

PHOTOCHEMICAL REACTIONS OF ALKYLBENZENES WITH BORON TRIBROMIDE¹

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Abstract—The photochemical reaction of toluene with boron tribromide followed by hydrolysis results in the formation of *o*- (12.7%), *m*- (7.5%), and *p*-tolueneboronic acids (54.8%) and a trace of ω -tolueneboronic acid. Ethylbenzene is similarly boronated to give *o*- (9.9%), *m*- (3.0%), and *p*-ethylbenzeneboronic acids (57.6%) together with α - (12.9%) and ω -ethylbenzeneboronic acids (2.6%). In the photoboronation of cumene, *o*- (1.9%), *m*- (4.5%), and *p*-cumeneboronic acids (73.6%) are obtained, but no α -cumeneboronic acid could be detected. Ring substitution, which may proceed via photochemical excitation of CT complexes between alkylbenzenes and boron tribromide, is favored. A small amount of side-chain boronated products is simultaneously obtained by a radical process involving a dibromoboryl radical ($\cdot\text{BBr}_2$).

THUS far reports on photoboronation are few, except for the photochemical reactions of substituted benzenes,² i.e., the reaction of benzene or halobenzenes with boron trihalides which gives on hydrolysis substituted boronic acids. For the reaction of benzene, an electronic excitation of charge-transfer complex (CT complex) between benzene and boron tribromide by irradiation accounts for the formation of dibromophenyl borane. On the other hand, the formation of *p*-phenylenebis(boron dibromide) from bromobenzene is thought to result from the attack of dibromoboryl radical ($\cdot\text{BBr}_2$) on the initially formed dibromophenyl borane. Thus, two different pathways, i.e., one via CT complex and another involving dibromoboryl radical, have been postulated.

The present paper describes the photochemical reactions of alkylbenzenes such as toluene, ethylbenzene, and cumene with boron tribromide. Mechanistic discussions will be presented on the basis of the product analysis.

RESULTS AND DISCUSSION

A mixture of toluene and boron tribromide in a molar ratio of 10:1 was irradiated in a sealed quartz tube for 50 hr with an unfiltered high pressure Hg lamp. The products obtained were hydrolyzed, giving tolueneboronic acids, ω -tolueneboronic acid, and bibenzyl (the sum of their yields was 75%). Table 1 shows the results on the similar photochemical reactions of ethylbenzene and cumene with boron tribromide. Analysis of boronic acids was carried out by IR and GLC as described in the experimental section.

No detectable reaction took place without UV light under these conditions. However, refluxing a mixture of toluene and boron tribromide in the dark under nitrogen atmosphere for 30 hr gave, after similar work-up, ω -tolueneboronic acid (2.0%), bibenzyl (19.2%), benzyl bromide (15.9%), *o*-cresol (10.6%), *m*- and *p*-cresols (6.8%) and bromotoluenes (6.1%) in the total yield of 60.6%. The pathway for the formation of cresols is uncertain.

TABLE 1. PHOTOCHEMICAL REACTIONS OF ALKYL BENZENES WITH BORON TRIBROMIDE AT ROOM TEMPERATURE FOR 50 HR

| Substrate R in RC ₆ H ₅ | Total yield of boronated products ^a , % | Ring substituted products, RC ₆ H ₄ B(OH) ₂ , % | | | Side-chain substituted products, % | Other products, % |
|---|--|--|------------|------------|--|-------------------------|
| | | <i>o</i> - | <i>m</i> - | <i>p</i> - | | |
| | | Me | 75 | 12.7 | | |
| Et | 86 | 9.9 | 3.0 | 57.6 | PhCH—CH ₃ (12.9), B(OH) ₂ PhCH ₂ CH ₂ B(OH) ₂ (2.6) | — |
| <i>i</i> -Pr | 80 | 1.9 | 4.5 | 73.6 | PhC(CH ₃) ₂ B(OH) ₂ (not detected) | — |

^a Based on the consumed boron tribromide.

Table 2 shows the correlation of the yields of boronic acids with molar ratios of toluene to boron tribromide. An excess of toluene gave the tolueneboronic acids in good yield, while an excess of boron tribromide gave no detectable amount of boronic acid. Similar trends have been reported in the photochemical reaction of bromobenzene with boron tribromide,^{2b} i.e., when the molar ratio of bromobenzene to boron tribromide was 1:1.6, benzeneboronic and *p*-phenylenediboronic acids were obtained via a radical process, while a large excess of bromobenzene gave only *p*-bromobenzeneboronic acid. The latter reaction may be explained to proceed via an electronic excitation of CT complex of bromobenzene with boron tribromide as has been observed for the reactions of benzene with boron trihalide.^{2a} The CT complex was confirmed in our hands by a new UV absorption maximum (296 mμ) with bromobenzene. In addition, λ_{max}, which may belong to the corresponding

TABLE 2. EFFECT OF MOLAR RATIOS OF TOLUENE AND BORON TRIBROMIDE ON THE YIELD OF C₇H₇B(OH)₂ AT ROOM TEMPERATURE

| Molar ratio of toluene: boron tribromide | Yield ^a % |
|---|-------------------------|
| 1:10 | ≈ 0 |
| 1:1 | 44 |
| 10:1 | 75 |

^a Based on the consumed boron tribromide.

CT complexes, in UV spectra of alkylbenzenes with boron tribromide are shown in Table 3. Absorption bands of boron tribromide in carbon tetrachloride and the alkylbenzenes in *n*-hexane appear below 260 m μ and 280 m μ , respectively.

TABLE 3. UV SPECTRA OF ALKYL BENZENE SOLUTIONS OF BORON TRIBROMIDE^a

| Substrate X in XC ₆ H ₅ | λ_{\max} m μ |
|--|-----------------------------|
| Me | 312 |
| Et | 301 |
| <i>i</i> -Pr | 281 |
| Br | 296 |
| H ^b | 315, 435 ^c |

^a After the solutions of sample were carefully degassed, the UV spectra were measured in a sealed square cell (path length 1 cm).

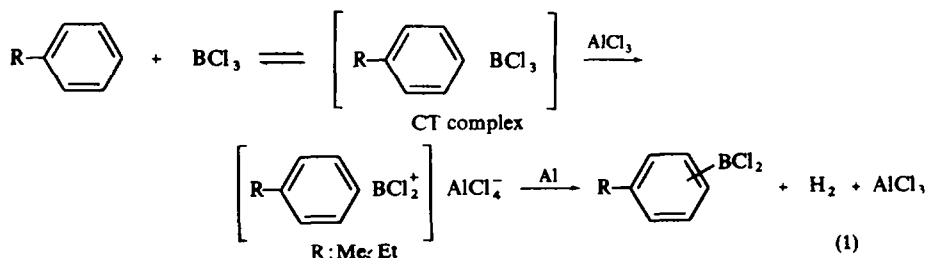
^b Reference 2a.

^c It is found that λ_{\max} of 435 m μ does not belong to the CT complex of benzene with BBr₃, but to that of Br₂ in benzene.

Photoboronation of toluene with boron tribromide also took place in a poor yield in a pyrex vessel in which the wavelength of light below 300 m μ was almost eliminated (Fig. 1). These poor yields may be ascribed to the decrease in light intensity by passing through pyrex. These facts would suggest that the photoboronation on the benzene ring proceeds via the excitation of CT complexes of alkylbenzenes and boron tribromide.

π -Electron densities of monosubstituted benzene, in which there is a single electron donating group ($-\text{CH}_2-$), have been calculated by LCAO MO method.³ According to the results, the π -electron densities at C atoms of benzyl anion in the ground state are 1.143 (*ortho*), 1.000 (*meta*), and 1.143 (*para*), while those in the first excited state are 1.250 (*ortho*), 1.250 (*meta*), and 1.000 (*para*). The present reaction occurs at the *ortho* and *para* positions having higher π -electron densities in the ground state.

The yields of *ortho*-products decreased in the order: toluene > ethylbenzene > cumene, i.e., in the order of the steric hindrance of alkyl groups. In contrast, only



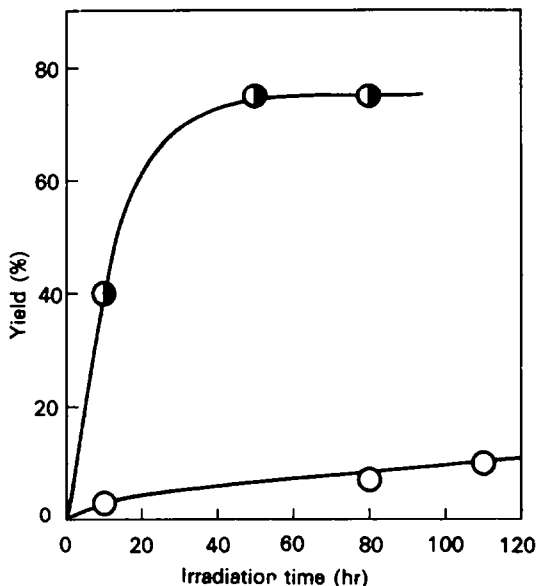


FIG. 1. Correlation curves of the yields of $C_7H_7B(OH)_2$ with irradiation time. —●—, in a sealed quartz tube; —○—, in a sealed pyrex tube, transmission of which is ca. 50% at 306 m μ .

p- and *m*- (but not *o*-) alkylbenzenboronic acids were obtained in the aluminum chloride-catalyzed boronation of alkylbenzenes with boron trichloride in the dark⁴ (Table 4). The steric hindrance of alkyl groups to a bulky reagent $[BCl_2^+][AlCl_4^-]$ at the *ortho* positions may explain these facts. Thus the orientations in the photo- and above dark-reactions are in accord with the electron density in the ground state.

The products in our dark reaction, i.e., tolueneboronic acids, bibenzyl, benzyl bromide, and bromotoluenes, may be derived from radical species produced by a homolysis:



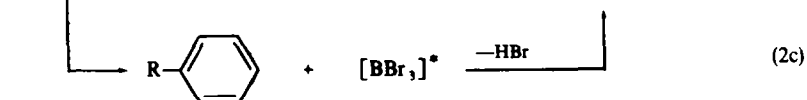
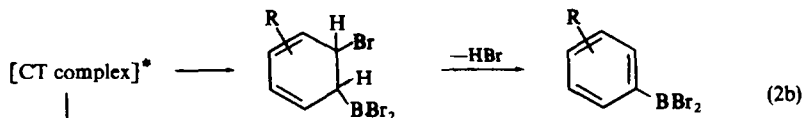
The same homolysis is also probable in the photochemical reactions.^{2b} Therefore, the side-chain substitutions under irradiation seem to be a result of an attack of dibromoboryl radical on the side-chain. The yield of side-chain substituted products is higher with ethylbenzene than with toluene, but negligible with cumene, probably owing to the steric hindrance of the two Me groups.

TABLE 4. MOLAR RATIO OF ISOMERIC ALKYLBENZENE BORONIC ACIDS FORMED ON PHOTOCHEMICAL REACTIONS OF ALKYL BENZENES WITH BORON TRIBROMIDE AT ROOM TEMPERATURE

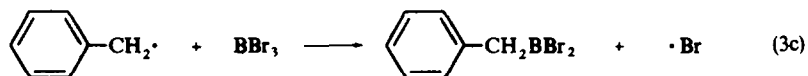
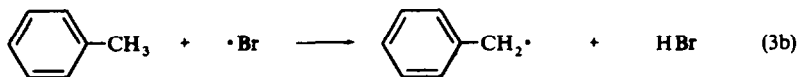
| Product $RC_6H_4B(OH)_2$ | Photoreaction | | | Dark reaction ⁴ | | |
|-----------------------------|---------------|------------|----------------|----------------------------|------------|----------------|
| | Substrate | | | Substrate | | |
| | CH_3Ph | C_2H_5Ph | $(CH_3)_2CHPh$ | CH_3Ph | C_2H_5Ph | $(CH_3)_2CHPh$ |
| <i>o</i> - | 1.0 | 1.0 | 1.0 | 0 | 0 | — |
| <i>m</i> - | 0.6 | 0.3 | 2.3 | 1 | 1 | — |
| <i>p</i> - | 4.4 | 5.8 | 37.9 | 4.6 | 5 | — |

It is clear from our results that the ring substitution predominates over the side-chain substitution. Probable processes in the photochemical boronation of alkylbenzenes on the ring and the side-chain are outlined in the following two schemes.

Ring substitution process:



Side-chain substitution process:



The formation of CT complex in the ground state followed by its excitation on irradiation results in the ring boronation. One pathway may be the transformation of CT complex into σ -complex of a hexadiene type^{2a} which eliminates then hydrogen bromide giving the products (Eq. 2b). Alternatively, the excited CT complex may dissociate into alkylbenzene in the ground state and excited boron tribromide $[\text{BBr}_3]^*$ ⁵ which can give boronated products via an electrophilic attack (2c). Since the yield of *m*-substituted product is poor, the CT complex does not seem to dissociate to excited alkylbenzene having higher π -electron densities at *meta* and *ortho* positions.³ But these evidences are not yet decisive.

On the other hand, the side-chain substitution may be explained as shown in the above scheme (Eq. 3a-c); i.e., excited boron tribromide, which is formed from the excited CT complex, eliminates a Br atom to give dibromoboryl radical (Eq. 3a), while benzyl radical formed by the H atom abstraction with bromo radical would react with boron tribromide to afford the side-chain substituted product.

A ring boronation by dibromoboryl radical is not feasible, since radical species may predominantly participate in a hydrogen atom abstraction from the side-chain.

EXPERIMENTAL

The UV spectra were measured by a Shimadzu recording spectrophotometer (Type SV-50A) and the IR spectra were recorded by a Perkin-Elmer Model 337 grating instrument. A Yanagimoto Model GCG-500F with a flame ionization detector was used for GLC.

Materials. Toluene, b.p. 109–110°, ethylbenzene, b.p. 135–136° and cumene, b.p. 151–152°, were purified by rectification of the first grade materials. BBr_3 was of commercial material. The authentic samples of *o*-tolueneboronic anhydride, m.p. 159–161° (lit.⁶ 160–161°), *m*-tolueneboronic anhydride, m.p. 156.7–159° (lit.⁷ 160–161.5°), and *p*-tolueneboronic acid, m.p. 238.5–240° (lit.⁷ 240°), were prepared by the reactions of the corresponding bromotoluenes with tri-*n*-butyl borate, b.p. 121–122° (22 mm) [lit.⁸ 114–115° (15 mm)].⁹ They were identified by the IR spectra. When the resulting boronic acids were heated at 80° for 2 hr under reduced press, they were easily converted to the corresponding anhydrides and the characteristic absorption bands of the anhydrides appeared at 685–725 cm^{-1} . The IR spectra of boronic acids and the anhydrides are summarized in Table 5.

TABLE 5. IR SPECTRA OF TOLUENEBORONIC ACIDS AND ANHYDRIDES

| $\text{CH}_3\text{C}_6\text{H}_4\text{B}(\text{OH})_2$ | OH Band cm^{-1} | Anhydride band cm^{-1} | B—O band ^b cm^{-1} |
|--|-----------------------------|------------------------------------|---|
| <i>o</i> - | 3300 (3260 ^a) | 685 (685 ^a) | 1350 (1350 ^a) |
| <i>m</i> - | 3250 | 725 | 1350 |
| <i>p</i> - | 3250 (3250 ^a) | 685 (685 ^a) | 1355 (1355 ^a) |

^a Values in the literature.¹⁰

^b This absorption band appears invariably in boronic acids and anhydrides.

p-Cresol was prepared from *p*-toluidine by the Sandmeyer reaction, b.p. 89.5–90.5° (12 mm).¹¹

m-Ethylphenol was prepared from nitroacetophenone as follows;¹² *m*-ethylamine obtained by the reduction of *m*-nitroacetophenone with hydrazine was converted to *m*-ethylphenol via its diazonium salt, b.p. 64–68° (1 mm) [lit.¹² 37° (0.05 mm)]. α -Phenethyl alcohol was prepared by the Meerwein-Ponndorf reduction of acetophenone, b.p. 90° (15 mm).¹³ Phenyl dimethyl carbinol was prepared by the Grignard reaction of acetone with bromobenzene, b.p. 105–108° (25 mm) [lit.¹⁴ 93° (11 mm)].¹⁴ Benzyl bromide was obtained by the photochemical reaction of toluene with bromine, b.p. 91.0–92.8 (20 mm)¹⁵ *o*-Ethylphenol, b.p. 82.5–86.5° (10 mm), and *p*-ethylphenol, m.p. 39.5–40.5 (lit.¹⁶ 45–08), b.p. 102–103 (15.5 mm) [lit.¹⁷ 95–101 (10 mm)], were prepared by the Clemmensen reduction of the corresponding *o*- and *p*-acetylphenols¹⁸ obtained by the Fries rearrangement of phenyl acetate.¹⁹ *p*-Isopropylphenol, b.p. 102–104 (10 mm), was prepared by the Sandmeyer reaction of *p*-cumidine,²⁰ b.p. 101–102° (9 mm) [lit.²¹ 103–105 (10 mm)], obtained by the reduction of *p*-nitrocumene. Bibenzyl was prepared by the Friedel-Crafts reaction of ethylene dichloride with benzene, m.p. 51.3–51.8°.²² *o*-Cresol, *o*-isopropylphenol, and β -phenethyl alcohol were of the first grade commercial materials, *m*-Cresol was of the guaranteed grade.

General procedure. Photochemical reactions were carried out in a sealed quartz tube (10 mm \times 300 mm) and a sealed pyrex (10 mm \times 300 mm) tube. The reagents were taken into the tube in a dry box under N_2 atm and the tube was sealed. The tube was irradiated with a Toshiba H-400P high pressure Hg lamp at 22–24° at the distance of 3–5 cm away from the reaction tube. After irradiation, the photoproducts were analyzed as follows: the reaction mixture was hydrolyzed with cold water to give alkylbenzeneboronic acids. The resulting boronic acids were treated with 30% H_2O_2 at 40–50° for 5 min affording the corresponding alkylphenols.^{4, 23, 24} The isomer composition of alkylphenols was determined by both IR spectrophotometry of the CS_2 soln using a 0.1 mm KBr cell and GLC operated with a 1 m \times 3 mm column packed with PEG 20M (10%) on Celite 545 of 80–100 mesh using N_2 as a carrier gas (25–30 ml/min) at 80–200° (4–6°/min) with a H_2 flow rate 20 ml/min. For tolueneboronic acids, the identification was performed by IR spectrophotometry by means of KBr disk technique using the authentic boronic acids. In a preliminary experiment, oxidation of boronic acids with hydrogen peroxide followed by the extraction of the resulting alkylphenols were confirmed to proceed almost quantitatively; *o*-, *m*-, and *p*-cresols were obtained from the corresponding tolueneboronic acids in the yields of 99.2%, 98.0%, and 100%, respectively. The yields were estimated by GLC on the basis of consumed boron tribromide in the photochemical reactions.

Photochemical reaction of toluene with boron tribromide. A mixture of toluene (4 g, 0.0435 mole) and BBr_3 (1.0 g, 0.0040 mole) were irradiated for 50 hr at 22–24°. After irradiation and succeeding hydrolysis, resulting products were extracted with ether. The ether extract (I) was dried with Drierite, and then the unreacted toluene and ether were distilled off in vacuum. There was obtained colorless crystals (II) of isomeric tolueneboronic acids (0.12 g). IR spectra of II showed ν_{max} 1350–1355 (B—O band), 730 (4H), 790 (3H), and 815 cm^{-1} (2H). On heating in vacuum at 80°, II was converted to anhydrides, ν_{max} 1350–1355 (B—O band), 730 (4H) and characteristic absorption band of *p*-tolueneboronic anhydride, 790 (3H), 815 (2H), 710 (characteristic absorption band of *p*-tolueneboronic anhydride), and 685 cm^{-1} (characteristic band of *o*- and *p*-tolueneboronic anhydrides). A small amount of bibenzyl was detected from I by GLC. Conditions for GLC were as follows: temp, 100–200° (6°/min); N_2 flow rate, 25 ml/min and the other conditions were the same as described above.

The residual aqueous layer (III) in the extraction work-up gave boric acid (0.17 g) derived from unreacted BBr_3 . III was treated with H_2O_2 (1 ml), extracted with ether and then the extract was dried. A trace of benzyl alcohol was detected from the extract by means of GLC. Conditions for GLC: temp, 80–200° (6°/min); N_2 flow rate, 25 ml/min.

The isomeric tolueneboronic acids (II) were treated with H_2O_2 (2 ml) to give cresol (75%). The ratio of the ring substituted isomers was estimated by means of the absorbance at 750 (4H), 775 (3H), and 820 cm^{-1} (2H). The ratio of *ortho*: (*meta* + *para*) was determined by GLC. Conditions for GLC: temp, 120–200° (4°/min); N_2 flow rate, 25 ml/min.

Photochemical reaction of ethylbenzene with boron tribromide. A mixture of ethylbenzene (4.3 g, 0.041 mole) and BBr_3 (1 g, 0.004 mole) was irradiated at 22–24° for 50 hr. After irradiation, the similar work-up gave the boronated products in the yield of 86%. Their characteristic absorption bands were 748 (4H), 775 (3H) and 825 cm^{-1} (2H) for ethylphenols, 755 (α -) and 745 cm^{-1} (β -) for phenethyl alcohols. The resulting isomers were determined by means of both IR spectrophotometry and GLC. Conditions for GLC: temp, 80–180° (6°/min); N_2 flow rate, 30 ml/min.

Photochemical reaction of cumene with boron tribromide. A mixture of cumene (4.8 g, 0.04 mole) and BBr_3 (1 g, 0.004 mole) was irradiated at 22–24° for 50 hr. After irradiation, the work-up similar to the photochemical reaction of toluene gave the boronated products in a yield of 80%. The characteristic absorption bands were 750 (4H), 780 (3H)²⁵ and 827 cm^{-1} (2H) for isopropylphenols. Conditions for GLC: temp, 130–200° (4°/min); N_2 flow rate, 25 ml/min. The analysis of the resulting ring substituted isomers was performed by using the molar extinction coefficients of the *o*-, *m*-, and *p*-ethylphenols reported previously.^{26,27}

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