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BORON PHOTOCHEMISTRY
III. PHOTOLYSIS OF SOME NAPHTHALENE-SUBSTITUTED BORATE COMPLEXES

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SUMMARY

The photolysis of two naphthalene-substituted "ate" complexes, lithium tetra-2-naphthylborate and lithium phenyltri-1-naphthylborate, has been carried out in the presence and absence of air. In both cases in the absence of air, the products are dihydrobiaryls, biaryls and diarylborinic acids. Air eliminates the dihydro derivatives to provide the biaryls and naphthols which result at the expense of the diarylborinic acids. The absence of biphenyl and phenylcyclohexadienes in the photolysis product of lithium phenyltri-1-naphthylborate indicates that the photolysis is intramolecular.

INTRODUCTION

We have previously described[1,2] the role of boron during photolysis of aqueous and alcoholic solutions of sodium tetraphenylborate (1). In the absence of oxygen the products were biphenyl (2) and a mixture of three dienes: 1-phenyl-1,4-cyclohexadiene (3), 1-phenyl-2,4-cyclohexadiene (4), 1-phenyl-1,3-cyclohexadiene (5). The major product was (3). In the presence of oxygen biphenyl (2), *m*-terphenyl (6), *p*-terphenyl (7) and small amounts of 3 were the products. According to a general mechanism which we outlined[1], formation of the dienes (3)–(5) and biphenyl (2) takes place when a phenyl group migrates from boron to an adjacent phenyl ring. The phenyl groups unite by formation of a bond between the carbons which were originally attached to boron. Thus, it was apparent that the boron atom in (1) controls the migration of the phenyl group. Such is also the case when the terphenyls (6 and 7) are formed in the presence of oxygen[2]. The photochemical reactions taking place at the boron atom in sodium tetraphenylborate (1) are intramolecular.

It was of interest to determine the scope of photochemical reaction which takes place when tetraarylborates are irradiated.

We find it of particular interest to vary the nature of the groups which can be caused to leave boron under the action of light. The boron atom retains control over the migration of the aryl groups since we have shown the reactions to be intramolecular[1,2]. Thus, by varying the aryl substituents on boron in tetraarylborates, it is possible to study both the tendency of groups to leave as well as the degree of control exerted on the same leaving groups by boron. We now wish to report the nature of the products which result when naphthalene substituted "ate" complexes are irradiated under the conditions previously described[1,2]. As in our previous communications, the products were characterized by means of zones isolated by preparative gas chromatography (SE-30 column). The isolated samples were submitted to UV and mass-spectrometric analysis.

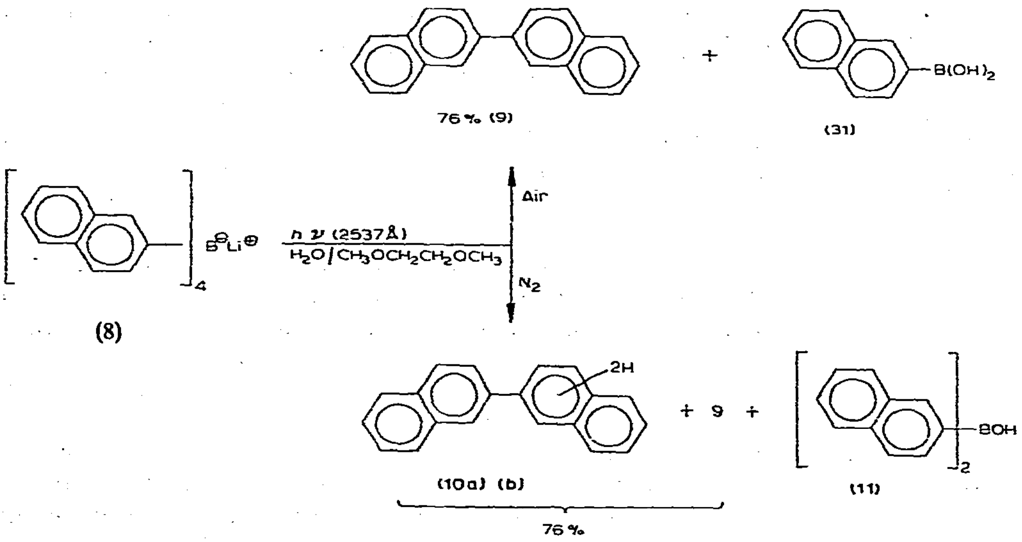
Since lithium tetra-2-naphthylborate (**8**) has not been previously reported, its synthesis was carried out according to the general method described by Wittig and Raff[3].

RESULTS AND DISCUSSION

In the absence of oxygen the course of the photolysis of solutions of (**8**) follows the same path as that described for (**1**). The products are a biaryl and the corresponding dihydro biaryls. Thus, 2,2′-binaphthyl (**9**) and two dihydro-2,2′-binaphthyl derivatives (**10a**) and (**10b**) are the photochemical products. Separation of 2,2′-binaphthyl (**9**) from the dihydro derivatives (**10a**) and (**10b**) is difficult since the high column temperature (270–300°) of the gas chromatograph leads to dehydrogenation of (**10a**) and (**10b**). By reinjection of collected zones the percent composition becomes richer in 2,2′-binaphthyl.

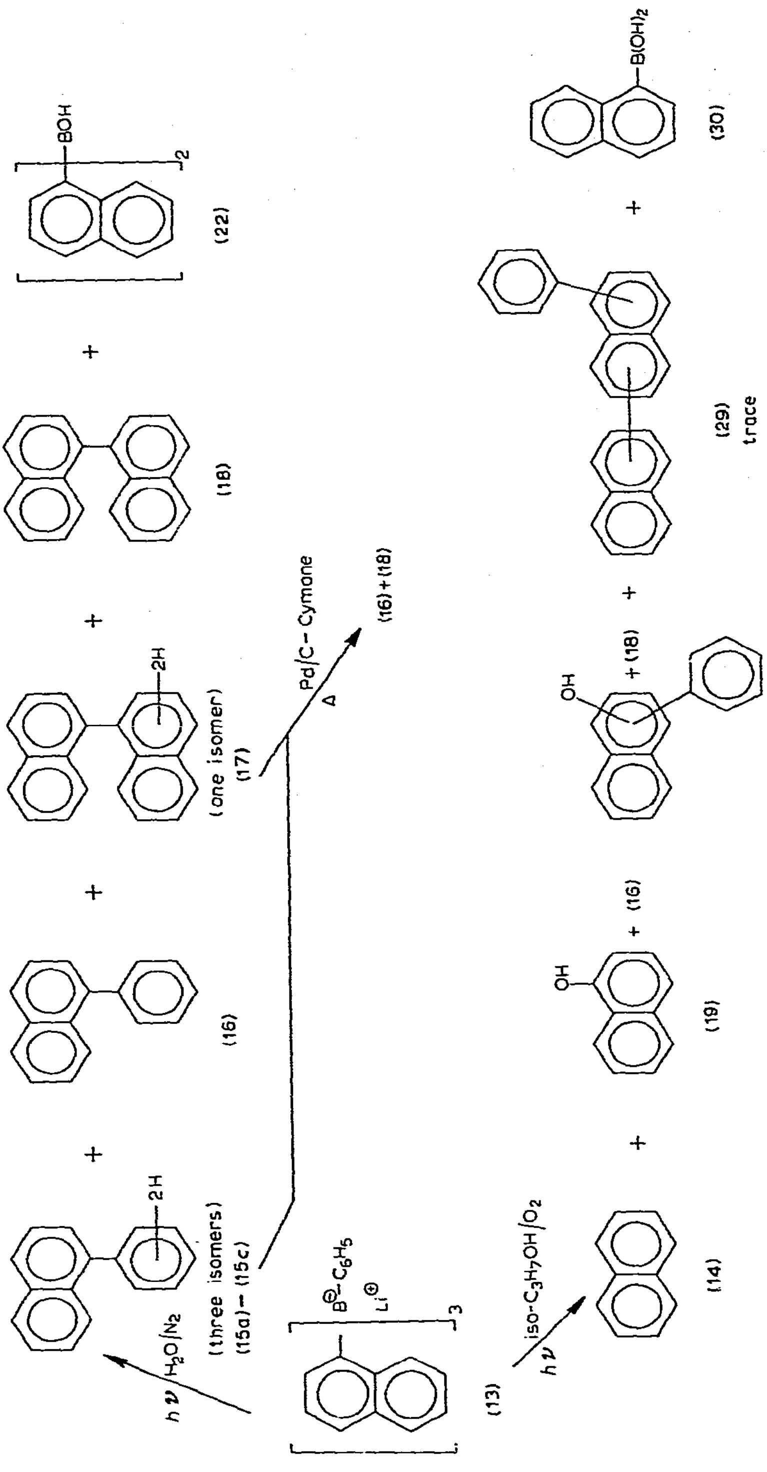
It was thus difficult to characterize the dihydro derivatives (**10a**) and (**10b**) by means other than mass spectrometry. The di-2-naphthylborinic acid (**11**) produced was isolated as its ethanolamine complex (**12**). In the presence of oxygen the photolysis of (**8**) leads to exclusive formation of (**9**). The yield of the hydrocarbon products is 76% in both cases.

CHART 1



We have not been able to synthesize the corresponding lithium tetra-1-naphthylborate. This failure is attributed to the high degree of steric interference

CHART 2

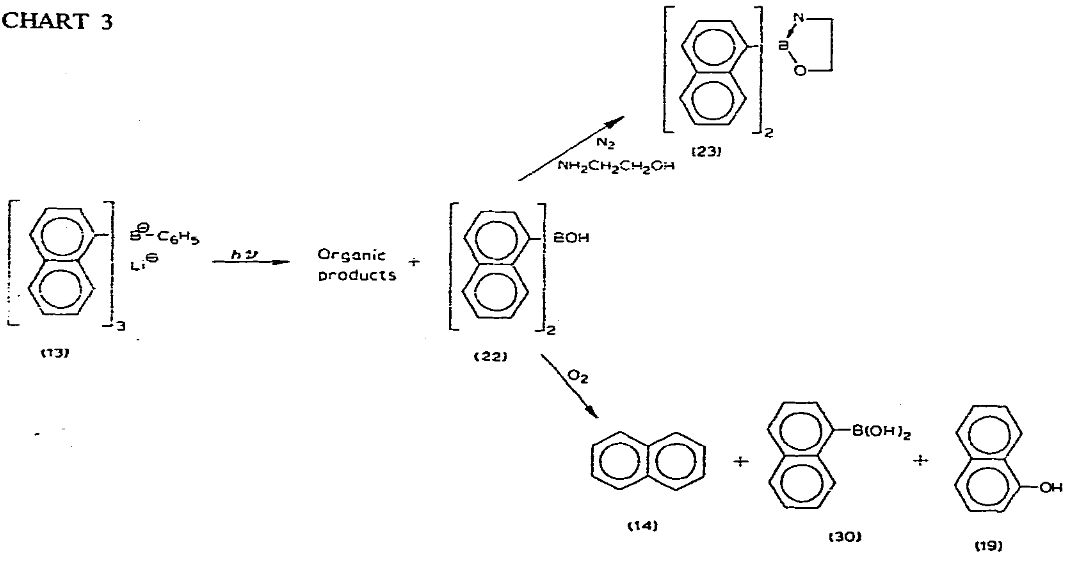

(13)
hν
H₂O/N₂
(three isomers)
(15a)—(15c)
2H
(16)
(one isomer)
(17)
2H
(18)
BOH
2
(22)
Pd/C - Cymane
Δ
(16)+(18)
hν
iso-C₃H₇OH/O₂
(14)
OH
(19)
+ (16)
OH
+ (18)
(20a)—(20c)
(29)
trace
B(OH)₂
(30)
3
Li⊕
B⊖–C₆H₅

which would result when four 1-naphthyl groups are attached to a central boron atom. As a result of this difficulty, we have instead irradiated lithium phenyltri-1-naphthylborate (**13**)[4].

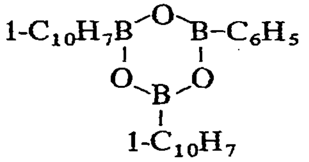
The UV spectra of the isolated gas chromatograph zones were compared with those of authentic samples of all products, with the exception of (**15a**)–(**15c**) and (**17**). The structures of (**15a**)–(**15c**) are assigned to be 1-cyclohexadienylnaphthalenes on the basis of their mass spectra (which show heaviest molecular ions at *m/e* 208 for $C_{16}H_{12}$) and their UV spectra which are essentially the same as that of naphthalene. The mass spectrum of compound (**17**) likewise, was found to have a molecular ion at *m/e* 256 corresponding to that of a dihydrobinaphthyl. The UV absorption spectrum of (**17**) was the same as that of naphthalene in the region of 270–340 mμ and did in no way resemble that of 1-phenylnaphthyl (**16**) or 1,1′-binaphthyl (**18**). Thus, the two additional hydrogens are located in one of the rings joining the two naphthalene nuclei. It is most significant that neither biphenyl (**2**) nor the phenylcyclohexadienes (**3**–**5**) were found. This result is in full agreement with our earlier results which showed that the reactions occurring on the photolysis of tetraarylborates are intramolecular.

In our preliminary irradiation experiments of (**13**) under a nitrogen atmosphere, amounts of naphthalene (**14**) as great as 12% were isolated from the reaction mixtures. Later we found that (**14**) was not produced by a photochemical reaction but during the product-isolation steps in the presence of air. During the photochemical conversion of (**1**) in the absence of oxygen to yield (**2**)–(**5**), diphenylborinic acid (**21**) is simultaneously produced[1]. In the case of (**13**), the photolysis results in the formation of a di-1-naphthylborinic acid (**22**). If oxygen is not carefully excluded during the isolation of the products from the photolysis of (**13**), naphthalene (**14**) results. Formation of naphthalene (**14**) can be avoided if ethanolamine is added to the photolysis mixture before the work-up steps are begun. Formation of the oxygen-stable ethanolamine complex (**23**) of di-1-naphthylborinic acid (**22**) results.

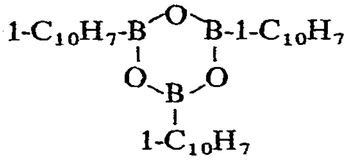
CHART 3



From acidified aqueous reaction mixtures which had been exposed to air before addition of ethanolamine, we have isolated fractions for which the *m/e* values correspond to the molecular ions of the following boronic acid anhydrides **(24)** and **(25)**:



(24)

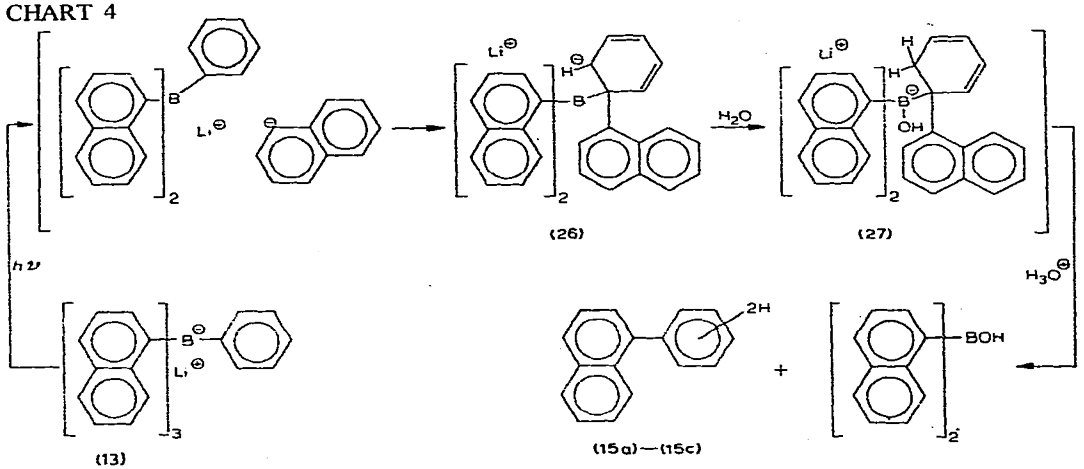


(25)

These cyclic trimers are not photoproducts but result from the in-solution recombination of phenylboronic acid **(32)** and 1-naphthylboronic acid **(30)**.

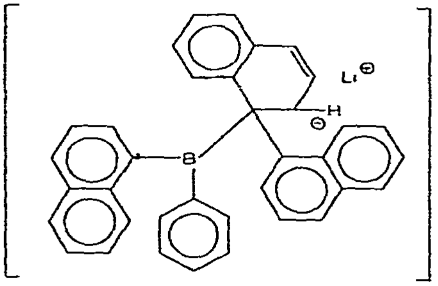
The absorption spectrum of **(1)** in water exhibits a large shoulder at 210 mμ, the value of absorption of which decreases rapidly (at 254 mμ the value of ε is 5900). Small absorption maxima appear at 266 mμ (ε 3260) and 274 mμ (ε 2160). Accordingly, the UV spectrum of **(1)** in water solution suggests that the transitions involved are $(\pi\rightarrow\pi^*)$ transition of the electrons of the individual phenyl groups. The possibility of a charge-transfer transition involving the phenyl rings and the negative boron atom cannot be ignored. Under the same conditions the absorption spectrum of **(13)** is characterized by a major absorption at 296 mμ (ε 18,000), with shoulders occurring at 285, 207 and 322 mμ. The UV spectrum of **(13)** in water is therefore characteristic of the $(\pi\leftarrow\pi^*)$ transitions of naphthalene. It is apparent that the electrons of the naphthalene nuclei of **(13)** are not delocalized between aryl groups via the boron atom. The three naphthyl groups of lithium phenyl tri-1-naphthylborate **(13)** have an inherently greater total value of "molecular" extinction than does the single phenyl group. The 1-naphthyl groups absorb the greater part of the light and are excited in preference to the single phenyl group. According to the mechanism outlined earlier for the photolysis of **(1)**, the aryl group which is excited reacts with an adjacent aryl group on boron. This "ate" type photochemical rearrangement occurs in such a manner that the aryl groups attached to boron combine by means of the carbons originally attached to boron[1]. We have proposed the intermediacy of an

CHART 4



anion at boron to explain the formation of the various products (**2**)–(**5**) resulting from the photolysis of tetraarylborate anions. In the case of lithium phenyltri-1-naphthylborate (**13**), the photolysis would thus proceed via intermediate (**27**) as shown in Chart 4.

Attack of a naphthyl anion on an adjacent naphthyl group can lead, alternatively, to (**28**), which in turn would lead to the binaphthyl-type products.

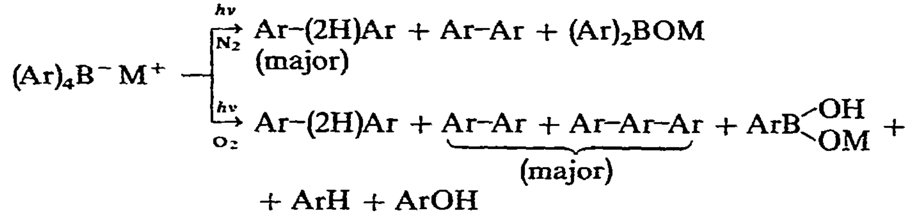


(28)

The effect of oxygen

The great influence of oxygen upon the nature of the products deserves comment. In the case of the photolysis of (**1**), oxygen increases the amount of biphenyl (**2**) and leads to the formation of the terphenyls (**6**) and (**7**) at the expense of the phenylcyclohexadienes (**3**)–(**5**) and the ring-opened products, the diphenylhexadienes[2]. In the case of the naphthyl-substituted tetraarylborate anions, the dihydro derivatives (**10a**),(**10b**), (**15a**)–(**15c**) and (**17**) are eliminated by the presence of oxygen in favor of (**11**), (**16**), and (**18**). The phenols (**19**) and (**20**) result most probably as the products from the attack of oxygen on a borinic acid or a trigonal intermediate. We wish to point out that the nature of the aromatic and dihydroaromatic products reflect the primary photochemical process and indicate the intramolecular control which the central boron atom exerts on the manner in which the aryl groups photomigrate. Moreover, the rearrangement retains its intramolecular character in the presence of oxygen[2]. Further evidence is given in the present work by the fact that no biphenyl (**2**) is formed during the photolysis of phenyltri-1-naphthylborate (**13**). The oxygen effect indicates that a trigonal intermediate or transition state is involved as at least one of the steps of the "ate" photochemical rearrangement.

We now believe that the rearrangement is general and can be described by the following scheme.



$$(\mathrm{Ar})_4\mathrm{B}^-\,\mathrm{M}^+ \begin{cases} \xrightarrow[\mathrm{N_2}]{h\nu} \mathrm{Ar{-}(2H)Ar + Ar{-}Ar + (Ar)_2BOM} \\ \quad \text{(major)} \\ \xrightarrow[\mathrm{O_2}]{h\nu} \mathrm{Ar{-}(2H)Ar} + \underbrace{\mathrm{Ar{-}Ar + Ar{-}Ar{-}Ar}}_{\text{(major)}} + \mathrm{ArB}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OM}\end{smallmatrix} + \\ \quad + \mathrm{ArH + ArOH} \end{cases}$$

EXPERIMENTAL

Irradiations

A typical irradiation was performed by dissolving the desired amount of the tetraarylborate salt in the desired amount of solvent, as indicated below. The solution was placed in a double-walled, water-cooled, all-quartz tube, the inside dimensions of which were 1 1/4 inch by 15 inches. 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 2537A 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.

Analytical procedures

Gas chromatographic analyses and preparative gas chromatography were carried out by means of an F and M Model 5750 Gas Chromatograph equipped with one-quarter inch, 8-foot-long columns packed with 20% SE 30 on Anakrom ABS support. The injection port was maintained at 230° and the detector at 320°. The helium flow was 90 ml/min. Before injection the column temperature was adjusted to 150°. After a 5-min post-injection period, the temperature was raised at a rate of 6°/min. Under these conditions the following adjusted retention times (Table 1) were found for authentic mixtures.

TABLE 1

ADJUSTED RETENTION TIMES

Compound	Adjusted retention time [Min (temp.)]
Naphthalene (14)	4.0 (150)
1-Naphthol (19)	11.4 (190)
1-Phenylnaphthalene (16)	17.7 (225)
2-Phenylnaphthalene	20.8 (235)
1,1'-Binaphthyl (18a)	27.5 (270)
2,2'-Binaphthyl (9)	30.0 (285)

The various spectra were determined on a Cary Model 15 (UV) instrument. Mass spectra were obtained on either a 60° sector-type or a CEC 21-110B instrument equipped with all glass heated inlet systems*.

Preparation of lithium tetra-2-naphthylborate (8)

The preparation of lithium tetra-2-naphthylborate (**8**) was carried out according to the scheme described for sodium tetra-*p*-tolylborate. This synthesis was essentially that of Wittig and Raff[3], with modification of the isolation of (**8**) as follows: By the reaction of an ether solution (100 ml) of 4.2 g of boron trifluoride–etherate with a solution from the reaction of 50 g of 2-bromonaphthalene with 165 ml of 2 *N* butyllithium there was obtained crude (**8**). The crude (**8**) was recrystallized from 1,2-dimethoxyethane to give the complex of (**8**) having three moles of crystallization of dimethoxy-

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* The system is described in ref. 5, but was constructed of glass.

ethane. The NMR and elemental analysis confirmed the structure corresponding to $C_{40}H_{28}BLi \cdot 3\,C_4H_{10}O_2$: Found: C, 78.5; H, 7.6; B, 1.1. $C_{52}H_{58}BLiO_6$ calcd.: C, 78.3; H, 7.3; B, 1.4%.)

Irradiation of lithium tetra-2-naphthylborate (**8**)

(*a*) *Under a nitrogen atmosphere.* A solution of 1.0 g of (**8**) in a mixture of 120 ml of H_2O and 80 ml of 1,2-dimethoxyethane was irradiated during 5 h at a temperature of 10° in an all-quartz, double-walled, water-cooled cell by means of a Rayonet 2537 photochemical reactor. To the photolysis mixture there was added excess aqueous potassium chloride. No potassium salt precipitated. The organic material was removed by filtration and dried (0.38 g). Ethanolamine (5 ml) was added to the filtrate. The resulting mixture was then distilled at the water pump. The receiver was cooled in a dry ice/acetone mixture and the distillation flask surrounded by water maintained at a temperature less than 50°. No organic material was found in the distillate. The residue was diluted with 25 ml of cold water and the solid, the ethanol amine complex (**12**) of di-2-naphthylborinic acid (**11**) was isolated and dried (0.11 g). The water filtrate was acidified with hydrochloric acid, saturated with solid potassium chloride, and extracted with two 25-ml portions of benzene. The benzene extracts were dried over magnesium sulfate. The benzene was distilled at reduced pressure to yield 0.09 g of the trimer of 2-naphthylboronic acid (**31**). The magnesium sulfate was rinsed with 25 ml of acetone, which, when evaporated, yielded an additional 0.015 g of the trimer of (**31**). The organic material was dissolved in benzene and submitted to gas-chromatographic analyses which revealed the presence of 5% (**10a**), 45% (**10b**) and 50% (**9**). The adjusted retention times of the dihydro derivatives are as follows: (**10a**), 27.1 min; (**10b**), 29.7 min. The ratios of (**9**), (**10a**) and (**10b**) do not represent the true values since reinjection of isolated zones of (**10b**) became richer in (**9**), indicating that dehydrogenation of (**10b**) was occurring in the gas chromatograph.

(*b*) *Under an air atmosphere.* Under the same irradiation conditions and similar isolation procedure, photolysis of (**8**) in the presence of air gave 76% yield of (**9**).

Irradiation of lithium phenyltri-1-naphthylborate (**13**)

(*a*) *Under a nitrogen atmosphere.* A solution of 1 g of lithium phenyltri-1-naphthylborate (**13**) in 200 ml of water was irradiated for 5 h, as described in (*a*) for (**8**). After the addition of 5 ml of ethanolamine, the solution was evaporated to about 5 ml by means of a rotary evaporator. The receiver was cooled in a dry ice/acetone bath. In order to trap any low-boiling products, a liquid nitrogen trap was placed in series with the evaporator. In this case no organic material was found in the water distillate. The residue was stirred with two portions of benzene and the combined extracts were dried over anhydrous magnesium sulfate. The benzene extracts were evaporated at reduced pressure and the residue was triturated with two 25-ml portions of cold hexane. The residue from the hexane consisted of 0.12 g of di-1-naphthylborinic acid–ethanolamine complex (**23**). The hexane was evaporated under reduced pressure to give 0.2 g of organic material which was composed as follows: 0.75% (**14**); 19%, (**15a**); 4.5%, (**15b**); 1.1% (**15c**); 34.3% (**16**); 1.5% (**17**); 36.5% (**18**). The corresponding adjusted retention times were for (**15a**), 15.5 min; (**15b**), 16.5 min; (**15c**), 18.5 min; and (**17**), 27 min. The following data summarize the physical properties of these products whose isomeric configurations have not been determined:

(**15a**), *m/e* 204; λ_{max} 270 (ε 3340), 263 (ε 2780) and 256 mμ (ε 3720);
(**15b**), *m/e* 204; λ_{max} 266 (ε 1040) and 220 mμ (ε 3200);
(**15c**), *m/e* 205; λ_{max} 290 (ε 980), 283 (ε 1250), 273 (ε 1080), 254 (ε 600) and 226 mμ (ε 10,500).

The ethanolamine residue from these benzene extractions was diluted with 200 ml of water and the solution saturated with sodium chloride. The resulting precipitate which was collected and dried was recovered sodium phenyltri-1-naphthylborate (0.49 g).

The organic material was dissolved in 2 ml of cymene. After the addition of a trace of palladium/charcoal catalyst, the whole was refluxed for 3 h. Gas chromatographic analysis of the cymene solution showed the presence of 1-phenylnaphthalene (**16**) and 1,1′-binaphthyl (**18**).

In a similar run, oxygen was not excluded during the addition of ethanolamine. As a result, the water distillate and the residue contained naphthalene (**14**). The residue was treated as just described. When the anhydrous magnesium sulfate from the benzene extract was rinsed with acetone and the acetone evaporated, a 0.2-g mixture of the cyclic trimers (**24**) and (**25**) resulted. For this reason oxygen must be completely eliminated during the irradiations and the work-up step, until after the addition of ethanolamine.

(*b*) *Under an air atmosphere.* Irradiation of 1 g of lithium phenyltri-1-naphthylborate (**13**) in 200 ml of isopropanol was carried out during 2.5 h, as described except that a current of air was passed through the photolysis mixture. The isopropanol was evaporated at reduced pressure. The isopropanol distillate contained 0.01 g of naphthalene (**14**). The residue was shaken with saturated potassium chloride. The insoluble material was removed by filtration, and then triturated with two 25-ml portions of benzene. The residue, recovered potassium phenyltri-1-naphthylborate, weighed 0.25 g. The benzene extract was evaporated to yield 0.53 g of a dark residue. Gas chromatographic and mass spectrometric analyses of this residue showed 3%, (**14**); 22% (**19**); 34%, (**16**); 10% (**20a**); 0.8%, (**20b**); 2%, (**20c**); 19% (**18**); and 3.2%, (**29**). Mass spectrometric examination of the crude residue indicated the presence of high-boiling products such as phenylbinaphthyl and trinaphthyl. These materials were too high boiling to pass through an SE 30 column at 290–300°. Accordingly, not all of the injected material passed through the column. Extraction of the crude residue with dilute sodium hydroxide gave a water solution which, when acidified, yielded 1-naphthol (**19**). The hydroxyphenylnaphthalene (**20**) could not be so extracted. The following data summarize the physical properties of these products, whose isomeric configurations we have not yet determined:

(**20a**); adjusted retention time 17 min; *m/e* 220; λ_{max} 333 (ε 907), 288 (ε 6250), 282 (ε 6430) and 225 mμ (ε 51,000);

(**20b**); adjusted retention time 18 min; *m/e* 220, λ_{max} 332 (ε 390), 282 (ε 1750) and 224 mμ (ε 7000);

(**20c**); adjusted retention time 19 min; *m/e* 220; λ_{max} 309 (ε 6500), 284 (ε 6100) and 225 mμ (ε 9700).

(**29**); adjusted retention time 38 min; *m/e* 330; λ_{max} 293 (ε 2300), 261 (ε 12,900) and 225 mμ (ε 156,000).

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