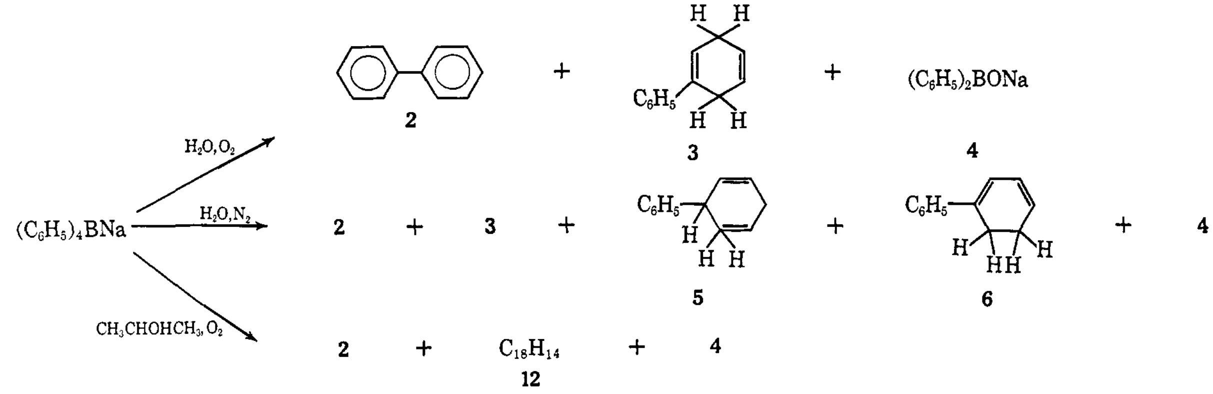
Boron Photochemistry. I. Irradiation of Sodium Tetraarylborates in Aqueous Solution

J. L. R. Williams, J. C. Doty, P. J. Grisdale, R. Searle, T. H. Regan, G. P. Happ, and D. P. Maier

Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. *Received March 16, 1967*

Abstract: The photolysis of aqueous solutions of sodium tetraphenylborate, with light of wavelengths in the region of 2537 A, has been carried out. The products which result in excess of 0.5% are biphenyl, 1-phenyl-1,4-cyclohexadiene, 3-phenyl-1,4-cyclohexadiene, and 1-phenyl-1,3-cyclohexadiene. In the presence of oxygen, biphenyl is the principal product, and, in its absence, 1-phenyl-1,4-cyclohexadiene predominates. The photochemical reaction leading to these products has been found to be intramolecular by use of substituents and by deuterium tagging. The quantum yield of decomposition of sodium tetraphenylborate in water is 0.22 to 0.26 at 2537 A.

In a previous communication[1] we outlined our preliminary work dealing with the photochemical conversion of sodium tetraphenylborate (**1**) to biphenyl (**2**), 1-phenyl-1,4-cyclohexadiene (**3**), and an isomer of **3**. Razuvaev and Brikina[2] had earlier tersely outlined the course of the photolysis of potassium tetraphenylborate in chloroform solution. The products were benzene, biphenyl, phenol, and potassium chloride. Thus far in our work we have photolyzed sodium tetraphenylborate (**1**) in water and in isopropyl alcohol solution. This paper deals with the course of the photolysis in water. The photochemistry of **1** in alcoholic solutions now being studied will be reported later. We find that the following reaction sequence depends on the presence or absence of oxygen when aqueous solutions of sodium tetraphenylborate are photolyzed, with light of wavelengths in the region of 2537 A, as indicated in Table I. One pathway for the photolysis of isopropyl alcohol solutions of **1** is also included.



Our work to date indicates that **2**, **3**, **5**, and **6** are the primary photochemical products, whereas diphenylborinic acid (**4**) results from the ensuing ground-state chemistry. Benzene (**12**), phenol (**9**), and phenylboronic acid (**10**) result from the further decomposition of **4** by reactions analogous to those suggested by Mirviss[3] to explain the aerobic oxidation of trialkylborons. Thus, the sodium salt of **4** can be attacked by oxygen to yield phenolate and phenylboronate anions.

We suggest that the phenol found by Razuvaev and Brikina[2] during the photolysis of potassium tetraphenylborate resulted from the oxidative decomposition of diphenylborinic acid (**4**). It is presumed that their photolysis[2] was carried out in a chloroform solution which was exposed to atmospheric oxygen since no description of protective conditions was given.

Thus, irradiation of **1** in aqueous solution leads to the formation of varying amounts of biphenyl (**2**) and to at least three dienes (**3**, **5**, **6**). The ratio of biphenyl to the dienes (**3**, **5**, **6**) increases when air is passed through the irradiation solution. For example, irradiation of an aqueous solution of **1** under a nitrogen atmosphere, by using an ultraviolet source rich in wavelengths in the region of 2537 A, leads to the formation of **2** (1%), 1-phenyl-1,4-cyclohexadiene (**3**, 97%), 3-phenyl-1,4 cyclohexadiene (**5**, 1%), and 1-phenyl-1,3-cyclohexadiene (**6**, 0.5%). In order to confirm the structure of the dienes **3**, **4**, and **6**, a general investigation of the methods of synthesis and characterization of all possible isomeric phenylcyclohexadienes was undertaken. The report of that investigation is in process.[4]

Linschitz and Grellman[5] have shown that flash photolysis of triphenylamine leads to the formation of N-phenylcarbazole.

---

[1] J. L. R. Williams, J. C. Doty, P. J. Grisdale, T. H. Regan, and D. G. Borden, *Chem. Commun.*, **3**, 109 (1967).

[2] G. A. Razuvaev and T. G. Brikina, *Zh. Obshch. Khim.*, **24**, 1415 (1954).

[3] S. B. Mirviss, *J. Am. Chem. Soc.*, **83**, 3051 (1961).

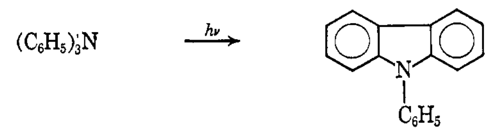
[4] P. J. Grisdale, T. H. Regan, J. C. Doty, J. Figueras, and J. L. R. Williams, submitted for publication.

[5] H. Linschitz and K. H. Grellman, *J. Am. Chem. Soc.*, **86**, 303 (1964).

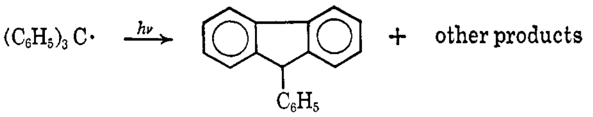
Table I. Photolysis of Alkali Metal Tetraarylborates in Water at 8° with a Rayonet 2537 Irradiation Apparatus

Borates	Borate soln, M	Water, ml	Atm	Irradiation time, hr	Yield,[e] g	Composition, %				$C_{18}H_{14}$ or greater	**4**, g	% conversion[d]
						2	**3**	**5**	**6**			
$NaB(C_6H_5)_4$	5.84×10^{-2}	250	Air[a]	5	0.35	6	93	1	<0.1	0.1		30
$NaB(C_6H_5)_4$	5.84×10^{-2}	250	Air[a]	5	0.35	4	95	1	<0.1	0.1		27
$NaB(C_6H_5)_4$	5.84×10^{-2}	250	N_2	5	0.65	2	97	1	0.1	0.3		36
$NaB(C_6H_5)_4$	5.84×10^{-2}	250	N_2	5	0.8	2	97	1	0.1	0.5		38
$NaB(C_6H_5)_4$	5.84×10^{-2}	250	Air[b]	5	0.50	59	39	<0.1	...	0.0		45
$NaB(C_6H_5)_4$	5.84×10^{-2}	250	Air[b]	5	0.58	58	42	<0.1	...	0.08		44
$NaB(C_6H_5)_4$	5.84×10^{-2}	250	Air[c]	5	0.90	42	60	<0.1	...	0		65
$NaB(C_6H_5)_4$	5.84×10^{-2}	250	Air[c]	5	1.05	40	60	<0.1	...	0		
$NaB(C_4H_5)_4$	5.84×10^{-2}	250	Air[a]	5	0.6	3	97	<1	<1		0.6	24
$NaB(C_4H_5)_4$	5.84×10^{-2}	250	Air[a]	4.5	0.5	5	93	1	1		0.43	23
$LiB(C_6H_5)_4$	3.08×10^{-2}	200	Air[a]	6	0.2	31	69	...	...	...		22
$NaB(C_6H_5)_4$-d_{20}	2.2×10^{-2}	50	Air[a]	3.5	0.2	20	77	3	...			95
$NaB(C_6H_5)_4$ $NaB(C_6H_5)_4$-d_{20}	2.2×10^{-2} 2.2×10^{-2}	50	Air[a]	4.8	0.23	13.5	85.5	1	...			50
						p-$C_{14}H_{14}$	$C_{14}H_{16}$					
$NaB(p\text{-}C_7H_7)_4$	4.2×10^{-4}	3000	Air[a]	5.5	0.05	86.5	13.5					
$LiB(p\text{-}C_7H_7)_4$	2.6×10^{-2}	200	Air[a]	5.0	0.5	40	60					55

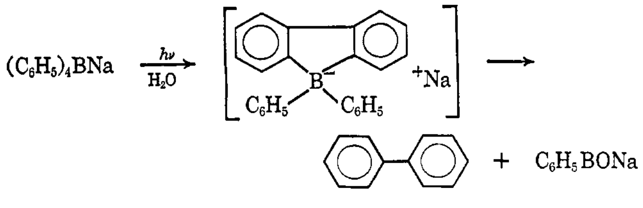
[a] Irradiation was stirred under an air atmosphere. [b] Air was admitted *via* a fritted disk into the bottom of the irradiation tube. [c] Air was passed as large bubbles through the irradiation mixture. More vigorous agitation resulted when air was passed through the irradiation tube at 0.5 to 1.0 l./min. [d] Per cent conversion is calculated on the basis of the potassium tetraarylborates recovered. [e] The yield signifies the nonvolatile organic hydrophobic products.



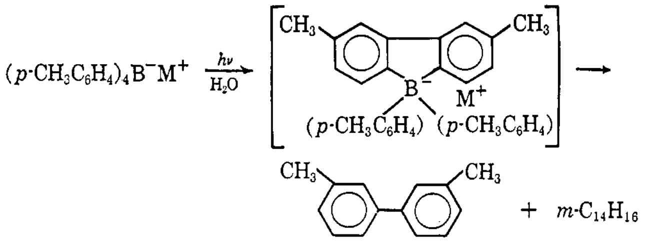
Two papers[6,7] have indicated that an analogous interphenyl cyclization can take place when triphenylmethyl radicals are photochemically produced.



We were interested to see if such an interphenyl cyclization would occur during the irradiation of solutions of sodium tetraphenylborate under air or inert gas atmospheres. We found no evidence of the formation of B-phenyl-9-borafluorene. However, in view of the instability of triphenylboron, B-phenyl-9-borafluorene would probably decompose in an analogous manner. The failure to isolate such an interphenyl cyclization product does not, however, exclude its transient existence during the formation of biphenyl (**2**) and dienes **3**, **5**, and **6**.



Similar intermediate five-membered products are indicated by the bisfluorenyl "ate" complex formed from the reaction of 2,2′-dilithium biphenyl and boron trifluoride.[8] In order to test this premise, sodium tetra-*p*-tolylborate and lithium tetra-*p*-tolylborate were synthesized from *p*-tolyllithium and boron trifluoride etherate by modification of known procedures.[9,10] The sodium salt showed very low solubility in water and hence was tedious to photolyze. The lithium salt was more soluble in water and therefore was used in larger runs as a matter of convenience. If the course of photolysis of sodium or lithium tetra-*p*-tolylborate involves an interphenyl cyclization, then the product should be *m*-bitolyl and the related dienes.



Only *p*-bitolyl and the related dienes were isolated from the two irradiations. The reaction mixture from the irradiation of lithium tetra-*p*-tolylborate was dehydrogenated over palladium–charcoal to yield a single product, *p*-bitolyl. Thus, the carbon atoms originally bonded to boron in lithium or sodium tetra-*p*-tolylborate form the link between the two rings in the products, biphenyl (**2**) and dienes **3**, **5**, and **6**.

The formation of **3**, **5**, and **6** requires the addition of two protons to two phenyl rings. When we irradiated **1** in deuterium oxide, biphenyl (**2**) and dienes **3**, **5**, and **6**, which were isolated by gas chromatography, contained

---

(6) R. L. Letsinger, R. Collat, and M. Magnusson, *J. Am. Chem. Soc.*, **76**, 4185 (1954).

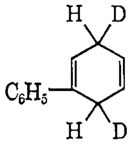
(7) H. G. Lewis and E. D. Owen, *Chem. Commun.*, **2**, 217 (1966).

(8) G. Wittig and W. Herwig, *Chem. Ber.*, **88**, 962 (1955).

(9) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

(10) G. Wittig and P. Raff, *Ann.*, **573**, 195 (1951).

deuterium distributed as follows: 46% $C_{12}H_{10}$ (biphenyl), 36% $C_{12}H_9D$, 21% $C_{12}H_8D_2$, and 1-phenyl-1,4-cyclohexadiene-d_2 (**3**). The other diene fractions (**5**, **6**), amounting to less than 1% of total products, were neglected. The nmr spectrum of diene **3**-d_2 had absorption peaks at exactly the same chemical shifts as those of the diene assigned structure **3**.[4] The spectrum of **3**-d_2 differed from that of **3** in that (1) the peak corresponding to the diallylic protons (δ 2.91) was reduced in intensity to slightly more than 2 H and was broadened slightly causing the loss of fine structure, and (2) the olefinic proton peaks differed slightly in fine structure from those in **3** but retained the same relative area. These facts are consistent with the structure in which two of the allylic protons have been replaced by deuterium. The most likely structure is



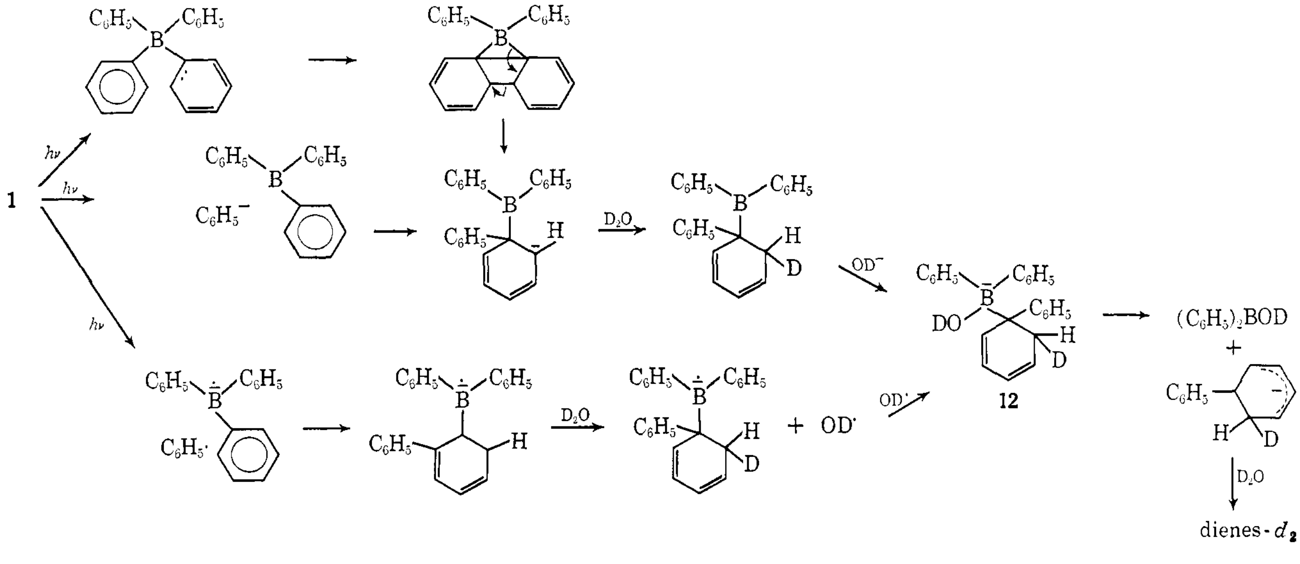
Thus there is no doubt that the two protons added are supplied by the solvent.

The work of DeTar and Long[11] dealing with formation of a phenylcyclohexadiene by the decomposition of benzoyl peroxide made it tempting to invoke a free-radical-type mechanism for the present work to explain the formation of **2** and dienes **3**, **5**, and **6**. If the reaction were to proceed *via* a typical free-radical mechanism, then one would expect that radicals from different individual anions of **1** would combine to form the ultimate photochemical products. When sodium tetraphenylborate-d_{20} (**1**) was irradiated in water through which air was bubbled, a mixture containing 80% **2** and 20% **3** resulted. The mass spectrum of the biphenyl (**2**) fraction collected by preparative gas chromatography showed that this fraction contained 75% $C_{12}D_{10}$ (**2**) and 25% $C_{12}D_9H$ (**2**). The mass spectrum of the 1-phenyl-1,4-cyclohexadiene (**3**) fraction showed the presence of only $C_{12}D_{10}H_2$. When an aqueous solution of equal parts of sodium tetraphenylborate (**1**) and sodium tetraphenylborate-d_{20} (**1**) was irradiated in a like manner, the products were 14% **2** and 84% **3**. Mass-spectrometric analysis showed the biphenyl (**2**) fraction to contain $C_{12}H_{10}$, $C_{12}D_{10}$, and $C_{12}D_9H$. The 1-phenyl-1,4-cyclohexadiene fraction contained both $C_{12}H_{12}$ and $C_{12}D_{10}H_2$. There was no evidence of $C_{12}D_5H_5$ (**2**) or of $C_{12}D_5H_7$ (**3**), which indicates that the reaction is essentially intramolecular or occurs within the anion-solvent cage. Only the minutest traces of the products of mixing between **1**-h_{20} and **1**-d_{20} could have been present but masked by fragment ions of the deuterated samples.

The quantum yield of decomposition of sodium tetraphenylborate (**1**) was measured in aqueous solution by use of potassium ferrioxalate actinometry. The extent of photodecomposition was determined by two methods: (1) by titration of the sodium hydroxide generated, and (2) by the carminic acid method. The difficulty of removing a small amount of unreacted **1** makes extreme accuracy hard to attain. The two methods, however, agree within the limits of experimental error. Nine samples analyzed by titration of the generated base gave quantum yields of 0.22 ± 0.03. Twelve samples analyzed by the carminic acid method gave values for the quantum yield of 0.26 ± 0.03.

We have indicated that irradiation of isopropyl alcohol solutions of **1** under an air atmosphere produced terphenyl in addition to **2** and **3**. Under the present aqueous irradiation conditions, the yield of terphenyl (**11**) or precursors has not exceeded 1%. On the basis of our present limited knowledge of the photolysis of sodium tetraarylborates, we are unable to choose between three possible mechanistic routes. These three possibilities, as shown in Chart I, have in common a proposed intermediate (**12**) which makes it possible to explain the formation of the three dienes isolated. Diphenylborinic anion (**4**) leaves the common intermediate (**12**) forming the dienes. Oxygen could penetrate the cage[12] of the triaryl system to lead to the formation of biphenyl (**2**).

Chart I



Experimental Section

The preparation of and gas-chromatographic methods of separating dienes **3**, **5**, and **6** have been described previously.[4] The

---

(11) D. F. DeTar and R. A. Long, *J. Am. Chem. Soc.*, **80**, 4742 (1958).

(12) H. C. Brown and V. H. Dodson, *ibid.*, **79**, 2302 (1957).

irradiations of the alkali metal tetraarylborate were conducted by using the conditions described in Table I, as follows.

Irradiation of Sodium Tetraphenylborate in Water. A typical irradiation was performed by dissolving the desired amount of sodium tetraphenylborate in the desired amount of water, as indicated in Table I. The solution was placed in a double-walled, water-cooled, all-quartz tube, the inside dimensions of which were 1.25 in. by 15 in. The quartz cooling jacket was equipped with a water inlet near the bottom and an outlet at the top. A small, Teflon-covered stirring bar was placed at the bottom of the tube and driven magnetically. The tube was placed at the center of a Rayonet photochemical reactor equipped with 2537-A tubes. If the atmosphere inside the reaction tube was to be controlled, the tube was closed with a large rubber stopper, equipped with a gas inlet tube reaching close to the bottom of the reaction tube, and a short outlet tube. After a few hours of irradiation, sufficient water-insoluble products were formed, as evidenced by the coating on the inside wall of the irradiation tube. The solids were removed mechanically and isolated by filtration. If further irradiation was desired, the clarified solution was returned to the tube and the irradiation continued. The air-dried solid was analyzed by gas chromatography. Analytical samples were collected when desired. The gas-chromatographic separation of these products has previously been described by us.[4]

The unreacted tetraphenylborate anion which was precipitated as the potassium salt by addition of excess potassium chloride was collected by filtration. The filtrate was made acid with 10% hydrochloric acid and extracted with two 50-ml portions of ligroin (bp 35–60°). The combined ligroin solution was dried over $MgSO_4$. Evaporation of the ligroin at room temperature and reduced pressure, followed by evacuation at 0.05 mm, gave diphenylborinic anhydride $(C_6H_5)_2B\text{–}O\text{–}B(C_6H_5)_2$, mp 108–119° (lit. 118°). The infrared spectrum was identical with that of an authentic sample prepared by the method of Neu[13] and Chremos, *et al.*[14] Since diphenylborinic acid and its anhydride decompose rapidly upon isolation and exposure to air, the amount of the salt of **4** formed during the irradiation could be alternatively determined by titrating an aliquot of the irradiation filtrate to pH 5.8 with 0.1 *N* hydrochloric acid. Mercuric chloride was then added to the aliquot, and the hydrochloric acid which was liberated was titrated with 0.1 *N* potassium hydroxide. After the addition of sorbitol, the boric acid complex was titrated with 0.1 *N* KOH to determine the total amount of boron in the solution. The titration was similar to that described by Neu,[13] except that the diphenylborinic acid was not isolated prior to titration.

Dehydrogenation of the Product Mixture from the Irradiation of Lithium Tetra-*p*-tolylborate. An 0.1-g portion of the mixture of bitolyl and the analogous substituted phenylcyclohexadiene obtained from the irradiation of lithium tetra-*p*-tolylborate in water was placed in a long test tube. A few milligrams of 25% palladium on charcoal was added, and the mixture was heated to 160° by means of a metal bath. After 30 min the sublimate on the sides of the tube was removed. It melted at 114–116°. The infrared spectrum was identical with that of an authentic sample of *p*-bitolyl (lit. mp 120°). Gas-chromatographic examination of the sublimed material revealed only one component, *p*-bitolyl.

Sodium Tetra-*p*-tolylborate. A 250-ml pressure-equalized dropping funnel equipped with a double-neck adapter carrying a stirrer and a reflux condenser was fitted to a two-necked 500-ml flask. The flask was equipped with a magnetic stirring bar and a nitrogen inlet tube. After the system had been flame-dried and flushed with nitrogen, boron trifluoride etherate (4.2 g) was added to the flask. Dry ether (100 ml) was added to *p*-bromotoluene (30 g) in the dropping funnel. An equivalent quantity of titrated *n*-butyllithium[9] in pentane solution (Arapahoe Chemicals) was added and the mixture stirred for 10 min. The resulting solution of *p*-tolyllithium was then added, dropwise, to the stirred boron trifluoride etherate solution while the whole was heated gently. The addition was continued until the Gilman test,[15] indicating the presence of excess aryllithium, was positive for 15 min. The suspension was then poured into water (300 ml) and the mixture extracted with two 500-ml portions of ligroin. The aqueous layer was separated and treated with solid sodium chloride until no additional white fluffy material was precipitated. The white solid material was isolated by filtration, washed with a small amount of water, and dried overnight *in vacuo* to yield 12 g of the crude sodium salt. The crude material (3.0 g) in chloroform (60 ml) was treated with 1,2-dimethoxyethane (6 ml) and the suspension cooled to −20°, with stirring. The cooled solution was filtered to remove traces of impurities and gently warmed to boiling, at which point the pure sodium tetra-*p*-tolylborate precipitated as white needles (2.2 g).

Anal. Calcd for $C_{28}H_{28}BNa$: C, 84.4; H, 7.1; B, 2.7. Found: C, 84.6; H, 7.3; B, 2.5.

Sodium Tetraphenylborate-d_{20}. Bromobenzene-d_5 was prepared by bromination of benzene-d_6.[16] Two distillations yielded a fraction with bp 156–158°. Mass-spectrometric analysis indicated that this material was at least 97% C_6D_5Br. The bromobenzene-d_5 was converted to the sodium tetraphenylborate-d_{20} by the method of Wittig and Raff.[10] The crude sodium salt was purified by the method employing the inverse solubility in chloroform–dimethoxyethane, as already described for sodium tetra-*p*-tolylborate.

Quantum Yield of Sodium Tetraphenylborate. The quantum yield of decomposition of sodium tetraphenylborate in aqueous solution was measured by comparing the extent of reaction to that of a potassium ferrioxalate actinometer solution.[17] Aqueous solutions of **1** were exposed to a compressed-spiral, Hanovia quartz-envelope, mercury resonance lamp. The cell containing the solution was held at a distance of 2$^1/_8$ in. from the lamp by a thin sheet of silica glass. A shutter was placed between the lamp and the cell. The solution was contained in a 1-cm spectrophotometer cell, the capacity of which was 3 ml. The light was not filtered by any means other than the air and the quartz equipment. Therefore, the output of the lamp as measured by the actinometer solution included all the light absorbed by the actinometer (200 to 590 mμ). The sodium tetraphenylborate solution absorbs principally longer wavelength light at the 2537-A mercury line and no light of longer wavelength than 290 mμ. The error can be calculated from the known output of the lamp and the known quantum yields of the actinometer at longer wavelengths. Since the output of the lamp is principally light of 1849 A (which is absorbed by the air and the quartz equipment) and 2537 A, the error amounted to no more than 3%. Fifteen exposures of 6×10^{-3} *M* solutions of a potassium ferrioxalate actinometer in water for periods of time ranging from 5 to 150 sec gave an average of 2.7×10^{16} atoms of Fe^{2+} produced per second. The accepted value of the quantum yield of the actinometer at 2537 A is 1.25; therefore, the output of the lamp is 2.2×10^{16} quanta/sec. Portions (3 ml) of sodium tetraphenylborate solutions of known concentrations between 0.1 and 0.01 *M* were irradiated for periods of time ranging from 4 to 7 min. The cell was turned and shaken periodically during the irradiation to keep the contents as homogeneous as possible. Two methods of analyses for the amount of reaction were used. In both cases the unreacted tetraphenylborate anion was precipitated by adding excess potassium chloride.

The first method employed to determine the amount of reaction required the titration of the diphenylborinic acid formed. The precipitated potassium tetraphenylborate and any insoluble reaction products were first removed by gravity filtration. The filtrate was titrated to a pH of 5.80 with 0.001 *N* HCl in the manner reported by Neu.[13] Excess solid mercuric chloride was added and hydrochloric acid liberated was titrated to pH 5.80 with 0.001 *N* KOH. Excess sorbitol was then added to complex the boric acid, and the complex was titrated with 0.001 *N* KOH. At the low borate concentrations involved, the phenylmercuric chloride that was formed after the addition of mercuric chloride did not immediately precipitate since the reaction tended to reach an equilibrium state. When the sorbitol was added, however, the mercuric chloride reaction was driven to completion. The total base used was equal to three times the number of moles of diphenylborinic acid, despite the fact that the two titrations rarely gave the proportions of 2:1, as expected by the stoichiometry of the two reactions.

Because of the difficulties involved in this determination of boron, a second method was employed. After irradiation, the contents of the cell were emptied into a centrifuge tube and the total volume was adjusted to 5 ml. After excess potassium chloride had been added, the solution was stirred and centrifuged. An unirradiated sample was prepared and treated in the same manner. A 2-ml

---

(13) R. Neu, *Chem. Ber.*, **87**, 802 (1954).

(14) G. N. Chremos, H. Neidmann, and H. K. Zimmerman, *J. Org. Chem.*, **26**, 1683 (1961).

(15) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(16) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Longmans Green and Co., London, 1961, p 535.

(17) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 783.

portion of the clear liquid from each sample was removed and the boron determined by the carminic acid method.[18]

Nine samples analyzed by titration gave a value of quantum yield of decomposition of 0.22 ± 0.03. Twelve samples analyzed by the carminic acid method gave values of 0.26 ± 0.03. The difficulties involved in removing the small amount of reacted material from the unreacted material and of accurately determining such small amounts of boron make a more accurate quantum yield determination very hard to obtain. Both methods agree within the limits of experimental error.

Mass Spectra. The mass spectra were obtained by using either a 60° sector-type mass spectrometer, or a Consolidated Electrodynamics Model 21-110B mass spectrometer. In either case, all samples were introduced *via* an all-glass inlet system operated at 230°. Exact mass determinations were made by electrical peak matching with the Consolidated Model 21-110B instrument.

---

(18) G. Charlot, "Colorimetric Determination of Elements," Elsevier Publishing Co., New York, N. Y., 1964, p 194.

Pentacoordinate Silicon. The Crystal Structure of Dimethylsilylamine Pentamer[1a,b]

Reuben Rudman,[2a] Walter C. Hamilton,[2a] Stewart Novick,[2b] and Theodore D. Goldfarb[2b]

Contribution from the Departments of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, and State University of New York at Stony Brook, Stony Brook, New York 11790. *Received April 19, 1967*

Abstract: X-Ray diffraction crystal-structure analysis of dimethylsilylamine (DMSA) at −120° reveals that the unusual physical characteristics of this compound are due to the formation of ten-membered, nearly planar rings of alternating silicon and nitrogen atoms. Each silicon is pentacoordinated in a trigonal bipyramidal arrangement with two long Si–N bonds (of the order of 1.95 A) in the apical directions and three hydrogen atoms at the corners of the triangular base. DMSA crystallizes in the monoclinic system, space group $P2_1/m$ (C_{2h}^2), a = 6.37 A, b = 19.53 A, c = 9.52 A, and β = 91.06°; there are ten formula units (two pentamers) per unit cell.

In 1954, Sujishi and Witz[3] demonstrated that dimethylsilylamine (DMSA) differs considerably from other silylamine compounds. It was found that DMSA melts at +3°, more than 100° higher than trisilylamine and methyldisilylamine, and that it has an appreciably higher ΔH of sublimation. Recently it was shown that the infrared absorption spectrum of crystalline DMSA differs radically from that of the gas phase.[4] These data were interpreted as indicating intermolecular association (of an unknown number of DMSA units) involving the nonbonding electrons on the nitrogen atom of one DMSA molecule and an empty silicon d orbital on an adjacent molecule. The present investigation was undertaken in an attempt to determine the crystal and molecular structure of crystalline DMSA.

The crystal data for $H_3SiN(CH_3)_2$ (mol wt 75.19) are: monoclinic, probable space group $P2_1/m(C_{2h}^2)$; a = 6.37 ± 0.3 A, b = 19.53 ± 0.10 A, c = 9.52 ± 0.05 A, β = 91.06 ± 0.10°; X-ray density = 1.054 g/cc for ten formula units/unit cell.

Experimental Section

DMSA was synthesized and purified according to the procedures described by Sujishi and Witz.[3] A small amount of material was condensed in an evacuated, thin-walled quartz tube of 0.3-mm diameter which was sealed and mounted on a precession camera. It was found that the presence of any impurities hindered single-crystal formation. Single crystals were grown from freshly purified samples using standard low-temperature X-ray diffraction techniques, and data were collected at −120°.

Zr-filtered Mo Kα radiation was used to investigate 12 reciprocal lattice layers (hkL, L = 0–4; hKl, K = 0–5; and hkk). The intensities were obtained by visually comparing the spots on the film with a standard intensity strip. All data processing was done with local versions of standard crystallographic computer programs. Lorentz polarization factors were applied; the data were scaled using the Hamilton, Rollett, and Sparks algorithm for interlayer scaling;[5] the over-all temperature factor and absolute scale factor were calculated; and E factors (normalized structure factors) were obtained.

The only systematically absent reflections were $0k0$, k odd, and the space group could be either $P2_1$ (C_2^2) or $P2_1/m$ (C_{2h}^2). Examination of the E factors indicated that the most probable space group is the centrosymmetric $P2_1/m$ (see below); this was subsequently verified by the structure determination.

	Theoretical[6] Centrosymmetric	Theoretical[6] Acentric	This investigation
$<\lvert E\rvert>$	0.798	0.886	0.66
$<\lvert E^2-1\rvert>$	0.968	0.736	1.01

The signs of the observed structure factors were determined using SORTE,[7] a computer program employing the Symbolic Addi-

---

(1) (a) Research performed under the auspices of the U. S. Atomic Energy Commission; supported in part by the U. S. Air Force Office of Scientific Research under Grants AFOSR 277-63 and AFOSR 837-65. (b) A preliminary report was presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

(2) (a) Brookhaven National Laboratory; (b) State University of New York at Stony Brook.

(3) S. Sujishi and S. Witz, *J. Am. Chem. Soc.*, **76**, 4631 (1954).

(4) T. D. Goldfarb and B. N. Khare, *J. Chem. Phys.*, **46**, 3384 (1967).

(5) W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, **18**, 129 (1965).

(6) I. L. Karle and K. Britts, *ibid.*, **21**, 532 (1966).

(7) Y. Okaya and A. L. Bednowitz, *ibid.*, **22**, 111 (1967).