J. Org. Chem. 1989, 54, 1627-1634

Photochemical Generation of the Diphenylborate(I) Anion from Metal Tetraphenylborates(III) in Aprotic Media: Repudiation of a Contravening Claim[1]

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Received June 27, 1988

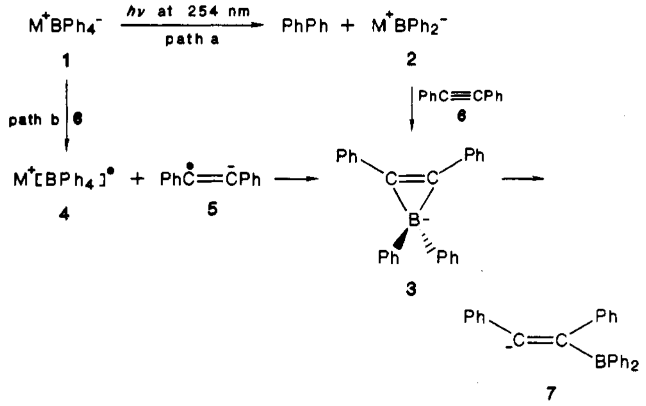
A detailed investigation is reported of the photolysis of sodium or lithium tetraphenylborate(III) at 254 nm in aprotic solvents, such as 1,2-dimethoxyethane and tetrahydrofuran, for periods up to 24 h. The nature of the photoreactions occurring under these conditions was ascertained by employing a series of chemical trapping agents: (1) DOAc to detect borohydrides, diarylborate(I) anions, and aryl–boron bonds; (2) 1-octyne to detect the presence of neutral boron hydrides; (3) benzyl chloride both to detect borohydride anions and to trap the diphenylborate(I) anion; and (4) diphenylacetylene as a trap for any boracarbenoid reactivity of the diphenylborate(I) anion. Upon the basis of these composite results and numerous control experiments, the conclusion is drawn that these tetraphenylborate(III) salts undergo two *ultimate* photoreactions under these conditions: (1) a principal reaction of ultimately eliminating biphenyl from the tetraphenylborate(III) salt to produce the diphenylbrate(I) anion and (2) a secondary isomerization of the tetraphenylborate(III) ion to a biphenylyldiphenylborohydride and, in part, finally to a terphenylylborohydride. Both reactions can be promoted by such photosensitizers as biphenyl, diphenylacetylene, and stilbenes. Since the diphenylborate(I) ion shows a moderate to low reactivity as a boracarbenoid intermediate, its chemical character seems rather to resemble that of the triphenylmethyl carbanion more closely. The present study was recently augmented in its scope in the light of a recent investigation of the photolysis of such tetraphenylborate(III) salts (Wilkey, J. D.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 2117), whose authors concluded that the diphenylacetylene was reacting with the tetraphenylborate anion to produce stilbene precursors in a photopromoted electron-transfer process, rather than reacting with a boracarbenoid diphenylborate(I) anion. However, the present study demonstrates that Wilkey and Schuster have overlooked two other sources of stilbene precursors in such photolyses: (1) photopromoted hydroboration of the diphenylacetylene by the arylborohydrides known to be generated in such photolyses and (2) the formation of stilbenes by the photolysis of the tetraphenylborate anion in THF or DME, even in the *complete absence of diphenylacetylene*. The present authors show that, accordingly, Wilkey and Schuster's evidence for an electron-transfer mechanism for the formation of stilbene precursors from diphenylacetylene and the tetraphenylborate(III) anion is inconclusive. Finally, they point out how Wilkey and Schuster have not taken into account all the evidence pointing to the photogeneration of the proposed diphenylborate(I) anion.

The photolysis of tetraarylborate salts in protic media, under anaerobic[3] or aerobic[4] conditions, has led to novel dihydrobiaryl or biaryl coupling products, respectively. As an extension of our interest in chemically induced 1,2-aryl shifts from boron to carbon,[5] we have been led to examine such rearrangements initiated photochemically under aprotic conditions and under nitrogen. By avoidance of hydroxylic solvents and prolonging the time of irradiation, we hoped to generate and detect the potentially interesting boron intermediates thought to be involved in these photochemical processes.

In a preliminary communication published in 1975, we reported several lines of evidence pointing to the photochemical generation of the boracarbenoid anion, diphenylborate(I), from metal tetraphenylborate(III) salts **1** in aprotic, donor solvents.[6] One line of evidence suggested that irradiation of such borate(III) salts at 254 nm in the presence of diphenylacetylene (**6**) led to a trapping of the diphenylborate(I) anion (**2**) by a carbene-like addition of Ph_2B^- to yield the boracyclopropenate anion **3**, which would open to form **7** (Scheme I, path a).

In a recent issue of this journal, Wilkey and Schuster published a study of the irradiation of the sodium or tetramethylammonium salt of the tetraphenylborate(III) anion in either acetonitrile or THF solution.[7] The nature of the photoproducts was examined either directly by ^{11}B NMR and UV–vis spectroscopy or indirectly after oxidative or hydrolytic workup. By working at short irradiation times, they were able to detect a bicyclic organoborate intermediate for which they proposed structure **19**. Also, photolyses were conducted in the presence of diphenylacetylene and the observed reduction of the alkyne to stilbenes was interpreted as a photopromoted electron-transfer process (Scheme I, path b), rather than as a sign of the photogeneration of the diphenylborate(I) anion (path a). On the basis of these studies, they concluded that "there are no experimental observations at all that suggest borene anion involvement in the photochemical reactions of tetraphenylborate."[7]

Scheme I



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[1] Paper 10 in the series Bora-Aromatic Systems. For paper 9, see: Eisch, J. J.; Shafii, B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 379.

[2] Current address: Department of Synthetic Chemistry, Kyoto University, Kyoto, Japan.

[3] Williams, J. L.; Grisdale, P. J.; Doty, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 4538.

[4] Williams, J. L. R.; et al. *J. Am. Chem. Soc.* **1967**, *89*, 5153; **1968**, *90*, 53; *J. Org. Chem.* **1971**, *36*, 544. Doty, J. C.; Grisdale, P. J.; Evans, T. R.; Williams, J. L. R. *J. Organomet. Chem.* **1971**, *32*, C35.

[5] Eisch, J. J.; Wilcsek, R. J. *J. Organomet. Chem.* **1974**, *71*, C21.

[6] Eisch, J. J.; Tamao, K.; Wilcsek, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 895.

[7] Wilkey, J. D.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 2118.

0022-3263/89/1954-1627$01.50/0

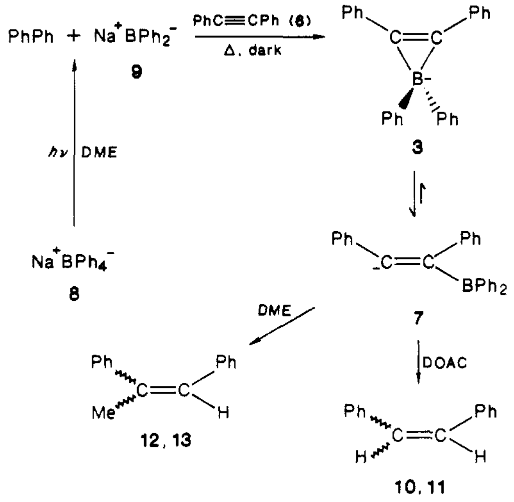
Readers of the Wilkey and Schuster article may be inclined to accept this report as a careful, thorough repetition of our photochemical study under exactly our experimental conditions. In fact, however, the reported experiments of Wilkey and Schuster differ significantly from ours in the manner in which they were carried out. From our studies, it was clear that the photoreactions are strongly dependent upon wavelength, time, metal ion, and solvent.[8] The majority of our studies were conducted on sodium or lithium salts of the tetraphenylborate(III) anion at 254 nm[9] in either tetrahydrofuran (THF) or especially in 1,2-dimethoxyethane (DME). As is stated in our paper, DME proved to be a superior solvent for the generation of **2**; THF is decidedly inferior.[6] All the results reported by Wilkey and Schuster were conducted in acetonitrile and in THF. Finally, our reactions were conducted for 24 h; Wilkey and Schuster make *no mention of time* for their direct irradiations. Since they have conducted their direct irradiation of tetraphenylborate(III) salts under conditions very different from ours, their claim that there is no experimental evidence at all for diphenylborate(I) anionic intermediates deserves further scrutiny.

Accordingly, in this paper we marshal the considerable body of evidence, both previously known and newly acquired, that points to the generation of the diphenylborate(I) anion in the photolysis of tetraphenylborate(III) salts; we show how Wilkey and Schuster's attempts to test our hypothesis that diphenylborate(I) is trapped by diphenylacetylene are invalid because of experimental defects, and we offer further proof for the existence of the diphenylborate(I) anion through its chemical trapping as benzyldiphenylborane.

Results

Trapping of the Diphenylborate(I) Anion by Diphenylacetylene. Wilkey and Schuster dismissed our suggestion that the diphenylborate(I) anion was generated directly in the prolonged photolysis of tetraphenylborate(III) salts, solely on the basis of their interpretation of the trapping experiment with diphenylacetylene. It is principally on the interpretation of this experimental observation, the mode of formation of the boron-substituted stilbene derivative **3** or **7**, that Wilkey and Schuster prefer an explanation different from ours. We suggest an ultimate elimination of BPh_2^- from BPh_4^- or their intermediate **19** at 254 nm and the direct formation of the biphenyl in the photoreaction mixture (path a); they favor a single-electron transfer from the BPh_4^- at 350 nm to yield radical-anions **4** and **5** and the subsequent direct transfer of $\dot{B}Ph_2$ from **4** to **5** with the formation of **3** or **7** (path b). Their interpretation differs from ours in their judging that no diphenylborate(I) is ever free in the reaction and that biphenyl is formed only in the presence of **6**. They searched without success by ^{11}B NMR spectroscopy for signs of **2** and they could observe no biphenyl formation in the irradiation of tetraphenylborates under their reaction conditions (short-term irradiation in THF or MeCN).

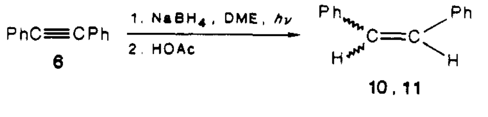
Scheme II



In the absence of further experimental evidence, the foregoing two modes of forming **3** and **7** (path a or path b) seem to be reasonable alternatives. However, an experimental test can readily be devised: path a is a thermal process and thus should proceed in the dark, while path b requires photopromotion.[10] Accordingly, we conducted a photolysis of sodium tetraphenylborate(III) in DME solution under the standard conditions (2.90 mM solution with degassed solvent under nitrogen for 24 h, with autogenous reactor temperature of 58 °C). Thereafter, the diphenylacetylene was added to the photolysate and the solution maintained in the dark for 24 h at 25 °C. Hydrolytic workup revealed the presence of both *cis*- and *trans*-stilbenes (45% of the acetylene consumed), together with α-methylstilbenes probably formed from the reactions of **7** with the DME[11] (Scheme II).

However, before we could conclude that stilbene precursors could be formed from diphenylacetylene and photolysate solutions of **8** in a dark reaction, we had to perform two control experiments: (1) irradiation of diphenylacetylene with $NaBH_4$ in DME and (2) irradiation of **8** alone either in DME or in THF. The former experiment was meant to determine whether the sodium arylborohydrides, which were known to be present in photolysates of **8** (cf. infra), could produce stilbenes by photopromoted hydroboration. The latter experiment was required to learn if stilbenes could arise in some unforeseen way.

Although heating diphenylacetylene with $NaBH_4$ in DME in the dark for 24 h and then treating with glacial acetic acid gave *no trace of stilbenes, repeating the same* reaction while irradiating at 254 nm did yield a 2% conversion of the diphenylacetylene to a 63:47 ratio of *cis*- and *trans*-stilbenes (eq 1). Moreover, a most remarkable

 (1)

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(8) As will be clear by comparing the data in this article and in the original communication (ref 6), the length of the irradiation period profoundly changes the nature and proportion of products produced by *protodeboronation; use of DME or THF changes the proportions of* products (Table I and hydrogen gas isotopes); the wavelength of irradiation used changes which organic photosubstrates are excited (ref 7); and the use of the lithium or sodium arylborate changes the proportions of products (ref 6).

(9) Wilkey and Schuster carried out their direct irradiations at 254 nm and their irradiations with diphenylacetylene present at 350 nm. The latter wavelength was chosen, so as not to have both the tetraphenylborate(III) and diphenylacetylene undergo simultaneous electronic excitation.

(10) In our original study we did in fact carry out such a dark reaction (photolysate solution of **8** allowed to react in the dark with diphenylacetylene (**6**)) and learned that organoboron stilbene precursors were formed. Since irradiation was not required to obtain the stilbene precursors, we performed our trapping reactions with the acetylene during the irradiations for the sake of convenience.

(11) Analogous alkylations of organometallics by ethers have been reported:

$$Ph_2CHLi + THF \rightarrow Ph_2CHCH_2CH_2CH_2CH_2OLi$$

cf. Eisch, J. J. *J. Org. Chem.* **1963**, *28*, 707.

Table I. Yields of Photoproducts from the Photolysis of Sodium Tetraphenylborate(III) at 254 nm and Subsequent Protodeboronation[a]

compound	reactn in DME[b]	reactn in THF[c]	reactn with PhPh (10 mol %)[d]	reactn with PhPh (20 mol %)[e]	reactn with PhC≡CPh[f] ($h\nu$)	reactn with PhC≡CPh[b] (Δ)
biphenyl[h]	23.0	22.0	45.0[k]	66.6[k]	35.7	22.5
terphenyls[h,i]	3.6	5.7	8.4	12.0	5.5	3.6
cis-stilbene[h,j]	0.24	0.47	0.80		1.8[l]	0.24
trans-stilbene[h,j]	0.38	0.47	0.35		2.4[l]	1.27
cis-α-methylstilbene[j]	0.80	0.90	0.80		0.42[l]	1.60
trans-α-methylstilbene[j]	0.80	1.6	0.80		0.33[l]	0.40

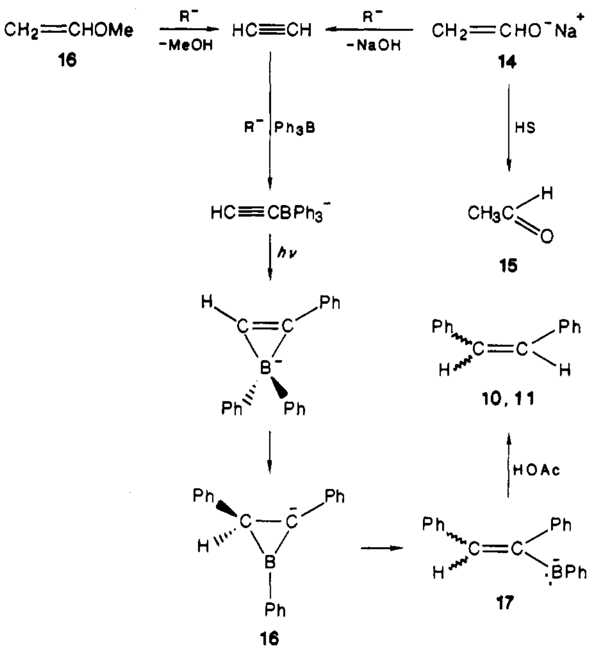
[a] Yields of all products have been calculated on the assumption that each product equivalent is formed with the consumption of 1 equiv of sodium tetraphenylborate(III)·mono-DME solvate (1.0 g equaling 2.31 mmol). Actually, of course, the stilbenes would require 2 or more equivalents of **8** for their formation in DME or THF alone and additional **8** could be consumed through attack on the solvent. [b] Irradiation in 80 mL of degassed DME for 24 h of a 1.0-g sample of $Na^+BPh_4^-$ recrystallized from a 1:1 mixture of DME and Et_2O and consisting of crystals of the monosolvate, $NaBPh_4$·DME. All ratios were determined by quantitative GC analysis using fluorene as the standard. [c] Irradiation in THF of a sample of $NaBPh_4$ recrystallized from a 1:1 mixture of THF and Et_2O and consisting of unsolvated $NaBPh_4$. [d] As in *b*, except that biphenyl (10 mol % of the $NaBPh_4$·DME employed) was present at the start of the 24-h irradiation period. [e] As in *b*, except that biphenyl (20 mol % of the $NaBPh_4$·DME employed) was present at the start of the irradiation period. [f] Reaction employing 1.0 g of $NaBPh_4$ in 80 mL of anhydrous, degassed DME and 1.0 g of diphenylacetylene for 24 h of irradiation. [g] As in *c*, except that the diphenylacetylene was added after the 24-h irradiation and allowed to react for 24 h at 25 °C in the dark. These percentages were reproducible within ±5% of these values. [h] Deuterium content was determined by MS comparison with deuteriated samples. [i] Terphenyls were 7:3 mixtures of para and meta isomers. [j] Samples of these hydrocarbons were collected and their identity established by ^1H NMR and MS examinations. [k] Additional biphenyl produced by irradiation. [l] Yields of stilbenes given in the table are based upon the amount of **8**; based upon the diphenylacetylene consumed (that is, not recovered), the yield of stilbenes is 45%.

outcome was obtained by the irradiation of $NaBPh_4$ at 254 nm in THF or in DME: both reactions led to the isolation of *cis*- and *trans*-stilbenes (**10**, **11**) and a *E*, *Z* mixture of α-methylstilbenes upon workup with glacial acetic acid. Apparently, in both solvents a base-induced elimination converts DME into methyl vinyl ether[12] and THF into sodium vinyloxide.[13] By further base-promoted elimination, acetylene itself can be generated.[14] The latter could form ethynyltriphenylborates, whose di-π-methane-like photorearrangement[15] could generate stilbene precursors (Scheme III).

The origin of the methyl groups required to generate the (*E*)- and (*Z*)-α-methylstilbenes in this photolysis is somewhat unclear. It is conceivable that photolysis of methyl vinyl ether (**16**) in DME solution or of any acetaldehyde (**15**) formed in THF solution could generate methyl radicals,[16,17] which in turn could attack boron intermediates such as **16** and **17** in Scheme III.

The results of these instructive control experiments demonstrate that the detection of stilbenes in photolysis mixtures of the tetraphenylborate anion cannot automatically be adduced as proof of the capture of the diphenylborate(I) anion by diphenylacetylene (path a, Scheme I), nor can it be taken as clear evidence of a photopromoted electron-transfer process (path b, Scheme I). For this reason, it was mandatory that the stilbene precursors be treated with *O*-deuterioacetic acid in the workup of photolysis reactions. It should be noted that only stilbenes formed from precursors **3** and **7** would be expected to yield α,α-dideuteriostilbenes with DOAc. Stilbenes formed via photoinduced hydroboration (eq 1) or from the photoinduced attack of **8** on the solvent, THF or DME, would be at most only monodeuteriated (**17**, Scheme III).

Scheme III



In Table I are summarized the molar ratios of the photoproducts obtained from sodium tetraphenylborate(III) in THF or DME solution. For ease in comparing the ratio of products, all product ratios were determined with an internal standard of fluorene, which was introduced at the conclusion of the photolysis or thermal reaction and before chromatographic analysis. The first two columns report the yields of biphenyl, terphenyls, stilbenes, and methylstilbenes generated in the photoreaction of sodium tetraphenylborate(III) (**8**) with the solvent in the *complete absence of any added diphenylacetylene*. Any increase in stilbenes over these threshold amounts would then represent stilbenes arising from attack on added diphenylacetylene, either by a photoproduced borohydride or by the diphenylborate(I) anion. From the dark reaction of **9** with **6** in Scheme II, the thermal reaction at 25 °C, it is clear that the stilbenes can be produced in a thermal process from the photolysate. By mass spectral analysis of such stilbenes, it is further shown that they are at least 25% dideuteriostilbenes, a substantiation that they were produced from intermediates **3** or **7**, rather than by hydroboration.

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(12) Walker, J. F.; Scott, N. D. *J. Am. Chem. Soc.* **1936**, *58*, 2442.

(13) Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1973**, *38*, 322.

(14) Reichstein, T.; Baud, J. *Helv. Chim. Acta* **1937**, *20*, 892.

(15) Eisch, J. J.; Shafii, B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 379.

(16) Murad, E. *J. Am. Chem. Soc.* **1961**, *83*, 1327.

(17) Calvert, J. G.; Pitts, J. N., Jr.; Thompson, D. D. *J. Am. Chem. Soc.* **1956**, *78*, 4239.

When the diphenylacetylene was present during the photolysis of sodium tetraphenylborate(III) in DME (Table I), somewhat more of the stilbene precursors was produced than in the thermal reaction with this alkyne (4.95% conversion versus 3.5%). However, it might be noted that the autogenous temperature of the photoreactor is somewhat higher (58 °C) and hence one cannot be certain that this is actually a photoacceleration of stilbene precursor formation. However, the irradiation of sodium tetraphenylborate in the presence of diphenylacetylene (2.4 molar equiv) did lead to a pronounced increase in the amount of biphenyl and of terphenyls formed upon protolysis of the photolysis products, namely, 1.6 times the amounts formed by irradiating **8** by itself. Thus, it is clear that diphenylacetylene promotes this photoreaction, possibly functioning as a triplet photosensitizer[18] for the series of reactions leading from **8** or **19** to **9**. In fact, by promoting the formation of the diphenylborate(I) anion, diphenylacetylene could thereby increase the proportion of the stilbene precursor.[19]

Compound **8** was irradiated in DME with 0.10 and with 0.20 molar equiv of biphenyl to learn whether photoproducts from **8** might also promote the photorearrangement of **8** itself. Upon protolysis of the photolysis, it was found that the amount of additional biphenyl generated had almost doubled (1.96 times) or tripled (2.9 times), respectively, over that generated from irradiating **8** alone (Table I). Therefore, biphenyl is a highly effective photosensitizer for the photorearrangement of **8**.[18]

From these results, therefore, there is no doubt that organoboron intermediate **3** and **7** can be formed in the absence of light. Indeed, there is no compelling evidence that light alone greatly accelerates their formation. These results are consistent with the presence of sodium diphenylborate(I) in photolysate solutions after irradiation has been discontinued. Accordingly, the photopromoted electron-transfer pathway suggested by Wilkey and Schuster to explain the formation of **3** and **7** (path b) is not required to obtain the observed stilbene precursors. Furthermore, Wilkey and Schuster cannot argue the necessity of this photopathway in dismissing our claim that we have trapped the diphenylborate(I) anion with diphenylacetylene in a thermal process.[20]

Protodeboronation of Organoboron Intermediates Formed in the Photolyses. But in focusing on the trapping experiment with diphenylacetylene, Wilkey and Schuster have not addressed the *totality of our other evidence*, obtained under different experimental conditions, which is offered in support of the generation of the diphenylborate(I) ion. This body of evidence is based upon protolysis and the deuterium-labeling of the deuteriodeboronation products of such photolysate solutions. In working such reaction mixtures up with degassed, glacial acetic acid, we observed that between 65 and 80% of one molecular equivalent of hydrogen gas was evolved (eq 2).

$$\underset{\substack{\mathbf{8}\\(1\ \text{mol})}}{\text{Na}^+\text{BPH}_4^-} \xrightarrow[\text{THF or DME}]{h\nu} \text{products} \xrightarrow{\text{HOAc}} \underset{(0.65\text{–}0.80\ \text{mol})}{\text{H}_2\uparrow} \qquad (2)$$

Parallel trapping experiments with benzyl chloride showed that only between one-quarter and one-half of the hydrogen gas could have come from B–H bonds in the photolysate[21] (eq 3). A further experiment of adding

$$\underset{\substack{\mathbf{8}\\(1\ \text{mol})}}{\text{Na}^+\text{BPh}_4^-} \xrightarrow[\text{THF or DME}]{h\nu} \text{products} \xrightarrow[\text{2. DOAc}]{\text{1. PhCH}_2\text{Cl}} \underset{(0.2\text{–}0.3\ \text{mol})}{\text{PhCH}_3} \qquad (3)$$

1-octyne to the photolysate and of failing to observe hydroboration ruled out the presence of neutral boron hydrides and thus pointed to the presence of borohydrides[22] (eq 4). The photolysate was sufficiently basic to abstract

$$\underset{\mathbf{8}}{\text{Na}^+\text{BPh}_4^-} \xrightarrow[\text{DME or THF}]{h\nu} \text{products} \xrightarrow[\text{2. DOAc}]{\text{1. C}_6\text{H}_{10}\text{C}\equiv\text{CH}}$$
$$\textit{no}\ \text{C}_6\text{H}_{13}\text{CH}{=}\text{CH}_2\ \textit{but}\ \text{C}_6\text{H}_{13}\text{C}\equiv\text{CD} \qquad (4)$$

the acetylenic hydrogen from 1-octyne, since workup with DOAc yielded 1-deuteriooctyne.

However, the treatment of the photolyzed sodium tetraphenylborate(III) solutions directly with degassed, glacial *O*-deuterioacetic acid (DOAc, 99%) proved to be most interesting: the evolved hydrogen gas contained significant amounts of D_2. With sodium tetraphenylborate(III) in THF, the 65% yield of hydrogen gas contained 20% D_2, 75% DH, and 5% H_2; with the borate salt in DME, an 80% yield of hydrogen gas containing 75% D_2, 25% DH, and *no* H_2 was obtained. Although the D–H can be attributed to the cleavage of the borohydride by the acid (eq 5), the D_2 must have arisen from the reaction of DOAc with

$$\text{Ar}_3\text{BH}^- + 4\text{DOAc} \rightarrow 3\text{ArD} + \text{H–D} + \text{B(OAc)}_3 + \text{OAc}^- \qquad (5)$$

a subvalent boron intermediate (e.g., Ar_2B^-) or with one having a boron–boron bond (eq 6 and 7).[23] Since there

$$\text{Ar}_2\text{B}^- + \text{DOAc} \rightarrow \text{Ar}_2\text{BD} + \text{OAc}^- \qquad (6)$$

$$\text{Ar}_2\text{BD} + 3\text{DOAc} \rightarrow 2\text{ArD} + \text{D}_2 + \text{B(OAc)}_3 \qquad (7)$$

are reports that hydrogen–deuterium exchange can occur between borohydrides and protic sources, such as H_2O, ROH, H_2SO_4, and HOAc,[23] one might consider that such an exchange in the present case could be the sole source of the observed D_2:

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(18) That the diphenylacetylene and biphenyl both promote the generation of biphenyl from **8** is open to various interpretations: (a) They might function as photosensitizers for one of the various photoprocesses leading from **8** to **19** to **19a**, possibly as a triplet photosensitizer. The triplet energy of diphenylacetylene has been estimated at 51 kcal/mol (Beer, M. *J. Chem. Phys.* **1956**, *25*, 745), that of biphenyl at 65 kcal/mol (Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537). Which step in this rather complicated photoconversion they might promote cannot be decided without a detailed mechanistic study. (b) They might function as SET agents, as suggested by Wilkey and Schuster (ref 7). It is not too difficult to accept that diphenylacetylene might be a participant in such an SET process, but it is doubtful whether biphenyl would display such electron affinity necessary for participation. In any event, both possibilities must be subjected to an experimental test.

(19) If the diphenylacetylene were acting as a triplet sensitizer for the photogeneration of **9**, the steady-state concentration of **9** would be higher during irradiation and hence its thermal addition to **6** thereby enhanced.

(20) Wilkey and Schuster's published experimental work with diphenylacetylene is inconclusive. Their workup was done with undeuteriated acetic acid. Therefore, the *cis*- and *trans*-stilbenes were unlabeled. Without deuterium labeling, they cannot conclude how the stilbenes were formed. If the borene transfer they favor were operative, DOAc would yield α,α-dideuteriostilbenes. But if the borohydrides known to be present in the photolysate led to a photochemical hydroboration, then DOAc workup would give α-deuteriostilbenes. It is also not ruled out that the stilbenes they observed stemmed not from the diphenylacetylene at all but from the photopromoted attack of **8** on THF (cf. our Scheme III).

(21) Borohydrides are known to reduce benzyl chloride smoothly to toluene. Workup of this reaction with DOAc gave only undeuteriated toluene. Cf. Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1973**, *95*, 1669.

(22) In the dark, neutral boron hydrides, but not borohydrides, cause the hydroboration of alkynes. But in this attempted reaction workup with HOAc gave no 1-octene.

(23) (a) Atkinson, J. G.; MacDonald, D. W.; Stuart, R. S.; Tremaine, P. H. *Can. J. Chem.* **1967**, *45*, 2583. (b) Cornforth, R. H. *Tetrahedron* **1970**, *26*, 4635.

$$\mathrm{Ar_3BH^- + DOAc \rightarrow Ar_3BD^- + HOAc} \qquad (8)$$

$$\mathrm{Ar_3BD^- + 4DOAc \rightarrow B(OAc)_3 + 3ArD + D_2 + OAc^-} \qquad (9)$$

$$\mathrm{Ar_3BH^- + 4DOAc \rightarrow B(OAc)_3 + 3ArD + HD + OAc^-} \qquad (10)$$

But were such exchange to be so extensive in eq 8, so that D_2 were the dominant product (eq 9), then the HOAc generated should produce some H_2 (eq 11). In fact,

$$\mathrm{Ar_3BH^- + 4HOAc \rightarrow B(OAc)_3 + 3ArH + H_2 + OAc^-} \qquad (11)$$

however, no H_2 was observed from the acetolysis of the photolysate 9 in DMF; only D_2 and HD were produced (75:25).

Even if such exchanges as depicted in eq 8 were to occur, it is highly improbable that they would occur to such an extent as to make D_2 as the principal acetolysis product from Ar_3BH and DOAc. For example, $NaBH_4$ and DOAc give 13% H-D exchange, $NaBH_4$ and D_2O give 10% exchange, and $NaBD_4$ and H_2SO_4–H_2O give 19% exchange.[23]

A bonus of information was obtained from these same deuteriolysis experiments: the biphenyl obtained in 30–70% overall yield[24] from these workups was 65:35 mixture of undeuterated and deuterated biphenyls for photolyses in THF. In DME, 85% of the biphenyl was undeuterated. Thus, at the end of 24 h of irradiation, the majority of the biphenylyl groups were *not attached to boron*. Only if an aryl–boron bond were present, would one find a deuterated biphenyl (eq 7). One might raise the objection that such absence of aryl–boron bonds in the photolysates of 8 might be due to photopromoted homolysis of such bonds and the abstraction of hydrogen from the solvent by such aryl radicals (eq 12 and 13). This

$$\mathrm{Ar_4B^- \xrightarrow{h\nu} Ar_3B^{\bullet -} + Ar^\bullet} \qquad (12)$$

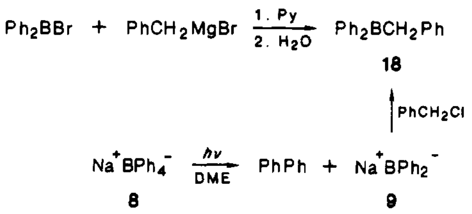
$$\mathrm{Ar^\bullet + H\text{–}S \rightarrow Ar\text{–}H + S^\bullet} \qquad (13)$$

possibility can be discounted in light of the failure of our group and of other workers ever to detect the presence of aryl radicals in such photolyses: (1) the photolysis of 8 in isopropyl alcohol-O-*d* occurred with the form biphenyl containing deuterium rather than incorporation of hydrogen by abstraction of the α-hydrogen from the isopropyl alcohol ($HCMe_2OD$), which a radical would choose to abstract;[25] (2) photolysis of the benzyltriphenylborate anion did not lead to preferential benzyl–boron cleavage, as a homolysis would favor, but rather coupling of the phenyl groups;[7] and (3) the separate photolysis of sodium phenyltri-*m*-tolylborate and of sodium phenyltri-*p*-tolylborate gave only the respective *m*- and *p*-methylbiphenyls and the *m,m'*- and *p,p'*-bitotyls.[6] No trace of biphenyl was detected, so that no intermolecular attack of free phenyl radicals was involved.

Even if one would concede the possibility that a small proportion of aryl–boron bond homolysis could occur, as suggested in eq 12 and 13, the combined observations of the large proportions of deuterium-free biphenyl and of deuterium gas require the generation of a reduced boron (Ph_2B^-) and an oxidized hydrocarbon (biphenyl from Ph_4B^-).

Thus, these two key observations, the formation of principally undeuteriated biphenyl and the formation of a large proportion of D_2 from the deuteriolysis of photolysates of borates in DME, are consistent with the generation of sodium diphenylborate(I) in DME, a solvent not studied in Wilkey and Schuster's investigation[7] (eq 14).

Scheme IV



$$\underset{8}{\mathrm{Na^+BPh_4^-}} \xrightarrow[\mathrm{DME}]{254\ \mathrm{nm}} \underset{9}{\mathrm{Na^+BPh_2}} + \mathrm{PhPh} \qquad (14)$$

Trapping of the Diphenylborate(I) Anion with Benzyl Chloride. If the diphenylborate(I) anion were present in such photolysate solutions, it might be expected to couple very readily with benzyl chloride. This expectation is based upon its similarity to anions of carbon and silicon (Ph_3C^- and Ph_3Si^-), both of which react readily (eq 15).[26]

$$\mathrm{Ph_3Si^-M^+ + PhCH_2Cl \rightarrow Ph_3SiCH_2Ph + MCl} \qquad (15)$$

In order to learn how benzyl chloride might react toward sodium tetraphenylborate(III) itself, two control experiments were performed: (1) 8 was allowed to react with benzyl chloride in a 1:1 molar ratio at 35 °C in THF for 24 h in the dark and (2) 8 and benzyl chloride were irradiated at 254 nm for 24 h in THF. Acetolysis of the dark reaction and gas chromatographic analysis showed the absence of toluene, biphenyl, diphenylmethane, and dibenzyl. Acetolysis of the photoreaction showed the presence of toluene, biphenyl (86%), terphenyls, and bibenzyl (35%).

Were the capture of the diphenylborate(I) anion by benzyl chloride to succeed, then benzyl(diphenyl)borane would be formed. Such unsymmetrically substituted triorganoboranes are known to be prone to redistribution of groups (eq 16),[27] although amine adducts tend to be

$$\mathrm{Ph_2BCH_2Ph \rightleftharpoons Ph_3B + PhB(CH_2Ph)_2 + B(CH_2Ph)_3} \qquad (16)$$

somewhat more stable. Accordingly, an authentic sample of benzyldiphenylborane (18) was synthesized as its pyridine adduct from bromodiphenylborane and benzylmagnesium chloride (Scheme IV). The crystalline product melted sharply (125–127 °C) and displayed the appropriate parent ions at *m/e* 256 and 255 in the expected 4:1 ratio, together with base peaks at *m/e* 165 and 164, signaling the loss of the benzyl group. However there were no peaks characteristic of Ph_3B (*m/e* = 242) or of $PhB(CH_2Ph)_2$ (*m/e* = 270). Once the crystalline 18 was dissolved in $CDCl_3$, however, the overall proton ratio of the α-pyridyl/aromatic/methylene region remained consistent with that expected for 18 (2:18:2), but there were now at least two methylene singlets. The mass spectrum of the recovered NMR sample thereafter showed peaks at *m/e* 242, 256, 270, and 294. From these observations and an HPLC analysis of 18, it is clear that 18 tends to undergo group redistribution, according to eq 16, in polar solution.

Equipped with this knowledge, we then introduced about 1 equiv of benzyl chloride and several equivalents of dry pyridine into a previously photolyzed solution of

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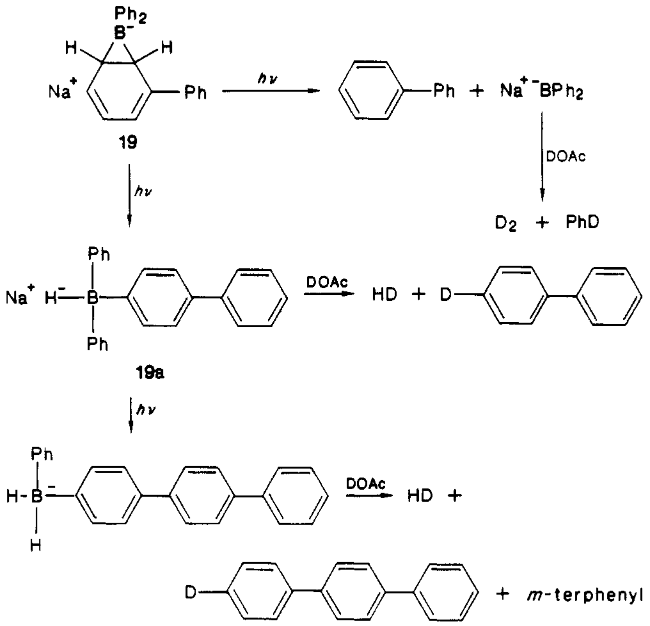
[24] Varying amounts of terphenyls (5–15%) and higher hydrocarbons were also isolated upon protolytic workup, but there was little or no sign of dihydrobiphenyls. This is yet another proof that Wilkey and Schuster's photoconditions differed from ours.

[25] Grisdale, P. J.; Babb, B. E.; Doty, J. C.; Regan, T. H.; Maier, D. P.; Williams. J. L. R. *J. Organomet. Chem.* **1968**, *14*, 63.

[26] Brook, A. G.; Wolfe, S. *J. Am. Chem. Soc.* **1957**, *79*, 1431.

[27] Onak, T. *Organoborane Chemistry*; Academic Press: New York, 1975; pp 24–26.

Scheme V

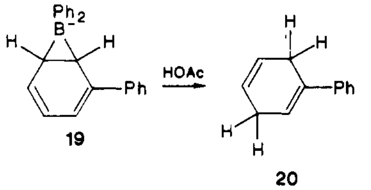


sodium tetraphenylborate(III) in DME. The deep red color of the photolysate solution was immediately discharged. Anaerobic removal of all volatiles under vacuum and subsequent extraction of the residue with pentane left a viscous, yellow oil, which was analyzed by mass spectrometry and HPLC separation. All the expected mass and chromatographic peaks were observed for Ph_3B, Ph_2BCH_2Ph, $PhB(CH_2Ph)_2$, and $B(CH_2Ph)_3$. From such HPLC peaks the overall yield of the various benzylphenylboranes was estimated to be about 20%. In addition, because of its unusual stability and high melting point, a triphenylborane–pyridine complex was isolated in the pure state from the yellow reaction residue by column chromatography on silica gel with $CHCl_3$ as eluent.

Discussion

The principal differences in experimental conditions between the studies of the Eisch group and of the Schuster group were in the solvent employed and the length of irradiation. The Eisch group performed most of their studies on the generation of the diphenylborate(I) anion in 1,2-dimethoxyethane over a period of 24 h. The Schuster group conducted their studies in THF and in acetonitrile for periods of time not specified in this publication, but apparently for less than 24 h.

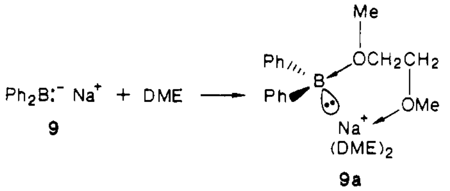
From the reported nature of the protodeboronation products from the two photolysis studies, it is clear that the Schuster group and the Eisch group had obtained different photoproducts. In Schuster's study, the interesting bicyclic organoborate(III) anion **19** was detected for the first time by NMR spectroscopy and its treatment with acetic acid led to 1-phenyl-1,4-cyclohexadiene (**20**) (eq 17).



(17)

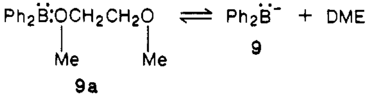
In the Eisch study, treatment of the organoborane photolysate led to little or *no* dihydrobiphenyl, but rather biphenyl itself and hydroen gas. It is evident that little or *no* **19** is present after 24 h of irradiation. As is consistent with the acetolysis products, and with the products obtained with DOAc (eq 5–7), it appears that upon prolonged irradiation (24 h) the Schuster intermediate **19** aromatizes, either by elimination of Ph_2B^- or by isomerization to a borohydride (Scheme V). As is depicted in Scheme V, it is comprehensible that treatment of photolysates with DOAc should give variable proportions of HD, D_2, biphenyl, and monodeuteriated biphenyl.

Both the modest amount of trapping with diphenylacetylene and the moderate amount of coupling with benzyl chloride are consistent with the presence of sodium diphenylborate(I) in the long-term photolysate solutions.[28] In DME solution it is likely that the tricoordinate anion $Ph_2B\!:^-$ is coordinated also to an oxygen of the DME (eq 18). Viewed in this way, the diphenylborate anion is not so much a boron analogue of a carbene, but rather analogous to the diphenylmethyl or the triphenylmethyl anion. Delocalization of the unshared electron pair on the boron center over the phenyl groups should stabilize such an anion.[29] The red color of solutions of sodium diphenylborate(I) in DME is suggestive of its electronic resemblance to tritylsodium, which also forms a red solution in ethyl ether.

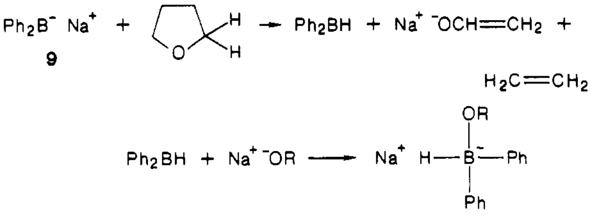


(18)

The relative slowness with which the diphenylborate(I) anion adds to diphenylacetylene may be connected with its solvated character; the solvent may have to be displaced by diphenylacetylene before reaction ensues (eq 19).[30]


$$\underset{\mathbf{9a}}{\mathrm{Ph_2\overset{-}{B}\!:\!\underset{\mid\atop Me}{O}CH_2CH_2\underset{\mid\atop Me}{O}}} \rightleftharpoons \underset{\mathbf{9}}{\mathrm{Ph_2\ddot{B}^-}} + \mathrm{DME} \qquad (19)$$

In addition to the borohydrides formed from **19** by isomerization (Scheme V), there are indications that the diphenylborate(I) anion can abstract protons with varying ease from the solvent (eq 20). This attack on solvent



(20)

would explain why THF might be less satisfactory than DME for generating the anion and why THF yields much more borohydride. Tetrahydrofuran is known to be much

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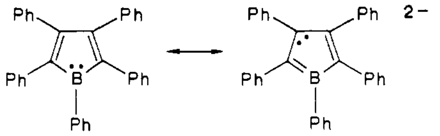
(28) As in our previous report, we cannot specify what the state of aggregation of **2** is (dimer or a higher cluster) nor whether it may be associated with the borohydrides present as a complex (such as $Ph_2B{=}BPh_2^{2-}$ or $Ph_2B\cdots H\cdots BAr_3^{2-}$).

(29) The dianion of pentaphenylborole is presumably stabilized by its Hückel aromaticity and the π-electron delocalization:



Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379.

(30) In a similar manner, the triphenylsilyl anion adds slowly to diphenylacetylene to give a small amount of adduct: Brook, A. G.; Tai, K. M.; Gilman, H. *J. Am. Chem. Soc.* **1955**, *77*, 6219.

more prone to proton abstracting by strong base.[13]

In conclusion, our chemical investigations of the photolysate solution of sodium tetraphenylborate(III) in DME strongly indicate, we believe, that sodium diphenylborate(I) or a similar subvalent boron salt exists in such solutions. Ultimately, of course, the most convincing proof of the structure and nature of this unusual compound must await its isolation as a pure substance. Because of the encouraging results of our chemical studies, therefore, we have undertaken an effort to generate and isolate such subvalent boron anions through photochemical means.

Experimental Section

Instrumentation. All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded either on a Perkin-Elmer Model 457 or Model 238B grating spectrophotometer and the samples were prepared in solution, as KBr pellets or as mineral oil mulls. The proton or heteroatom nuclear magnetic resonance spectra (^{1}H NMR) were measured with a Varian spectrometer, Model EM 360, and with a Bruker 300-MHz instrument equipped with an Aspect 3000 computer. The values are reported on the δ scale in parts per million with reference to internal tetramethylsilane, followed by the relative proton intensities and the coupling constants (J) in hertz. Mass spectra were determined either with an MS/902 CIS 2 instrument coupled with a V6 Datasystem 2040 computerized recorder, with a Varian MAT spectrometer, Model CH5, or with a Hewlett-Packard GC/MS apparatus, Model 5993, equipped with capillary GC columns (OV-101). Vapor-phase chromatographic analysis (GC) and isolations were carried out on an F&M chromatograph, Model 720, equipped with a 6 ft × 0.125 in. column of 10% SE-30 silicone gum rubber on Chromosorb P or with a Hewlett-Packard gas chromatograph, Model 588A, equipped with GC columns packed with OV-101. Liquid chromatographic analyses were performed with a Perkin-Elmer HPLC apparatus, Model 400, equipped with silica columns (10 μm) coated with LCI-100. Irradiations were conducted in quartz vessels for the organic solutions of sodium tetraphenylborate(III), under anhydrous conditions where both solvent and reaction vessel were maintained under an atmosphere of dry nitrogen, by means of a Rayonet photochemical reactor, Model 100. The reactor was provided with a cylindrical array of lamps emitting 254-nm irradiation and the cylindrical cavity of the lamp bank had a diameter of 24 cm.

Inert Reaction Media. All preparations and reactions involving air- and moisture-sensitive organometallic intermediates were conducted under an atmosphere of dry, oxygen-free nitrogen, with adherence to published procedures.[31] Solvents of reagent grade were used in all reactions. Specifically, peroxides were removed from 1,2-dimethyoxyethane (DME) and tetrahydrofuran (THF) by passing such solvents through a column of neutral alumina under nitrogen. The eluted solvents were then allowed to reflux over $LiAlH_4$ for 5 h and then distilled under an atmosphere of dry nitrogen just before use.

Starting Materials and Products. Sodium Tetraphenylborate(III) (8). This compound could be purchased commercially (Aldrich, 99+%, A.C.S. reagent) or prepared by the reliable procedure of Wittig and Raff via the lithium salt.[32] Either source of 8 provided a sample that was then recrystallized from DME (40 mL per 5.0 g). The 8 was crystallized at −78 °C as a colorless powder. The powder was dried *in vacuo* for 24 h at 25 °C; the resulting solid was shown by ^{1}H NMR spectroscopy to be 8 solvated with 1 mol of DME. Upon heating to 125 °C, the solvated 8 released the DME. A mass spectrum of the purified 8 showed the complete absence of even traces of mass peaks attributable to phenol (94) or to biphenyl (154), telltale products of partially oxidized 8. Alternatively, this salt could be recrystallized from DME–Et_2O or THF–Et_2O mixtures (1:1, v:v).

Hydrocarbons. Authentic samples of mono- and dideuteriated biphenyls were available for comparison of mass spectra,[33] as were samples of (*E*)- and (*Z*)-stilbenes, (*E*)- and (*Z*)-α-methylstilbenes, α-deuteriotoluene, 1-deuteriooctyne, *p*-terphenyl, and both *p,p′*- and *o,o′*-quaterphenyls.

Irradiations of Sodium Tetraphenylborate(III) (8). General Procedure. In a quartz photoreactor, thoroughly dried and then flushed and maintained under dry nitrogen were placed 80 mL of 1,2-dimethoxyethane or of tetrahydrofuran, which were freshly distilled from $LiAlH_4$. Then 1.0 g (2.92 mmol) of pure, dry sodium tetraphenylborate(III) was added and the initially colorless solution irradiated in the Rayonet reactor for 24 h. The ambient temperature in the reactor chamber attained 58 °C during the irradiation. After irradiation a deep-red solution had formed. This solution was then subjected to various chemical reactions.

(a) Irradiation of Sodium Tetraphenylborate(III) (8) in Various Solvents with Subsequent Treatment with Glacial Acetic Acid. One-gram samples of 8, which had been recrystallized from THF–Et_2O or from DME–Et_2O (1:1, v:v), were irradiated in 80 mL of THF or of DME for 24 h. Then 3.0 mL of degassed glacial acetic acid was added under a nitrogen atmosphere and the mixture stirred for 15 h at 20–30 °C and for 15 h at reflux. After cooling to 25 °C, 500 mg of pure fluorene was introduced as a standard for GC analysis. The reaction mixture was concentrated to a volume of about 5 mL and then diluted with 20 mL of ether. The resulting organic layer was extracted with two 5-mL portions of saturated, aqueous $NaHCO_3$ and then with water. The organic layer was dried over anhydrous $MgSO_4$ and then concentrated to a volume of 5 mL. The mixtue was analyzed by GC, GC/MS, and, in most cases, by HPLC techniques. The reaction components and their amounts are reported in Table I. The components were collected by GC and their identity verified by IR, ^{1}H NMR, and MS measurements.

(b) Irradiation of Sodium Tetraphenylborate(III) (8) in the Presence of Diphenylacetylene (6). This irradiation and workup were performed as in section a, except that 1.00 g of pure diphenylacetylene (6) was present. The results of the analysis of the hydrocarbons formed upon hydrolysis are given in Table I. In a parallel reaction, workup of the photolysate with *O*-deuterioacetic acid (99%) gave a mixture of (*Z*)- and (*E*)-stilbenes and (*Z*)- and (*E*)-α-methylstilbenes. Under these conditions, the isomeric stilbenes were formed in comparable amounts (Table I). In earlier irradiations with an air-cooled radiation chamber (<45°C) and with shorter heating periods with glacial acetic acid, the cis–trans ratio obtained was 7:1. The yield of stilbenes, based upon diphenylacetylene consumed and allowing for the stilbenes produced from the DME (Scheme III), was 45%.

Analysis of the *cis*-stilbene isolated from the workup with DOAc by ^{1}H NMR and MS measurements showed it to consist of 20% of α,α'-dideuteriated, 40% of α-deuteriated, and 40% of undeuteriated stilbenes.

(c) Treatment with *O*-Deuterioacetic Acid. In this experiment 20 mol % of biphenyl was introduced into the reaction mixture before irradiation. The reactor tube was connected to a mercury-filled gas buret and then 2 mL of CH_3CO_2D (99%) pure introduced into the reaction mixture from irradiating 8 in DME. The evolved gas was dried and collected; adjusted to STP, the volume of gas obtained was 42.5 mL. This corresponds to 1.90 mmol. Mass spectral analysis showed the gas to consist of 73% of D_2 and 27% of HD. No H_2 was detected.

The reaction mixture was concentrated under nitrogen by distillation to a clear, pale yellow solution. This solution was heated at reflux for 16 h and then diluted with water. The mixture was extracted with 4–15-mL portions of ether, the combined ether extracts washed with 10% aqueous NaOH and with water, and the resulting solution dried over solid $MgSO_4$. After solvent removal the residue was analyzed by quantitative gas chromatography using bibenzyl and *o*-terphenyl as standards. In this manner it was shown that the yield of additional biphenyl (over the 20 mol % employed) was 66.6% and that of *p*-terphenyl was 12%. By sublimation of this residue and recrystallization from methanol, pure samples of biphenyl and *p*-terphenyl were isolated. The mother liquor was shown by GC to contain *m*-terphenyl and unknowns. By preparative GC a pure sample of *m*-terphenyl was isolated.

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[31] Eisch, J. J. *Organometallic Syntheses*; Academic Press: New York, 1981; Vol. 2, pp 1–52.

[32] Wittig, G.; Raff, P. *Justus Liebigs Ann. Chem.* **1951**, *573*, 195.

[33] Eisch, J. J.; Hallenbeck, L. E.; Han, K. I. *J. Am. Chem. Soc.* **1986**, *108*, 7763.

Mass spectral analysis of the biphenyl showed it to contain 85% of undeuteriated and 15% of monodeuteriated biphenyls. The *p*-terphenyl was 61% undeuteriated, 34% monodeuteriated, and 6% dideuteriated; the meta isomer had 49% d_0, 48% d_1, and 4% d_2.

An analogous irradiation of **8** in THF and treatment with *O*-deuterioacetic acid gave a 65% yield of hydrogen gas, which was a 20:75:5 mixture of D_2, HD, and H_2. The biphenyl was a 65:35 mixture of undeuteriated and monodeuteriated biphenyls.

(d) Treatment with Benzyl Chloride. The reddish brown solution was treated under nitrogen with 712 mg (5.64 mmol) of freshly distilled benzyl chloride and the solution allowed to stir at 25 °C for 24 h. The mixture was warmed at 60 °C in vacuo for 12 h, in order to remove the excess benzyl chloride. At this point an aliquot of the reaction mixture was treated with a nonane standard and analyzed by gas chromatography. A 24% yield of toluene was determined, based upon the starting borate.

The residue was dissolved in 5 mL of THF and the solution treated, in turn, with 1 mL of 3 N aqueous NaOH and 1.7 mL of 30% H_2O_2. The temperature then rose to 65 °C. Workup and gas chromatographic analysis, using diphenylacetylene as a standard, revealed a 3.8% yield of bibenzyl.

An identical photolysate solution of **8** in DME under nitrogen was treated first with 1.10 g (9.85 mmol) of benzyl chloride and then allowed to stir for 40 h at 35 °C. Addition of 2 mL of CH_3CO_2D after this time caused the evolution of only 2 mL of hydrogen. The solvent was removed and the residual liquid was heated at reflux for 16 h. Usual workup gave an organic extract, from which toluene was separated by gas chromatography. The toluene was shown by mass spectrometry to be completely toluene-d_0.

(e) Treatment with 1-Octyne. An identical reddish brown photolysate solution of **8** in THF was treated with 1.0 mL of pure 1-octyne and the mixture heated at reflux for 2 h. Neither a color change nor a gas evolution was observed. But when 2 mL of CH_3CO_2D was added, 54 mL (2.41 mmol) of gas was collected at STP, an 82% yield of hydrogen. By mass spectrometry this gas consisted of 18.4 of D_2, 76.7% of HD, and 4.9% of H_2.

The solvent was removed by distillation, under nitrogen, and the residue heated at reflux for 16 h. Usual workup and gas chromatographic analysis showed that no 1-octene was present. The octyne was recovered and was shown by infrared and mass spectral analysis to be 1-deuteriated. The biphenyl and the *m*- and *p*-terphenyls were found to be present in 40% and 15%, respectively. By mass spectrometry the biphenyl consisted of 68% d_0, and 32% d_1 and the terphenyls 76% d_0, 16% d_1, and 8% d_2.

(f) Treatment with Diphenylacetylene (6). The reddish brown photolysate solution was carefully shielded from light and then treated with 1.00 g of diphenylacetylene. The reaction mixture was stirred in the dark for 24 h at 25 °C and then worked up with HOAc in the usual manner.

Irradiation of Diphenylacetylene (6) in the Presence of Sodium Borohydride. In 80 mL of DME, 1.00 g of $NaBH_4$ and 1.00 g of **6** were irradiated for 24 h. Workup with glacial acetic acid showed a 2% yield of a 63:47 mixture of *cis*- and *trans*-stilbenes.

In a control experiment, treatment of an unirradiated mixture of $NaBH_4$ and **6** with HOAc gave no stilbenes.

Synthesis of Benzyldiphenylborane–Pyridine (12). Benzylmagnesium chloride was prepared in the usual manner from 1.9 g (15 mmol) of benzyl chloride and 700 mg (3 mg-atom) of magnesium turnings in 20 mL of anhydrous diethyl ether. In a separate flask under nitrogen was prepared a solution of 2.5 g (10 mmol) of bromodiphenylborane in 50 mL of THF at 0 °C. To this was added 0.8 mL (10 mmol) of dry pyridine; after 30 min at 25 °C a thick, white mixture had formed. Thereupon, the benzyl Grignard reagent was slowly added to the borane–pyridine suspension. With a slight exotherm, the white suspension gradually dissolved to yield a clear, light brown solution. The solution was stirred at 25–30 °C for 2 h and then was treated slowly with a saturated, aqueous NH_4Cl solution. The organic layer was separated, dried over solid Na_2SO_4, and evaporated to leave a yellow-brown viscous oil, which upon dissolution in 30 mL of methanol deposited 1.7 g (51%) of off-white needles. A further recrystallization from methanol provided colorless needles, mp 125–127 °C.

Anal. Calcd for $C_{24}H_{22}BN$: C, 85.98; H, 6.61. Found: C, 86.31; H, 6.44.

Although a MS analysis of this product showed only a parent-peak duo at 256 and 255 in a 4:1 ratio, dissolution in $CDCl_3$ for recording the ^1H NMR spectrum led to at least two methylene peaks. The MS analysis of the recovered organoborane now showed parent peaks at *m/e* 242, 256, 270, and 294.

Isolation of Benzyldiphenylborane–Pyridine from the Photolysate of Sodium Tetraphenylborate(III) (8). After a standard 24-h irradiation of 1.00 g of **8** in 80 mL of DME, the mixture was cooled down and then treated with 1.0 mL of carefully dried and degassed pyridine (no color change observed). After 30 min a portion of freshly distilled benzyl chloride was introduced; this amounted to 2.0, 0.8, or 0.3 mL in three different experiments. The color of the reaction mixture immediately changed from dark reddish brown to light yellow. The mixture was stirred at 25–30 °C for 24 h while still under nitrogen and then volatiles were removed at the same temperature under reduced pressure. The residue material was treated as an air- and moisture-sensitive system during all subsequent analyses.

The material was examined by TLC, HPLC, ^1H NMR, and MS (deep-insertion probe) after the majority of hydrocarbons was removed by extraction with portions of pentane at 25 °C. The fractions collected by HPLC had the same components as exhibited by an authentic sample of benzyldiphenylborane–pyridine (cf. supra **12**). The composite yield of all these peaks was estimated at 20%. By mass spectrometry these components had parent ions at *m/e* 242, 256, 270, and 294, which correspond to the redistribution products of benzyldiphenylborane and the loss of complexed pyridine: Ph_3B, Ph_2BCH_2Ph, $PhB(CH_2Ph)_2$, and $B(CH_2Ph)_3$.

Column chromatography of such a reaction mixture on silica gel and elution with methanol permitted the isolation of triphenylborane–pyridine, mp 215–217 °C dec, as verified by MS and IR comparison with an authentic sample.

Acknowledgment. We are indebted to the National Science Foundation for the support of the initial research on this topic under the auspices of Grant GP-34204. For the most recent studies, we acknowledge the support of the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant 85-0108, and of Akzo Corporate Research America, Inc.