an explanation has been proposed to account for the stability of trimesitylborane toward oxidation.[3]

(3) H. C. Brown and V. H. Dodson, *J. Amer. Chem. Soc.*, **79**, 2302 (1957).

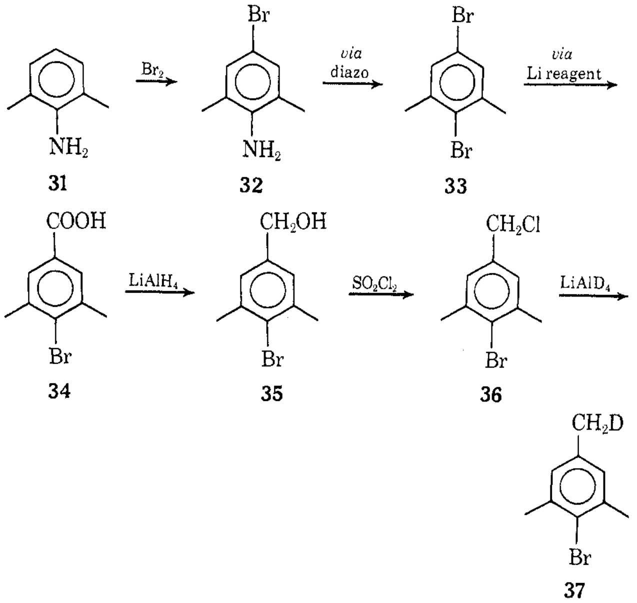
SCHEME II



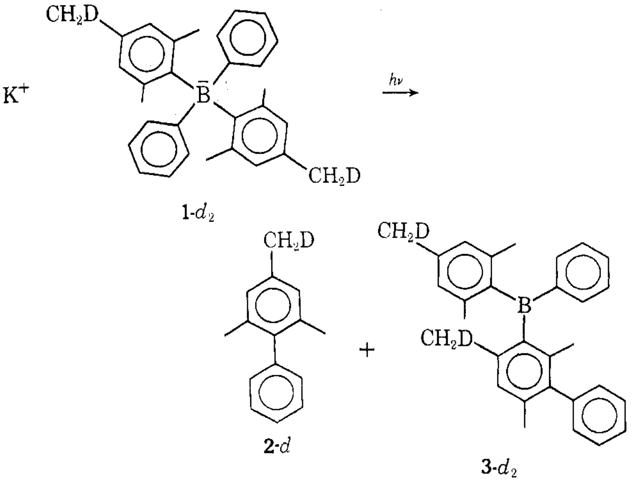
Compounds **29** and **30** have steric crowding similar to **3** and consequently, if they were formed, one would expect them to be isolable. We suspected that these products were not formed because an unexpected rearrangement had taken place during the photolysis, which in the case of **27** had produced neither **29** nor **30**, but isomeric triarylboranes in which four methyl groups were no longer ortho to the boron atom. Such compounds would be easily oxidized. The unexpected rearrangement would go unobserved during the photolysis of **1** owing to the symmetry of the mesityl groups. We have, therefore, labeled each of the 4-position methyl groups of **1** with a single deuterium atom to enable us to determine if any rearrangement of the diarylboron group occurs during the photolysis. The route to the required intermediate, monodeuterated bromomesitylene (**37**), is shown in Scheme III.

The monodeuterated bromomesitylene (**37**) was converted to dimesitylfluoroborane-d_2 and potassium dimesityldiphenylborate-d_2 (**1**-d_2) by the methods mentioned previously.[1] We have studied the photolysis of this compound as described previously[1] and examined the products, 2,4,6-trimethylbiphenyl-*d* (**2**-*d*) and the (2,4,6-trimethyl-3-biphenylyl)mesitylphenylborane-d_2 (**3**-d_2), by nmr spectroscopy. We have already published the nmr data for the undeuterated compounds.[1] These data and those for the deuterated compounds are compared in Table I. The resonances corresponding to the CH_2D– groups appeared as 1 : 1 : 1 triplets in **2**-*d* and **38**-*d*. The triplet signal for the CH_2D– in **3**-d_2 was less clearly defined than those for this group in **2**-*d* and **38**-*d*, but integrated as a two-proton resonance. An inspection of the data for the isolated **2**-*d* clearly establishes the structure as 4-deuteriomethyl-2,6-dimethylbiphenyl. This is in agreement with our previous observations that the biaryl fractions are formed by coupling of the aryl groups at positions originally linked to boron.[4]

SCHEME III



The nmr data for **3**-d_2 are inconclusive. One CH_2D– residue is, of course, on the mesityl group linked to boron, while the second could occupy either of positions "b" of the trimethylbiphenylyl group. Compound **3**-d_2 was degraded with mercuric acetate and bromine[1] to yield the 3-bromo-2,4,6-trimethylbiphenyl derivative (**38**-*d*). This procedure introduces a bromine atom in the position originally bonded to boron. A comparison of the nmr data for **38**-*d* and **38** clearly fixes the position of the CH_2D– group in position 4 relative to the phenyl group. As a further check on the correctness of our assignments for the spectrum of **38**, we have debrominated **38**-*d* *via* its lithium derivative to yield **2**-*d*, identical with



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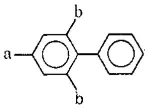
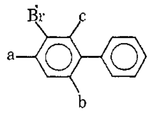
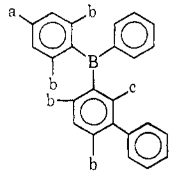
[4] J. L. R. Williams, J. C. Doty, P. J. Grisdale, R. Searle, T. H. Regan, G. P. Happ, and D. P. Maier, *J. Amer. Chem. Soc.*, **89**, 5153 (1967).

TABLE I

SHIFTS FOR THE METHYL PROTON RESONANCES OF THE DEUTERATED AND UNDEUTERATED COMPOUNDS[a]

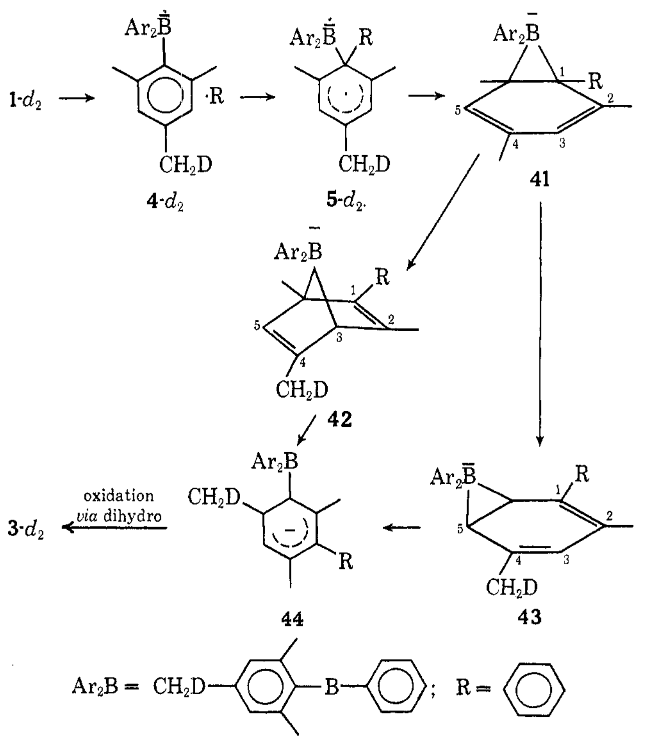
Compd	No.	CH_3^a	CH_3^b	CH_3^c
	**2** **2**-*d*	137 (3 H) 138 (2 H)	119 (6 H) 120 (6 H)	
	**38** **38**-*d*	146 (3 H) 146 (2 H)	116 (3 H) 116 (3 H)	128 (3 H) 128 (3 H)
	**3** **3**-d_2	138 (3 H) 136 (2 H)	123 (12 H) 124 (11 H)	103 (3 H) 106 (3 H)

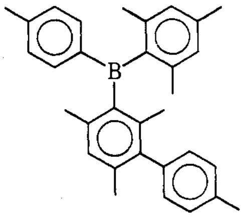
[a] In hertz downfield from TMS in $CDCl_3$.

the 4-deuteriomethyl-2,6-dimethylbiphenyl (**2**-*d*), which we obtained as a direct photolysis product. The overall reaction is, therefore, that given above.

The phenyl group in **3**-d_2 occupies the position originally occupied by the diarylboron group which has undergone a 1,3 shift. A possible reaction mechanism to account for these facts is shown in Scheme IV. Such a scheme requires that (a) the reaction be intramolecular, and (b) the phenyl ring be bonded to the mesityl ring at the C atom originally bonded to boron. Both requirements are met. We have photolyzed a mixture of potassium dimesityldiphenylborate (**1**) and potassium dimesityldiperdeuteriophenylborate (**1**-d_{10}) and examined the triarylborane fraction **3**. It consisted of **3** (m/e 402), **3**-d_{10} (m/e 412), but no **3**-d_5 (m/e 407). We have also photolyzed potassium dimesityldi-*p*-tolylborate (**39**). The structure of the triarylborane **40** derived from this photolysis was determined by comparison with an authentic sample. This finding established the position of the bonding in the tolyl group. Our reasons for favoring the original generation of a radical species have already been presented.[1] The intramolecularity of the reaction necessitates the caged radical pair **4**-d_2.

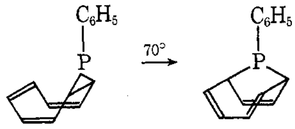
SCHEME IV





40

The intermediate **41** is the analog of one proposed recently by us to account for the production of 1,1- and 1,6-diphenylhexadiene from the photolysis of sodium tetraphenylborate.[5] The proposed concerted rearrangements **41** → **42** and **41** → **43** are of interest. If one considers the symmetry of the orbitals involved in the phenylpentadienyl system ($R-C_1C_2C_3C_4C_5$),[6] then the C_1-C_3 bond migration to yield **42** is photochemically allowed but thermally forbidden, while the C_1-C_5 bond migration to yield **43** is photochemically forbidden and thermally allowed. Since both proposed intermediates lead to the same product, either thermal or photochemical processes could be involved. There is a very close analogy here to the rearrangement of the cyclic phosphorus compound **45** reported recently by Katz.[7] An



45 **46**

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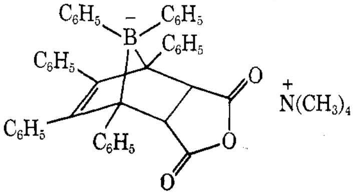
[5] J. L. R. Williams, P. J. Grisdale, and J. C. Doty, presented at the Fourth International Conference on Organometallic Chemistry, Bristol, England, 1969.

[6] A. Streitweiser and J. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. 1, Pergamon Press, New York, N.Y., 1965, p 90.

[7] T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Amer. Chem. Soc.*, **88**, 3832 (1966).

alternative description would involve π-allyl complex intermediates with delocalization of the π electrons on just three carbon atoms of the mesityl ring.[8] Such bonding is well known for transition metal–allyl interactions, but the stability of such complexes is due partly to interaction of the d orbitals of the metal with the antibonding π orbitals of the allyl system.[9]

So far, attempts to obtain direct evidence of bridged or cyclic intermediates have failed. Bridged aluminates analogous to our intermediate **42** have recently been synthesized and do open readily with water to yield trisubstituted aluminum derivatives.[10] We have recently reported on the first boron-containing analog **47**



47

of the norbornene system, which is a stable crystalline material.[11] However, we have been unsuccessful in preparing the corresponding norbornadiene analog.

Experimental Section

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.[12] All the deuterated products described below were more than 95% enriched unless otherwise stated (mass spectral analyses). Glc analyses were run on a Model 5750 F & M gas chromatograph equipped with a 0.25-in. stainless steel column 10 ft long, packed with 5% SE-30 on Chromosorb G, acid washed, DMCS treated. The column temperature was usually programmed from 150 to 300° at 10°/min. Preparative glc separations were performed under similar conditions on an F & M Model 776 instrument equipped with a $^3/_8$-in. stainless-steel column 7 ft long.

Photolyses.—Solutions of the potassium tetraarylborates, 1.0 g, 0.23 mmol, were photolyzed with a mixture of dimethoxyethane (DME) and water (or deuterium oxide) as described previously.[1] The neutral products were isolated and the following results obtained. Potassium dimesityldiphenylborate (**1**) in DME-D_2O yielded 2,4,6-trimethylbiphenyl (**2**) (10% monodeuterated by mass spectral analysis, 0.1 g) and (2,4,6-trimethyl-3-biphenylyl)mesitylphenylborane (**3**, 0.28 g). A mixture of potassium dimesityldiphenylborate (**1**) and potassium dimesityldiperdeuteriophenylborate (**1**-d_{10}) yielded a mixture of 2,4,6-trimethylbiphenyls (**2** and **2**-d_5) (0.11 g), and a mixture of the boranes **3** and **3**-d_{10} (0.29 g), but *no* **3**-d_5. Potassium dideuteriomesityldiphenylborate (**1**-d_2) yielded 4-deuteriomethyl-2,6-dimethylbiphenyl (**2**-*d*, 0.12 g) and (4-deuteriomethyl-2,6-dimethyl-3-biphenylyl)(4-deuteriomethyl-2,6-dimethylphenyl)phenylborane (**3**-d_2, 0.25 g). Potassium diphenyldi-2,6-xylylborate (**27**) yielded only 2,6-dimethylbiphenyl (**28**, 0.1 g). The nmr ($CDCl_3$) spectrum showed that the methyl groups were equivalent and a six-proton absorption band occurred at δ 2.0. The uv spectrum was identical with published data,[13] and the mass spectrum indicated a parent ion at *m/e* 182. Potassium dimesityldi-4-tolylborate (**39**) gave a tetramethylbiphenyl (mass spectrum *m/e* 210) with a characterless uv spectrum typical of a hindered biphenyl. In addition, (2,4,4′,6-tetramethyl-3-biphenylyl)mesityl-4-tolylborane (**40**), 0.32 g, mp 186–187°, was produced. It was identical in every respect with an authentic sample (see below).

Degradation Experiments.—The degradation of the (4-deuteriomethyl-2,6-dimethyl-3-biphenylyl)(4-deuteriomethyl-2,6-dimethylphenyl)phenylborane (**3**-d_2) was carried out as described previously using bromine.[1] The crude bromo compounds (0.2 g) after separation by glc yielded 3-bromo-4-deuteriomethyl-2,6-dimethylbiphenyl (**38**-*d*, 0.075 g), identical in retention time with the undeuterated analog.[1] (For nmr data see Table I.) This bromo compound (0.075 g) in 20 ml of dry ether was treated with 2 *M* butyllithium solution (0.2 ml). After 15 min, water was added and the ether layer was washed, dried, and evaporated. The residue was chromatographed to yield unchanged starting material and 4-deuteriomethyl-2,6-dimethylbiphenyl (**2**-*d*, 0.017 g), *identical in retention time with the undeuterated analog*.[1] (For nmr data see Table I.)

Materials.—All operations involving lithium and Grignard reagents were conducted under a nitrogen atmosphere. Fluorodimesitylborane was prepared by the method of Brown and Dodson.[3] The potassium tetraarylborates were prepared *via* their lithium salts by the general method described by Wittig and Herwig[14] from 2 mol of aryllithium and 1 mol of fluorodimesitylborane. The following example is typical but utilizes the fluorodi-2,6-xylylborane.

Potassium Di-2,6-xylyldiphenylborate (**27**).—A solution of 2,6-dimethylbromobenzene (148 g, 0.8 mol) in dry ether (200 ml) was added slowly with stirring and heating to magnesium turnings (20 g) and dry ether (100 ml). When the magnesium had dissolved, the Grignard reagent was treated with boron trifluoride ethyl etherate (55 g, 0.39 mol) in ether (100 ml) and the resulting solution heated under reflux for 1 hr. Dry hexane (500 ml) was then added and the supernatant liquid decanted from the residue. The liquid was evaporated to yield the crude fluoroborane. It was distilled at 153–155° (6 mm) giving 50 g, 54%, of pure product, which was converted to the tetraarylborate as follows. A solution of phenyllithium prepared from bromobenzene (32 g, 0.2 mol) and *n*-butyllithium (95 ml, 2 *M* solution) in dry ether (300 ml) was added to a stirred solution of fluorodi-2,6-xylylborane (21 g, 0.09 mol). The resulting mixture was heated under reflux for 2 hr and then poured into water (1000 ml). The ether layer was dried and evaporated yielding the crude lithium tetraarylborate. This was dissolved in water and the aqueous solution washed with hexane and then treated with a solution of potassium chloride. The white potassium salt was filtered off, washed with water, and dried under vacuum, yield 14 g, 38%.

Anal. Calcd for $C_{28}H_{28}BK$: C, 81.1; H, 6.8; B, 2.6; K, 9.4. Found: C, 80.7; H, 7.0; B, 2.6; K, 9.1.

4-Bromo-3,5-dimethylbenzoic Acid (**34**).—1,4-Dibromo-3,5-dimethylbenzene (26 g, 0.1 mol), prepared from 2,6-dimethylaniline by bromaintion[15] and a Sandmeyer reaction,[16] was dissolved in ether (300 ml). The resulting solution was chilled in an acetone–Dry Ice bath and treated with *n*-butyllithium solution (50 ml, 2 *M* solution). This solution was allowed to warm slowly to room temperature and then poured onto crushed Dry Ice. When the mixture had warmed up, the solid was filtered off and dissolved in water and the aqueous solution was treated with concentrated hydrochloric acid. The white solid was collected and recrystallized from acetonitrile to give the desired 4-bromo-3,5-dimethylbenzene acid as white needles, 10.0 g, 48%, mp 217–219° (lit.[17] 214–215°).

4-Hydroxymethyl-2,6-dimethylbromobenzene (**35**).—Lithium aluminum hydride (0.95 g, 0.025 mol) in dry ether (60 ml) was added slowly to a solution of 4-bromo-3,5-dimethylbenzoic acid (5.0 g, 0.02 mol) in dry ether (60 ml). After 15 min the solution was treated with water and dilute hydrochloric acid. The ether layer was washed with dilute hydrochloric acid, dried, and evaporated to yield the crude product, mp 50–53°. It was

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[8] We are grateful to Dr. P. Heimbach (Mülheim-Ruhr) for helpful discussion on this point.

[9] A reviewer has pointed out that a π-allyl bond requires that the boron atom adopts an sp^2 hybridization since the $+++$ symmetry of the allyl group must be matched by a $+$ orbital on the boron, and the higher energy $+\ 0\ -$ symmetry on the allyl must be matched by a $+-$ symmetry orbital on the boron. Hybrid sp^3 orbitals on boron would not fulfill these conditions.

[10] H. Lehmkuhl, *Justus Liebigs Ann. Chem.*, **719**, 20 (1968).

[11] P. J. Grisdale and J. L. R. Williams, *J. Organometal. Chem.*, **22**, C19 (1970).

[12] The system is described by V. J. Caldecourt, *Anal. Chem.*, **27**, 1670 (1955), but was constructed of glass instead of metal.

[13] G. H. Beaven and E. A. Johnson, *Spectrochim. Acta*, **14**, 67 (1959).

[14] G. Wittig and W. Herwig, *Chem. Ber.*, **88**, 962 (1955).

[15] E. Noelting, A. Braun, and G. Thesmar, *ibid.*, **34**, 2242 (1901).

[16] J. J. Blanksma, *Recl. Trav. Chim. Pays-Bas*, **25**, 171 (1906).

[17] H. J. Schmitz, *Justus Liebigs Ann. Chem.*, **193**, 174 (1878).

crystallized from ligroin (bp 60–65°) giving the pure product, 3.5 g, 85%, mp 53–54°.

Anal. Calcd for $C_9H_{11}BrO$: C, 50.2; H, 5.1; Br, 37.2. Found: C, 50.6; H, 5.4; Br, 37.6.

4-Chloromethyl-2,6-dimethylbromobenzene (36).—The 4-hydroxymethyl derivative (26 g, 0.12 mol) in dry benzene (100 ml) was treated with thionyl chloride (25 g). After 30 min the benzene was evaporated and the residue recrystallized from ligroin (bp 35–40°) at low temperature to yield the pure product, 20 g, 75%, mp 43–44°.

Anal. Calcd for $C_9H_{10}BrCl$: C, 46.2; H, 4.3; Br, 34.2. Found: C, 46.5; H, 4.5; Br, 33.8.

4-Deuteriomethyl-2,6-dimethylbromobenzene (37).—The chloromethyl derivative (19 g, 0.08 mol) in dry ether (200 ml) was treated with lithium aluminum deuteride (5 g, 0.12 mol). The mixture was heated under reflux for 6 hr and then treated with water and dilute hydrochloric acid. The ether layer was separated, dried, and evaporated to yield the crude deuterated product. It distilled at 225–227° (lit.[18] 225°, undeuterated), 13 g, 81%. The nmr ($CDCl_3$) spectrum showed absorption bands at δ 6.85 (s, 2 H), 2.37 (s, 3 H), and 2.2 (1:1:1 t, 2 H).

3-Bromo-2,4,6,4′-tetramethylbiphenyl.—A solution of *p*-toluidine (53 g, 0.5 mol) in water (100 ml) and concentrated hydrochloric acid (100 ml) was diazotized at 0–5°. The resulting solution was added to 2-bromomesitylene (250 ml). To this mixture was added, with vigorous stirring, ice-cold 50% sodium hydroxide solution until the mixture was basic. The organic layer was separated, washed with water, dried, and evaporated to yield a colored residue. This residue was treated with ligroin (1000 ml, bp 60–65°) and the solution poured through a 3 × 3 in. column of alumina (Woelm neutral activity grade I). Evaporation of the eluent afforded a pale yellow oil (10 g) which was distilled under vacuum to give a fraction, bp 114–118° (0.3 mm), 8.0 g, 6%.

Anal. Calcd for $C_{16}H_{17}Br$: C, 66.4; H, 5.9; Br, 27.7. Found: C, 66.8; H, 6.3; Br, 27.7.

***n*-Butoxymesityl-4-tolylborane.**—4-Tolylboronic acid was heated with *n*-butyl alcohol providing the di-*n*-butoxy-4-tolylborane. This diester (124 g, 0.5 mol) in dry ether was vigorously stirred and treated at −70° with the Grignard reagent prepared from 2-bromomesitylene (100 g, 0.5 mol) in dry ether. The resulting suspension was allowed to warm to room temperature overnight and then washed with 10% aqueous hydrochloric acid. The ether layer was separated, washed with water, dried, and evaporated to yield a colorless residue. It was treated with *n*-butyl alcohol (30 ml) and then fractionated to give the desired compound, 66 g, 45%, bp 182–185° (1.4 mm).

Anal. Calcd for $C_{20}H_{27}BO$: C, 81.6; H, 9.2; B, 3.7. Found: C, 81.3; H, 9.6; B, 3.6.

(2,4,4′,6-Tetramethyl-3-biphenylyl)mesityl-4-tolylborane (40).—The mesityltolyl ester (2.9 g, 0.01 mol) in dry ether (30 ml) was treated with a solution of the lithium reagent prepared from the 3-bromo-2,4,4′,6-tetramethylbiphenyl (2.9 g, 0.01 mol) and *n*-butyllithium (5 ml, 2 *M* solution) in dry ether (20 ml). The solution was then heated under reflux for 1 hr and poured into dilute hydrochloric acid. The ether layer was washed with water, dried, and evaporated to give a pale yellow oil. This oil was triturated with methanol (two 5-ml portions) and the methanol discarded. The oil was scratched under ether (5 ml) to yield a crystalline residue, mp 178–182°. This residue was washed with warm ether to yield the pure borane, 1.1 g, 26%, mp 185–186°.

Anal. Calcd for $C_{32}H_{35}B$: C, 89.3; H, 8.2; B, 2.5. Found: C, 89.1; H, 8.4; B, 2.8.

Registry No.—**1**, 20623-88-5; **1**-d_2, 26985-33-1; **2**-d, 26965-68-4; **3**-d_2, 26965-69-5; **27**, 26985-34-2; **35**, 27006-02-6; **36**, 26965-70-8; **38**-d, 26965-71-9; **40**, 26992-54-1; 3-bromo-2,4,4′,6-tetramethylbiphenyl, 26941-22-0; *n*-butoxymesityl-4-tolylborane, 26941-23-1.

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Displacement of Tertiary Phosphines from Methylolphosphonium Salts by Tributylphosphine

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Tributylphosphine displaces tris(hydroxymethyl)phosphine (II), triphenylphosphine, and, to a limited extent, butylbis(hydroxymethyl)phosphine (Vb) from the corresponding methylolphosphonium salts. No formaldehyde is liberated. Tetrakis(hydroxymethyl)phosphonium chloride (I) reacts with mercuric chloride in ethanol giving the mercuric chloride adduct of II, $(HOCH_2)_3P\cdot HgCl_2$, in 88% yield.

In connection with some other work in these laboratories on the flameproofing of cotton, we had a need for a method of preparing formaldehyde-free methylolphosphines and, in particular, tris(hydroxymethyl)phosphine (II). Methylolphosphines such as Va or Vb [$RP(CH_2OH)_2$, R = Me or Bu] can be rendered formaldehyde-free by repeated distillation, but II decomposes when distilled under vacuum.[2]

Methylolphosphines are usually prepared from the corresponding methylolphosphonium salts by treatment with a base (B) such as sodium hydroxide[3] or triethylamine.[4] Formaldehyde (1 equiv) is liberated in the process by either reagent.

$$\underset{\text{I}}{(HOCH_2)_4PCl} + B \longrightarrow \underset{\text{II}}{(HOCH_2)_3P} + CH_2O + B\cdot HCl$$

Gordon's method,[5] in which the base was sodium sulfite, was an effort to overcome this problem by tying up the formaldehyde as the bisulfite addition compound. This procedure, however, requires a careful attention to pH, as the sodium hydroxide liberated in the formation of the bisulfite addition compound is capable of destroying the product.[6a]

In this paper, we report our investigation of the use of a tertiary phosphine as the base, on the premise that tertiary phosphines, unlike tertiary amines,[7] are

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[7] Crystalline *N*-methylol compounds having the composition $R_3NCH_2OH^+Cl^-$ can be prepared from tertiary amines, but decompose in water; see T. D. Stewart and H. P. Kung, *J. Amer. Chem. Soc.*, **55**, 4813 (1933).