Boron Photochemistry. II. Irradiation of Sodium Tetraarylborates in Alcohol Solutions

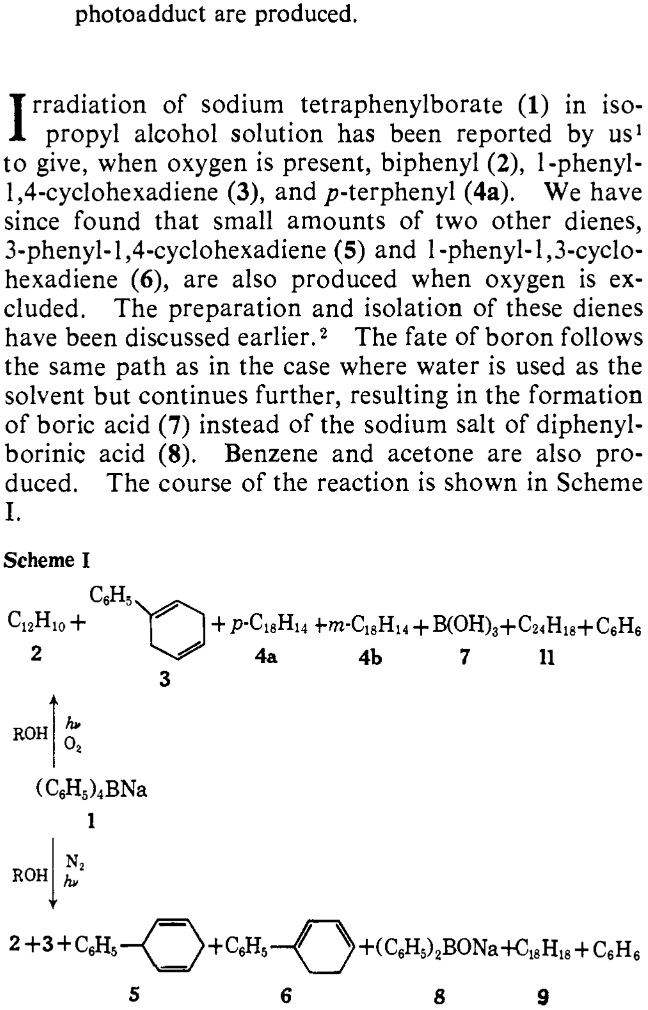
J. L. R. Williams, J. C. Doty, P. J. Grisdale, T. H. Regan, G. P. Happ, and D. P. Maier

Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. *Received June 23, 1967*

Abstract: Photolysis of sodium tetraphenylborate and related tetraarylborates has been conducted in methyl, ethyl, isopropyl, and *t*-butyl alcohol solutions. In all the alcohols thus far tested as solvents, photolysis of sodium tetraphenylborate in the presence of air yields biphenyl as the major product. The abundance of biphenyl depends on the amount of oxygen present and on the irradiation time. In addition, irradiation of sodium tetraphenylborate in ethyl, isopropyl, or *t*-butyl alcohol solution produces various amounts of *p*-terphenyl and *m*-terphenyl as follows: *t*-butyl > isopropyl > ethyl alcohol. It has been shown that the biphenyl and terphenyl are produced by intramolecular reaction around the boron atom of the tetraarylborate anion. In methyl, ethyl, and isopropyl alcohol solutions under a nitrogen atmosphere, the products are biphenyl, 1-phenyl-1,4-cyclohexadiene, 3-phenyl-1,4-cyclohexadiene, 1-phenyl-1,3-cyclohexadiene, and at least three isomeric diphenylhexadienes. In methyl and ethyl alcohols, the corresponding photoadducts 1-phenyl-1-alkoxy-2-cyclohexenes are isolated in addition to the products mentioned. In *t*-butyl alcohol, neither the diphenylhexadienes nor the corresponding *t*-butoxy photoadduct are produced.

Irradiation of sodium tetraphenylborate (**1**) in isopropyl alcohol solution has been reported by us[1] to give, when oxygen is present, biphenyl (**2**), 1-phenyl-1,4-cyclohexadiene (**3**), and *p*-terphenyl (**4a**). We have since found that small amounts of two other dienes, 3-phenyl-1,4-cyclohexadiene (**5**) and 1-phenyl-1,3-cyclohexadiene (**6**), are also produced when oxygen is excluded. The preparation and isolation of these dienes have been discussed earlier.[2] The fate of boron follows the same path as in the case where water is used as the solvent but continues further, resulting in the formation of boric acid (**7**) instead of the sodium salt of diphenylborinic acid (**8**). Benzene and acetone are also produced. The course of the reaction is shown in Scheme I.

Scheme I



We have not preparatively investigated products occurring in amounts of less than 1% of the total isolatable hydrocarbon materials. However, when the untreated hydrocarbon products from an isopropyl alcohol irradiation mixture of **1** were subjected to mass spectrometric analysis, the mass spectrum of the crude mixture consisted of masses corresponding to biphenyl (**2**) and its reduction products (**3**, **5**, and **6**) and terphenyls (**4a**, **4b**). In addition, peaks associated with quaterphenyl (**11**) and one of its dihydro derivatives were observed. We have shown[3] that the photochemical transformation of **1** to form **2** and **3** in aqueous solution involves an intramolecular phenylation reaction around the boron atom of **1**. Such is also the case when the terphenyls (**4a**, **4b**) are formed. This fact has been established by mass spectrometric analysis of the gas chromatographic zones from the reaction product of the aerobic irradiation of an equimolar mixture of **1** and **1**-d_{20} in isopropyl alcohol. The **4a**–**4b** fraction isolated consists uniquely of molecular species corresponding to $C_{18}H_{14}$, $C_{18}D_{14}$, and $C_{18}D_{13}H$. The **2** isolated from the same photolysis mixture corresponded to $C_{12}H_{10}$, $C_{12}D_{10}$, and $C_{12}D_9H$. The formation of biphenyl (**2**), the dienes (**3**, **5**, **6**), and the terphenyl fraction (**4a**, **4b**) proceed by an *intramolecular reaction around the boron atom of the "ate" complex.*

Mass spectrometry indicates approximately 1 part of quaterphenyl (**11**) per 3000 parts of **3** in the photolysis mixture. Up to the present time the photolysis of **1** has not produced sufficient yields of quaterphenyl (**11**) for isolation. The possibility of the presence of phenyl radicals in the photolysis mixture cannot be ignored, since varying amounts of benzene are formed during the irradiation of **1**. Thus, either the phenyl radicals resulting from excitation of diphenylborinic acid (**8**) or those formed by excitation of the photochemically produced benzene molecules from **8** could attack *p*-terphenyl (**4a**) to form **11** when oxygen is present. With a limited oxygen supply, a dihydro derivative of **11** also results.

We have shown that *coupling between the first two phenyl rings occurs at the same carbons of the phenyl rings which were originally bonded to boron in* **1**. Irradiation of sodium tetra-*p*-tolylborate (**12**) in isopropyl alcohol solution under an air atmosphere has

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

(2) P. J. Grisdale, J. C. Doty, T. H. Regan, and J. L. R. Williams, *J. Org. Chem.*, in press.

(3) J. L. R. Williams, J. C. Doty, P. J. Grisdale, T. H. Regan, G. P. Happ, and D. P. Maier, *J. Am. Chem. Soc.*, **89**, 5153 (1967).

yielded *p*-bitolyl (**13**). Furthermore, the same sort of *para*-position coupling occurs when lithium or sodium tetra-*p*-tolylborates (**14**, **12**) are irradiated in water.[3] To investigate further the position of coupling and the possibility of species mixing during coupling, particularly in the terphenyl series, we irradiated an equimolar mixture of **1** and **12** in isopropyl alcohol. The products were 38% **2**, 11% (**4a**), and 51% *p*-bitolyl (**13**). Neither *p*-methylbiphenyl nor a methylterphenyl was detected by gas chromatographic analysis.

Irradiation of **1** in methyl alcohol solution in the presence of air produces biphenyl (**2**) and traces of 1-phenyl-1,4-cyclohexadiene (**3**). No terphenyl is produced. In ethyl alcohol solution under the same conditions, biphenyl (**2**) prevails but with yields of 3–4% of *p*- and *m*-terphenyls (**4a** and **b**). Isopropyl alcohol directs the photolysis to formation of biphenyl and *p*-terphenyl (**4a**) under the same conditions. In *t*-butyl alcohol, the yield of biphenyl (**2**) drops in favor of larger amounts of *p*-terphenyl as well as 8.5–12.5% of a dihydroterphenyl in the products. In all cases, quaterphenyl is detected by mass spectrometric analysis. No *o*-terphenyl has been found to be present in any of the photolysis mixtures.

The various products cited were isolated, with the exception of quaterphenyl (**11**), by preparative gas chromatography. Mass spectrometric analysis of the crude photolysis mixtures obtained in the presence of air in alcohol resulted in the finding of *m/e* values corresponding to the following compounds which appear in amounts of less than 1%: phenol, a hydroxybiphenyl, and a hydroxyterphenyl. Subsequently, small zones corresponding to these products have been found in the gas chromatograms of the aerobic alcohol photolysis mixtures.

Under a nitrogen atmosphere, or in a degassed system, the photochemical products in isopropyl alcohol solution were **2**, **3**, **5**, **6**, and a $C_{18}H_{18}$ fraction (**9**). The mass spectrum of this fraction showed an ion peak at *m/e* 234, assigned to the molecular ion of $C_{18}H_{18}$. When the total reaction products obtained under nitrogen were subjected to gas chromatography, fraction **9** appeared as a group of zones of much longer retention times than the zones of **2** and **3**. In fraction **9**, the major component was **10**, a $C_{18}H_{18}$ compound which can comprise as much as 25% of the total photolysis product. The remaining zones of fraction **9** appeared as satellites to **10**. Four zones of fraction **9** were isolated by preparative gas chromatography and also showed mass spectral peaks at *m/e* 234, as molecular ions, with fragmentation patterns consistent with the presence of a mixture of $C_{18}H_{18}$ isomers.

Our earlier work[1,3] dealing with the photolysis of **1** in water demonstrated the production of the four products **2**, **3**, **5**, and **6**, which, when submitted *in toto* to gas chromatographic analysis, yielded zones which had retention times appearing as a group of satellites around the main zone of **3**. We were not surprised therefore that the next higher phenylog (**10**) should appear as one of a group of satellites in fraction **9**.

These results dealing with terphenyls prompted us to consider first that the fraction **9**, which contained **10** as the principal constituent, was composed of tetrahydroterphenyls ($C_{18}H_{18}$ or *m/e* 234). The ultraviolet spectra and retention times of the zones of **9** isolated by preparative gas chromatography were inconsistent with those of known samples of tetrahydroterphenyls. A total photolysis mixture resulting from the irradiation of **1** in isopropyl alcohol in the absence of oxygen was subjected to dehydrogenation conditions. After treatment in boiling *p*-cymene with palladium-on-charcoal catalyst, the following products were obtained: phenylcyclohexane (**15**), biphenyl (**2**), and hydrogenated derivatives of fraction **9**, **16** (*m/e* 236), and **17** (*m/e* 238). Furthermore, when the same photolysis mixture was subjected to catalytic hydrogenation at a pressure of 40 psi of hydrogen in the presence of a palladium-on-charcoal catalyst, the products were the same: **15** **2**, **16** (minor), and **17**. The similar behavior of the photolysis mixture toward hydrogenation and dehydrogenation conditions was surprising. The ultraviolet absorption spectra of the zones so produced (which were isolated by preparative gas chromatography) were inconsistent with the spectra of hexahydro- (*m/e* 236) and octahydroterphenyls (*m/e* 238). Furthermore, the mass spectrometric fragmentation patterns of the various components of fraction **9** were very similar, indicating that the structures of various zones had much in common. The samples of zone **9** showed, in common, a molecular ion peak at *m/e* 234 and a peak of M − 91 (*m/e* 143). The loss of the 91 fragment suggested the existence of at least one benzylic residue in all of the similar structures of the components of fraction **9**. The ultraviolet absorption spectra, together with nmr and mass spectrometric data, indicated the existence of a series of diphenylhexadienyl structures for the various fractions. We therefore envisaged *that the ring-opened compounds (fraction* **9**) *consisted of a mixture of cis–trans and bond isomers of diphenylhexadiene* (**10**). When a sample of 1,6-diphenylhexatriene (**19**) was hydrogenated over palladium on carbon, the product was 1,6-diphenylhexane (**20**), the retention time of which was identical with the retention time of **17** (*m/e* 238). Furthermore, the nmr spectra, mass spectrometric fragmentation patterns, and the infrared absorption spectra of **17** and **20** were identical. We are continuing the investigation in detail of the nature of fraction **9**, the results of which will form a later communication.

When we irradiated methanol solutions of **1** under a nitrogen atmosphere, *photoaddition of the alcohol occurred.* The photoadduct, 1-phenyl-1-methoxy-2-cyclohexene (**21**), was formed in addition to **2**, **3**, **5**, **6**, and fraction **9**. Under similar conditions in ethyl alcohol, the analogous addition product was 1-phenyl-1-ethoxy-2-cyclohexene (**22**). To date, the analogous compounds have not been found in isopropyl or *t*-butyl alcohol irradiation mixtures of **1**. The photoaddition of alcohols to diene systems has already been reported for cholestadiene derivatives.[4,5]

More closely related to our system is the report of addition of alcohols to 1-ethyl-1,4-cyclohexadiene[6] and addition of alcohols to 1-menthene.[7]

Samples of the two 1-phenyl-1-alkoxy-2-cyclohexenes (**21** and **22**) were isolated by preparative gas chromatography and their structures determined by nmr,

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(4) W. G. Dauben and F. G. Wiley, *Tetrahedron Letters*, 893 (1962).

(5) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

(6) P. J. Krupp, *J. Am. Chem. Soc.*, **88**, 4091 (1966).

(7) J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966).

infrared, and high-resolution mass spectrometric techniques. If the irradiation of **1** is conducted in the presence of air, neither **21** nor **22** is produced.

Irradiation of solutions of **1** in *t*-butyl alcohol under a nitrogen atmosphere led to a mixture of 20% biphenyl (**2**) and 80% 1-phenyl-1,4-cyclohexadiene (**3**). No products corresponding to addition of *t*-butyl alcohol to the phenylcyclohexadienes nor formation of fraction **9** were detected by gas chromatographic or mass spectrometric analysis.

A rigorously degassed solution of **1** in isopropyl alcohol was irradiated by using a quartz–mercury resonance lamp to a conversion of 20%. It is of interest to note that, despite the absence of oxygen, a mixture as rich as 21% in biphenyl (**2**) and as low as 57% in 1-phenyl-1,4-cyclohexadiene (**3**) resulted. A comparable irradiation conducted to 95% conversion, made with nitrogen bubbling through the mixture, with a Rayonet 2537 apparatus, yielded 19% of **2** and 15% of **3**. In the two runs, the yields of fraction **9** were 14 and 55%, respectively. We are further investigating the role of the hydrogen-transfer pair, isopropyl alcohol–acetone, in this system.

Experimental Section

Irradiation and Analytical Procedure. In general, the irradiation techniques, ultraviolet, infrared, nmr, and mass spectrometric methods were the same as those described previously.[2,3] All irradiations, except where otherwise noted, were conducted by using a Rayonet 2537 apparatus. A summary of the irradiation conditions used for the various runs is given later in the paper. The isolation and identification of the longer retention time components of the various irradiation mixtures were carried out in a manner analogous to that previously described[2,8] but at higher column temperatures. Isolation of products occurring in amounts of less than 1% has been thus far neglected. Following is the sequence of appearance of the various zones when a typical methyl alcohol photolysis mixture was analyzed by means of an F and M Model 720 gas chromatograph equipped with 20% SE 30 on Anakrom ABS column: **5**, **2**, **6**, **3**, **21**, and **9**. Any modifications of the general procedure are noted.

Modified Procedure for the Photolysis of 1 in *t*-Butyl Alcohol. A solution of 10 g of **1** in 250 ml of *t*-butyl alcohol was irradiated under a nitrogen atmosphere for 24 hr. The photolysis mixture was concentrated at reduced pressure to a volume of 150 ml and then diluted with 250 ml of water. The resulting mixture was cooled to 10°, and the solids were separated and dried. Gas chromatographic analysis of the solid (1.4 g) showed it to contain 20% biphenyl (**2**) and 80% 1-phenyl-1,4-cyclohexadiene (**3**). There were no other products. The filtrate was treated with excess potassium chloride solution and the potassium tetraphenylborate collected and dried (7.1 g; photolysis conversion, 29%). Thus 8.5×10^{-3} mole of **1** was photolyzed to yield 8.4×10^{-3} mole of hydrocarbon products (99% yield).

Irradiation of a Degassed Solution of Sodium Tetraphenylborate (1) in Isopropyl Alcohol. A solution of 5.0 g (1.47×10^{-2} mole) of sodium tetraphenylborate (**1**) in 100 ml of isopropyl alcohol was placed in a quartz ampoule which was equipped with a Pyrex–quartz graded seal. The solution was freeze-degassed three times, after which time the ampoule was sealed. The ampoule was placed in a thermostated water bath at a distance of 5 cm from a Hanovia quartz–mercury resonance lamp. Irradiation was conducted at 8–10° for 8 hr, during which time the ampoule was shaken periodically. The contents of the ampoule were then evaporated at reduced pressure in such a manner that the volatiles were trapped. Benzene was detected in the distillate by means of its ultraviolet absorption spectrum. The residue was stirred with 100 ml of ice water, and the resulting solids were collected by filtration (dry weight 0.45 g). Gas chromatographic analysis of the solid showed it to be composed of 2% of **5**, 21% of **2**, 6% of **6**, 57% of **3**, and 14% of **9**. The aqueous filtrate was treated with excess potassium chloride and the resulting potassium tetraphenylborate collected (dry weight 4.2 g, 1.17×10^{-2} mole). The filtrate was titrated for phenyl groups and boron according to the scheme previously described[3] and was thus shown to contain 3×10^{-3} mole of both sodium ion (as sodium hydroxide) and boron, as well as the presence of 4.7×10^{-3} mole of phenyl groups. The phenyl groups not remaining on the boron and not recovered as the potassium salt of **7** can be accounted for by the benzene and **9**.

Irradiation of Sodium Tetraphenylborate (1) and Sodium Tetraphenylborate (1-d_{20}) in Ethanol. A solution of 2.9×10^{-3} mole of 1-d_{20} in 250 ml of ethanol was irradiated for 5 hr (air). The product mixture (0.65 g) consisted of 78% of **2**, 8.7% of **4a**, 12.2% of **4b**, and 1% of **5**. The conversion based on recovered tetraphenylborate was 88%.

Irradiation of Sodium Tetra-*p*-tolylborate (12) in Isopropyl Alcohol. A solution of 1.2×10^{-2} mole of **12** in 200 ml of isopropyl alcohol was irradiated under an air atmosphere for 6 hr. The product was *p*-bitolyl. The conversion was 100%.

Irradiation of Sodium Tetraphenylborate (1) and Sodium Tetra-*p*-tolylborate (12) in Isopropyl Alcohol. A solution of 2.9×10^{-3} mole of **1** and 2.9×10^{-3} mole of **12** in 200 ml of isopropyl alcohol was irradiated under an air atmosphere during 17 hr to a conversion of 100%. The product consisted of 38% of **2**, 11% of **4a**, and 51% of *p*-bitolyl.

Irradiation of 1.48×10^{-3} *M* Solutions of Sodium Tetraphenylborate (1) in Various Alcohols (250 ml). For the following alcohols at the noted irradiation times[8] and atmosphere,[8] the per cent conversion,[9] yield of organic product (g),[10] and per cent products are given.

Methyl Alcohol. 5 hr, N_2, 65%, 1.05 g: **2**, 20%; **3**, 59%; **5**, 8%; **9**, 1%; **21**, 12%. 15 hr, N_2, 95%, 2.1 g: **2**, 30%; **3**, 21%; **5**, 30%; **9**, 5%; **21**, 13%. 5 hr, air, 79%, 1.3 g: **2**, 97%. 15 hr, air, 93%, 1.8 g: **2**, 97%; **3**, 1%; **5**, 1%; **6**, 1%.

Ethyl Alcohol. 5 hr, N_2, 63%, 1.25 g: **2**, 12%; **3**, 58%; **5**, 5%; **6**, 1%; **9**, 18%; **22**, 2%. 15 hr, N_2, 95%, 2.1 g: **2**, 21%, **3**, 24%; **5**, 19%; **9**, 33%; **22**, 3%: 5 hr, air, 95%, 1.78 g: **2**, 93%; **4a**, 3%, **4b**, 2%.

Isopropyl Alcohol. 5 hr, N_2, 54%, 0.5 g: **2**, %; **3**, %; **5**, %; **9**, %. 15 hr, N_2, 95%, 1.7 g: **2**, 19%; **3**, 15%; **5**, 4%; **6**, 3%; **9**, 55%. 5 hr, air, 55%, 0.73 g: **2**, 88%; **4**, 12%. 15 hr, air, 93%, 1.5 g: **2**, 83%; **4a**, 16%; **4b**, 1%.

t-Butyl Alcohol. 24 hr, N_2, 29%, 0.2 g: **2**, 20%; **3**, 80%. 5 hr, air, 33%, 0.4 g: **2**, 68%; **3**, 6%; **4a**, 16%; **4c**, 8.3%. 15 hr,[11] air, 75%, 0.9 g: **2**, 49%; **3**, 3%; **4a**, 31%; **4b**, 1%; **4c**, 12.5%.

Structure Determination of Alcohol Adducts 21 and 22. The nmr spectrum of **21** in CCl_4 solution has absorptions at δ 7.0–7.4 (5 H, aromatic), 5.67 (m, olefinic, 2 H), 2.95 (s, 3 H, OCH_3), 2.43 (m, 2 H, allylic), 1.93 (m, 4 H, cycloaliphatic). The presence of two olefinic hydrogens coupled with the absence of a signal for –C(–O)H requires the phenyl and methoxyl to be *gem* substituted. The presence of only two allylic hydrogens locates the double bond adjacent to the tetrasubstituted carbon. Assignment of 1-phenyl-1-methoxy-2-cyclohexene as the structure of **21** is consistent with these data.

The ethanol adduct, **22**, has an exactly analogous nmr spectrum: δ 7.1–7.4 (m, 5 H, aromatic), 5.67 (m, 2 H, olefinic), 3.12 (m, 2 H, OCH_2), 2.45 (m, 2 H, allylic), 1.95 (m, 4 H, cycloaliphatic), 1.07 (t, 3 H, O–C–CH_3). The O–CH_2 absorption is complex since the ethoxyl is substituted on an asymmetric carbon and the two hydrogens are nonequivalent. Assignment of 1-phenyl-1-methoxy-2-cyclohexene as the structure of **22** is consistent with these data.

The adducts **22** and **23** were subjected to high-resolution mass spectrometry. Exact mass measurement produced the following results: Calcd for $C_{13}H_{16}O$ (**22**): *m/e* 188.1201. Found: *m/e* 188.1200. Calcd for $C_{14}H_{18}O$ (**23**): *m/e* 202.1358. Found: *m/e* 202.1365.

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(8) The appropriate gas was bubbled through the photolysis for 15 min prior to and during the irradiation period.

(9) The conversion is based on recovered tetraphenylborate, as the potassium salt.

(10) The yield is reported as grams of nonboron-containing organic products.

(11) 2.94×10^{-3} mole of 1.