*Inorganica Chimica Acta,* 12 (1975) 45–51

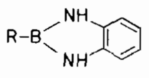
# A Study of the Reaction of 2-Phenyl-1,3,2-benzodiazaborolidine with Benzoyl Chloride[1]

W. R. PURDUM and E. M. KAISER[2]
*Department of Chemistry, University of Missouri, Columbia, Mo. 65201, U.S.A.*
Received June 14, 1974

*Reaction of 2-phenyl-1,3,2-benzodiazaborolidine* (**2**) *with benzoyl chloride afforded N,N′-dibenzoyl-o-phenylenediamine* (**8**) *regardless of the amount of the acid chloride employed. Depending on the work-up procedure, the 2-phenylboron moiety was isolated as either phenylboronic acid or phenylboronic acid anhydride. In the absence of added bases, the reaction was observed to be susceptible to solvent assistance by ethers, presumably by coordination with the empty p-orbital of boron. In the presence of added amines, the extent of benzoylation was altered considerably. With pyridine as a co-reagent, small amounts of 1,3-dibenzoyl-2-phenyl-1,3,2-benzodiazaborolidine mono- or dihydrochloride were isolated though this compound readily underwent hydrolysis or oxidation upon standing. Interaction of* **2** *with sodium hydride in tetrahydrofuran caused ionization of only one of the two hydrogens bound to nitrogen even upon extended reflux. Benzoylation of the heterocycle under these latter conditions again afforded only the dibenzoylated compound* **8**.

## Introduction

Although numerous reports have appeared concerning the synthesis of various 2-substituted 1,3,2-benzodiazaborolidines (**1**)[3,4] the chemistry of such compounds appears limited. For example, earlier investigators[3,4c] observed that treatment of 2-phenyl-1,3,2-benzodiazaborolidine (**2**) with dilute sodium hydroxide solutions or aqueous hydrochloric acid rapidly converted it to benzeneboronic acid (**3**) and *o*-phenylenediamine (**4**) (Eq. 1). A later kinetic study attempted to relate this hydrolytic instability to the stereochemistry involving boron during hydrolysis and the amount of $\pi$-character present in the initial diazaborolidine ring.[5] It has also been reported that treatment of **2** with gaseous hydrogen chloride in refluxing toluene afforded the dihydrochloride derivative **5** which, upon trituration with dilute sodium carbonate solution in diethyl ether, was reconverted to **2** (Eq. 2).[4c]



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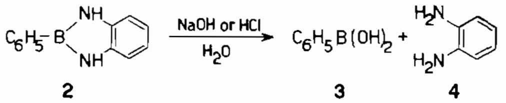

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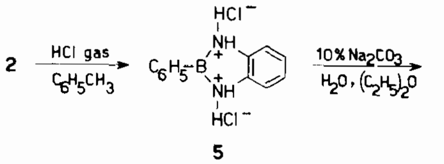

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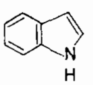

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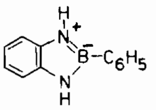
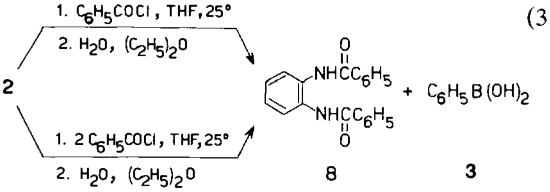


**7**

Previous workers noted that the basic ring system of **2** is isoelectronic with indole (**6**) and that the ultraviolet spectra of the two compounds are very similar.[3] As a result, it was considered feasible that the $\pi$-electron distribution of **2** would be similar to that of **6** such that the two nitrogen atoms bonded to the boron of **2** would exhibit different reactivities with respect to each other. This hypothesis is even more apparent with the zwitterionic form **7**[5] of **2** in which one of the nitrogen atoms possesses considerable positive character; the extreme canonical form would possess a full positive charge as in quaternary nitrogen salts.

## Results and Discussion

As part of our investigation concerning the reactivity of selected boron–nitrogen heterocycles with organoalkalies and electrophiles,[6] the chemistry of **2** with a



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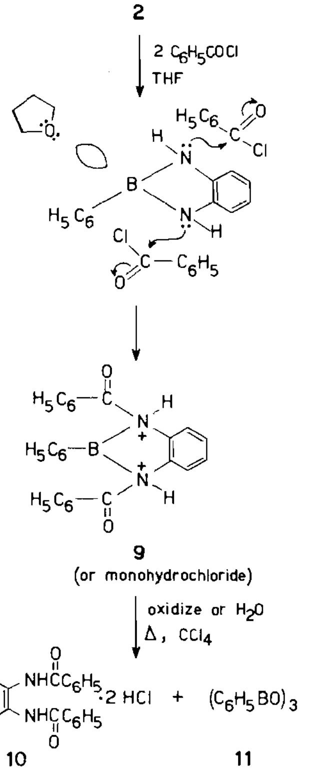
Scheme I



selected electrophile, benzoyl chloride, was studied. It was first of interest to investigate the relative nucleophilicity of the nitrogens of **2** with benzoyl chloride in the absence of any other base. Thus, **2** was treated separately with one and two equivalents of this acid chloride in anhydrous tetrahydrofuran (THF) (Eq. 3) to give a precipitate which did not redissolve upon standing. Hydrolysis of the precipitate afforded N,N'-dibenzoyl-*o*-phenylenediamine (**8**) in yields of 98% and 93% (based on benzoyl chloride), respectively; none of the expected mono- and dibenzoylated derivatives of **2** were present. In both reactions, the 2-phenylboron moiety was isolated and characterized as phenylboronic acid (**3**).

In order to explain the unexpected dibenzoylation along with ring cleavage regardless of the amount of benzoyl chloride employed, factors which may have influenced the pathway of the reaction were examined.

TABLE I. Reaction of 2-Phenyl-1,3,2-benzodiazaborolidine with Two Equivalents of Benzoyl Chloride in Various Solvents.

| Solvent | Time; Temperature | Appearance of Precipitate (minutes) | % Yield |
|---|---|---|---|
| Tetrahydrofuran | 6 hr; 25°C | 90 | 78[a] |
| 2-Methyltetrahydrofuran | 12 hr; 25°C | 35 | 77[a] |
| 2,5-Dimethyltetrahydrofuran | 12 hr; 25°C | 15 | 75[a] |
| Benzene | 24 hr; reflux | 24 hr | 35[b] |

[a] Based on the N,N'-dibenzoyl-*o*-phenylenediamine dihydrochloride isolated. [b] Based on the N,N'-dibenzoyl-*o*-phenylenediamine isolated.

Besides the probable different nucleophilicity of the nitrogens, the possibility of solvent participation also existed as suggested in Scheme I. To test the latter hypothesis, the reaction of **2** with two equivalents of benzoyl chloride was conducted in THF, its 2-methyl and 2,5-dimethyl derivatives, and in benzene (Table I). In each case, a precipitate formed that was insoluble in the respective solvents both at 25°C and at reflux. However, the stronger the solvent as a base, the sooner this precipitate initially appeared (Table I). Thus, solid first appeared after only 15 minutes in 2,5-dimethyltetrahydrofuran, after 35 minutes in the less basic 2-methyltetrahydrofuran, and after 90 minutes in THF itself. In contrast, initial appearance of solid in the non-ethereal solvent benzene was observed only after 24 hours of refluxing; in benzene, moreover, the yield of benzoylated product was substantially lower than that realized in THF and its derivatives. Thus, it seems certain that ethereal solvents do indeed participate in benzoylations of **2**.

The initial precipitate formed in the benzoylations described in Table I may have been 1,3-dibenzoyl-2-phenyl-1,3,2-benzodiazaborolidine dihydrochloride (**9**) or the corresponding monohydrochloride salt. Though the compound was not specifically characterized, indirect evidence was obtained that it was such a salt when it was collected by filtration in the open atmosphere and subjected to Soxhlet extraction to afford the dihydrochloride of N,N'-dibenzoyl-*o*-phenylenediamine (**10**) and phenylboronic anhydride (**11**). Presumably, the initial precipitate had undergone autoxidation or hydrolysis to give **10** and **11**. Of course, the initial precipitate in the reaction flask before exposure to the atmosphere could itself have been a mixture of **10** and **11** however, the reaction mixture was protected during this time by an atmosphere of helium. Thus, such autoxidation or hydrolysis seems unlikely until the precipitate was collected or transferred to the Soxhlet apparatus.

The instability of the 1,3,2-benzodiazaborolidine ring system in the current reactions may be attributed to the delocalization of the electron pairs on the nitrogen atoms into the carbonyl groups thus increasing the ability of the vacant *p*-orbital of boron to react with molecular oxygen or water. Also, cleavage of the ring system may be facilitated by hydrogen chloride side-product. To eliminate the latter possibility, the reaction of **2** with benzoyl chloride was conducted in the presence of certain tertiary amines in anticipation that by-product hydrogen chloride would be precipitated by the amine and thus be unable to effect ring-cleavage. Also, such tertiary amines could themselves coordinate with the vacant *p*-orbital of boron and prevent autoxidation.

First, it was determined that triethylamine as the added base had a considerable influence on the reaction since N,N'-dibenzoyl-*o*-phenylenediamine (**8**) was obtained in only 26% yield; moreover, the reaction required a five hour reflux period before a precipitate formed. That **8** was formed at all suggested that autoxidation or hydrolysis of intermediates was not prevented even though triethylamine hydrochloride was obtained in 30% yield; unreacted **2** was recovered to the extent of 63% of the theoretical amount.

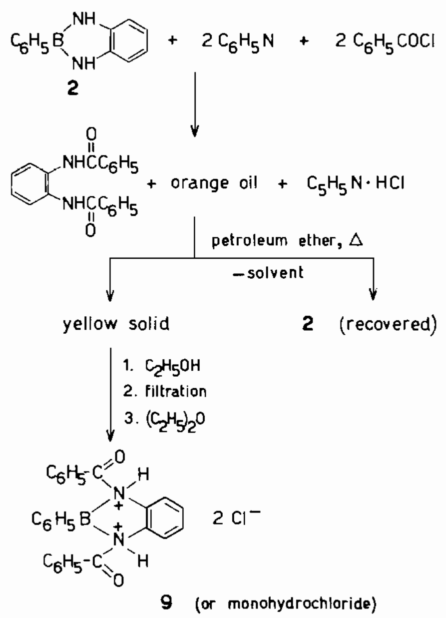
As a result of the previously observed difference between pyridine and triethylamine in dehydrohalogenations involving boron,[7] the benzoylation was next conducted in the presence of pyridine (Scheme II). In this case, a small amount of 1,3-dibenzoyl-2-phenyl-1,3,2-benzodiazaborolidine dihydrochloride (**9**) or the corresponding monohydrochloride salt was isolated. Though the compound was not sufficiently stable to permit elemental analysis, the structure of **9** was supported by the presence of an ir absorption band at 2701 $cm^{-1}$ characteristic of quaternary nitrogen atoms, and by appropriate nmr resonances for N–H protons (in addition to all of the expected aromatic resonances.) Furthermore, the addition of deuterium oxide to the nmr sample not only caused a collapse of the resonances to a multiplet characteristic of phenylboronic acid (that had also been treated with deuterium oxide), but also caused the precipitation of N,N'-dibenzoyl-*o*-phenylenediamine (**8**) Interestingly, compound **9** (or the monohydrochloride salt) decomposed to **3** and **8** upon standing in a closed vial for only 48 hours.

TABLE II. Reaction of 2-Phenyl-1,3,2-benzodiazaborolidine with Sodium Hydride Followed by Nmr.

| Time (Minutes) | Solution Color | No. of NH[a] | Resonance Position (δ, ppm) |
|---|---|---|---|
| 0 | light-brown | 2.0 | 8.13 |
| 15 | dark-brown | 1.4 | 8.13 |
| 45 | dark-brown | 1.25 | 8.13 |
| 60 | dark-green | 1.0 | 8.15 |
| 105 | dark gray-brown | 0.89 | 8.11 |
| 195 | gray-brown | 1.10 | 8.10 |

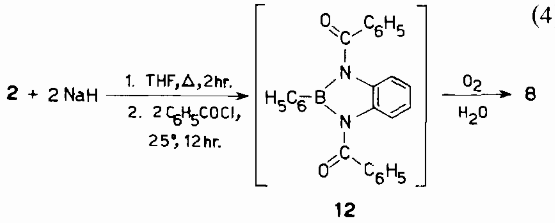
[a] Relative to the aromatic C–H protons; sodium hydride is not considered capable of metallating aromatic hydrogen atoms.

Scheme II



Although the presence of tertiary amines had an effect on the amount of benzoylation, the complete removal of hydrogen chloride by these added bases was not realized. Moreover, in no case were monobenzoylated derivatives of **2** obtained. The absence of the latter compound suggests that benzoylation may occur virtually simultaneously at both nitrogen atoms of **2** despite their different reactivities and that both N–H bonds might, therefore, be susceptible to ionization by bases stronger than tertiary amines. To test this, **2** was reacted with two equivalents of sodium hydride and the reaction was followed by nmr as a function of time (Table II). However, only one proton was observed to be acidic with this base even after 195 minutes of refluxing the reaction mixture.

Finally, benzoylation of **2** was attempted in the presence of sodium hydride as the added base. In this case, though **8** was the only benzoylated product isolated (Eq. 4), the presence of the dibenzoylated heterocycle **12** was indicated in the nmr spectrum of an aliquot of



(4)

the reaction mixture before work-up. This observation suggests that decomposition of **12** is occurring upon work-up.

In conclusion, diazaborolidine **2** readily condenses with benzoyl chloride but the desired benzoylated heterocycle is so reactive towards oxygen and/or water that it is not isolable. Other acid halides should behave similarly. Studies of this and related heterocycles with other types of electrophiles are anticipated in the future.

## Acknowledgement

The authors wish to thank the Shell Oil Company for the support provided to W.R.P. in the form of a research fellowship.

## Experimental

Melting points were obtained on a Thomas–Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 237B spectrophotometer, and only those vibrations are reported which were considered necessary for structural confirmation. Nmr spectra were obtained at 60 mc. on a Varian A-60 spectrometer using tetramethylsilane as an external standard. Commercial anhydrous tetrahydrofuran (Mallinckrodt Chemical Works) was distilled from solutions containing excess *n*-butyllithium and stored over type 5-A molecular sieves. Other commercial anhydrous solvents were purified according to standard procedures.

### *Preparation of Phenylboronic Acid*

The method of Bean and Johnson was used.[8] The preparation was conducted on a scale of 0.29 mol and afforded, upon recrystallization from a minimum of water, 33.5 g (95%) of phenylboronic acid (**3**); mp 210–212°C [lit.[8] mp 214–216°C (corr.)].

### *Preparation of 2-Phenyl-1,3,2-benzodiazaborolidine*

The procedure of Nyilas and Soloway was employed in a modified form.[4f] A 1 liter, 3-necked, round-bottomed flask, equipped with a mechanical stirrer and a Dean–Stark separator, was charged with 30.0 g (0.28 mol) of *o*-phenylenediamine and 33.8 g (0.28 mol) of phenylboronic acid in 500 ml of toluene. The resulting mixture was refluxed for 8 hr with continuous removal of water. The solvent was then concentrated *via* distillation at atmospheric pressure to a volume of 150 ml. Upon cooling the solution, a tan solid precipitated and was collected by filtration. This solid was dissolved in 250 ml of diethyl ether and filtered to remove any phenylboronic acid anhydride. Removal of the solvent *in vacuo* afforded a white solid which, upon two recrystallizations from benzene, gave 50.0 g (92%) of 2-phenyl-1,3,2-benzodiazaborolidine (**2**): mp 213–214°C (lit.[4c] mp 212–214°C); ir (Nujol) 3407 cm$^{-1}$ (NH), 1601, 744 and 697 cm$^{-1}$ (aromatic), 1425 cm$^{-1}$ (possibly $^{11}$BN); nmr (DMSO) $\delta$ 9.08 (S, 2, N$H$), 7.95 (m, 2, $C_6H_5$), 7.16 (m, 7, $C_6H_4$ and $C_6H_5$); mass spectrum (70 ev) m/e (relative intensity); 194 (100.0), molecular ion.[9]

### *Reaction of 2-Phenyl-1,3,2-benzodiazaborolidine (2) with Benzoyl Chloride*

*(A) 1:1 Ratio*

A solution of 0.80 g (0.004 mol) of 2-phenyl-1,3,2-benzodiazaborolidine in 30 ml of anhydrous THF was treated with 0.60 g (0.0045 mol) of benzoyl chloride. The reaction vessel was stoppered and set aside at room temperature with the appearance of a small amount of a pink precipitate. At the end of three days, the solution was pale-yellow and contained a white precipitate. This precipitate was collected by filtration, washed with diethyl ether, acetone, and then water and recrystallized from glacial acetic acid to afford 0.70 g (98%, based on one-half of the available benzoyl chloride) of N,N′-dibenzoyl-*o*-phenylenediamine (**8**): mp 299–301°C (lit.[10] mp 300–301°C); ir (Nujol) 3267 cm$^{-1}$ (NH), 1658 cm$^{-1}$ (C=O), 1577 cm$^{-1}$ (NH bending), 1599, 757, 713 and 685 cm$^{-1}$ (aromatic).

Concentration of the aqueous filtrate afforded 0.1 g (41%) of phenylboronic acid: mp 211–213°C [lit.[8] mp 214–216°C (corr.)]; ir (Nujol) 3250 cm$^{-1}$ (OH, broad), 1604, 762 and 696 cm$^{-1}$ (aromatic), 1359 cm$^{-1}$ (BO).

*(B) 1:2 Ratio*

A solution of 0.80 g (0.004 mol) of 2-phenyl-1,3,2-benzodiazaborolidine in 30 ml of anhydrous THF was treated with 1.2 g (0.0085 mol) of benzoyl chloride. The reaction vessel was stoppered and set aside at room temperature with the appearance of a small amount of a pink precipitate. At the end of three days, isolation and purification of the precipitate as in (A) afforded 1.2 g (93%, based on 2-phenyl-1,3,2-benzodiazaborolidine) of N,N′-dibenzoyl-*o*-phenylenediamine (**8**): mp 299–302°C (lit.[10] mp 300–301°C); ir spectrum identical with (A).

Concentration of the aqueous filtrate afforded 0.1 g (41%) of phenylboronic acid: mp 216–218°C [lit.[8] mp

214–216 °C (corr.)]; ir spectrum identical with that of (A).

### *Reaction of 2-Phenyl-1,3,2-benzodiazaborolidine* (**2**) *with Benzoyl Chloride in Selected Solvents*

#### *(A) Tetrahydrofuran*

A solution of 4.9 g (0.025 mol) of 2-phenyl-1,3,2-benzodiazaborolidine in 125 ml of anhydrous THF in an atmosphere of helium was treated during 2 min with 7.0 g (0.05 mol) of benzoyl chloride in 50 ml of THF. After stirring for 90 min at room temperature, the solution became cloudy and a white precipitate formed. At the end of 6 hr, the precipitate was collected by vacuum filtration, subjected to a Soxhlet extraction with carbon tetrachloride for 24 hr, removed from the thimble, and dried to afford 6.2 g of solid: mp 273–274 °C; ir (Nujol) 3267 $\mathrm{cm^{-1}}$ (NH), 2600 $\mathrm{cm^{-1}}$ (NH, quaternary), 1657 $\mathrm{cm^{-1}}$ (C=O), 1582 (NH, bending), 1597, 759, 714, and 690 $\mathrm{cm^{-1}}$ (aromatic). Since the infrared spectrum was almost identical with that of N,N′-dibenzoyl-*o*-phenylenediamine (**8**), 3.0 g of the solid was treated with 4.0 g of pyridine in ether for 1 hr to give 2.5 g of **8**: mp 294–296 °C; ir (Nujol) 3268 $\mathrm{cm^{-1}}$ (NH), 1656 $\mathrm{cm^{-1}}$ (C=O), 1580 $\mathrm{cm^{-1}}$ (NH bending), 1600, 758, 714 and 690 $\mathrm{cm^{-1}}$ (aromatic).

Concentration of the carbon tetrachloride extract *in vacuo* afforded 1.9 g (73%) of phenylboronic acid anhydride: mp 214–216 °C (lit.[8] mp 217 °C); ir (Nujol) OH absent, 3174, 3151 and 3123 $\mathrm{cm^{-1}}$ (aromatic CH), 1607, 762 and 701 $\mathrm{cm^{-1}}$ (aromatic), 1362 $\mathrm{cm^{-1}}$ (broad, BO); nmr ($CH_2Cl_2$) $\delta$ 2.98 (m, 2, $C_6H_5$), 2.28 (m, 3, $C_6H_5$); the resonance positions are relative to $CH_2Cl_2$ as 0.0 ppm.

The unreacted benzoyl chloride was recovered upon basic hydrolysis as benzoic acid.

#### *(B) 2-Methyltetrahydrofuran*

A solution of 4.9 g (0.025 mol) of 2-phenyl-1,3,2-benzodiazaborolidine in 125 ml of anhydrous 2-methyltetrahydrofuran was treated with 7.0 g (0.05 mol) of benzoyl chloride during a 2 min period. The resulting clear solution became cloudy with formation of a white precipitate after stirring for 35 min at room temperature. After an additional 12 hr, the precipitate was collected by filtration, subjected to a Soxhlet extraction with carbon tetrachloride for 24 hr, removed from the thimble, and dried to afford 6.1 g of a pink solid: mp 273–274 °C. Treatment of this solid as a slurry in diethyl ether with a dilute potassium carbonate solution followed by filtration afforded 4.2 g (53%) of N,N′-dibenzoyl-*o*-phenylenediamine (**8**): mp 295–297 °C; mmp with an authentic sample showed no depression.

Concentration of the carbon tetrachloride extract *in vacuo* yielded 2.0 g (77%) of phenylboronic acid anhydride: mp 216–218 °C; mmp with an authentic sample showed no depression.

#### *(C) 2,5-Dimethyltetrahydrofuran*

A solution of 4.9 g (0.025 mol) of 2-phenyl-1,3,2-benzodiazaborolidine in 125 ml of anhydrous 2,5-dimethyltetrahydrofuran was treated with 7.0 g (0.05 mol) of benzoyl chloride in 125 ml of 2,5-dimethyltetrahydrofuran during 2 min. After stirring for 15 min at room temperature, the mixture became cloudy with formation of a white precipitate. At the end of 12 hr, the precipitate was collected by filtration, subjected to a Soxhlet extraction with carbon tetrachloride for 24 hr, removed from the thimble, and dried to yield 6.0 g of pink solid: mp 273–274 °C; ir spectrum identical to that of (A). Treatment of this pink solid as a slurry in diethyl ether with a dilute potassium carbonate solution caused loss of the pink color and yielded 4.5 g (57%) of N,N′-dibenzoyl-*o*-phenylenediamine (**8**), mp 295–297 °C; mmp with an authentic sample showed no depression.

Concentration of the carbon tetrachloride extract *in vacuo* afforded 1.9 g (73%) of phenylboronic acid anhydride: mp 218 °C (lit.[8] mp 217 °C); ir spectrum identical with that of (A).

#### *(D) Benzene, refluxing*

A solution of 1.94 g (0.01 mol) of 2-phenyl-1,3,2-benzodiazaborolidine in 50 ml of anhydrous benzene was treated with 2.8 g (0.02 mol) of benzoyl chloride in 50 ml of benzene and refluxed for 24 hr. Upon cooling, the clear solution deposited a white solid. This solid did not redissolve when the mixture was briefly heated to reflux again. After 48 hr at room temperature, the mixture was heated to boiling and subjected to a hot vacuum filtration. Recrystallization of the white solid from $CHCl_3$:DMF (1:1) afforded 1.1 g (35%) of N,N′-dibenzoyl-*o*-phenylenediamine (**8**): mp 298–301 °C; mmp with an authentic sample showed no depression.

### *Reaction of 2-Phenyl-1,3,2-benzodiazaborolidine with Benzoyl Chloride in the Presence of Triethylamine*

A solution of 4.9 g (0.025 mol) of 2-phenyl-1,3,2-benzodiazaborolidine in 75 ml of anhydrous THF was treated separately but simultaneously with 2.5 g of triethylamine in 50 ml of THF and 3.5 g (0.025 mol) of benzoyl chloride in 50 ml of THF. After refluxing for 5 hr and standing at room temperature for 12 hr, a white precipitate formed that was collected by filtration, dried *in vacuo*, and recrystallized from absolute ethanol to afford 1.0 g (30%) of triethylamine hydrochloride: mp 257–258 °C (lit.[11] mp 253–254 °C).

Removal of the solvent from the THF filtrate left a viscous oil which, upon trituration with 50 ml of hot benzene, afforded a white solid. Collection of this solid by a hot filtration and recrystallization from glacial acetic acid yielded 1.5 g (26%) of N,N′-dibenzoyl-*o*-

phenylenediamine (**8**): mp 299–302°C (lit.[10] mp 300–301°C).

Concentration of the cooled benzene filtrate *in vacuo* to approximately 20 ml gave 3.5 g of a precipitate which, after collection and recrystallization from a minimum amount of benzene, afforded 3.1 g (63%) of recovered 2-phenyl-1,3,2-benzodiazaborolidine: mp 204–206°C; mmp with authentic sample 205–208°C.

The residual oil from the initial benzene filtrate was stirred with 25 ml of a 10% sodium hydroxide solution for 12 hr yielding a white precipitate upon acidification with 6 *N* hydrochloric acid. Recrystallization of this solid from water afforded 2.05 g of benzoic acid (68% of initial benzoyl chloride recovered): mp 120–121°C; ir spectrum identical with standard benzoic acid.

### *Reaction of 2-Phenyl-1,3,2-benzodiazaborolidine with Benzoyl Chloride in the Presence of Pyridine*

A solution of 4.9 g (0.025 mol) of 2-phenyl-1,3,2-benzodiazaborolidine in 100 ml of anhydrous THF was treated with 4.0 g (0.05 mol) of pyridine, followed by the addition of 7.0 g (0.05 mol) of benzoyl chloride in 25 ml of THF. The resulting clear solution was refluxed for 12 hr with formation of a white precipitate within 60 min. The solid was collected, washed with water, and dried *in vacuo* to afford 1.1 g (14%) of N,N′-dibenzoyl-*o*-phenylenediamine (**8**): mp 299–301°C; mmp with authentic sample showed no depression.

Removal of the solvent from the THF filtrate left a bright orange residue, which, upon trituration with boiling petroleum ether (bp 60–70°C), yielded a bright yellow solid and a clear solution. The solid was collected by filtration, washed with diethyl ether, dried *in vacuo*, dissolved in a minimum amount of absolute ethanol, filtered, and re-precipitated by the drop-wise addition of diethyl ether to afford 1.1 g of what appears to be 1,3-dibenzoyl-2-phenyl-1,3,2-benzodiazaborolidine dihydrochloride; mp 185–187°C (color change: yellow to green), 195–197°C decomposition; ir (Nujol) 3401, 3324, and 3251 cm$^{-1}$ (NH), 2701 cm$^{-1}$ (NH, quaternary), 1654 and 1626 cm$^{-1}$ (C=O), 1568 cm$^{-1}$ (NH bending), 1601 and 726 cm$^{-1}$ (aromatic); nmr (DMSO) $\delta$ 9.22 (m, NH) 8.52 (m, broad, 11, NH and $C_6H_5$), 7.95 (m, broad, 2, $C_6H_5$), 7.28 (m, 7, $C_6H_5$ and $C_6H_4$). Treatment of this sample in the spin tube with deuterium oxide caused a collapse of the resonance to a multiplet centered at 7.4 ppm and an HOD resonance at 4.6 ppm. In addition, a white precipitate immediately formed in the tube which, after collection, was identified as N,N′-dibenzoyl-*o*-phenylenediamine (**8**): mp 299–301°C.

Removal of the solvent from the ethanol–diethyl ether filtrate *in vacuo* afforded 3.7 g (75%) of recovered 2-phenyl-1,3,2-benzodiazaborolidine: mp 206–208°C.

An identical experiment with only 6 hr reflux yielded similar results.

### *Reaction of 2-Phenyl-1,3,2-benzodiazaborolidine (2) With Two Equivalents of Sodium Hydride (Followed by NMR)*

A 100 ml, 3-necked, round-bottomed flask, equipped with mechanical stirrer, Friedrich's condenser, helium inlet, and rubber septum was charged with a slurry of 0.84 g (57% dispersion in mineral oil, 0.02 mol) of sodium hydride in 25 ml of anhydrous THF. This mixture was treated with 1.9 g (0.01 mol) of 2-phenyl-1,3,2-benzodiazaborolidine in 40 ml of anhydrous THF. The resulting light-brown mixture was refluxed for 3.3 hr during which time the reaction was followed by the nmr spectrum of aliquots placed in helium flushed spin tubes at selected time intervals; time (minutes), color of the solution, $\delta$ values in ppm (assignments): 0 minutes, light-brown, 8.13 (broad, 2, N$H$), 7.73 (m, 2, $C_6H_5$), 7.25 and 6.83 (m, 7, $C_6H_5$ and $C_6H_4$); 15 minutes, dark brown, 8.13 (broad, 1.4, N$H$), 7.72 (m, 2, $C_6H_5$), 7.25 and 6.83 (m, 7, $C_6H_5$ and $C_6H_4$); 45 minutes, dark brown, 8.13 (broad, 1.25, N$H$), 7.75 (m, 2, $C_6H_5$), 7.26 and 6.83 (m, 7, $C_6H_5$ and $C_6H_4$); 60 minutes, dark green, 8.15 (broad, 1, N$H$), 7.77 (m, 2, $C_6H_5$), 7.28 and 6.83 (m, 7, $C_6H_5$ and $C_6H_4$); 105 minutes, dark gray-brown, 8.11 (broad, 0.89, N$H$), 7.78 (m, 2, $C_6H_5$), 7.3 and 6.83 (m, 7, $C_6H_5$ and $C_6H_4$); 195 minutes, gray-brown, 8.10 (broad, 1.10, N$H$), 7.76 (m, 2, $C_6H_5$), 7.28 and 6.83 (m, 7, $C_6H_5$ and $C_6H_4$).

### *Reaction of 2-Phenyl-1,3,2-benzodiazaborolidine (2) with Benzoyl Chloride in the Presence of Sodium Hydride*

A slurry of 2.1 g (57% dispersion in mineral oil, 0.05 mol) of NaH in 150 ml of anhydrous THF was treated with 4.9 g (0.025 mol) of 2-phenyl-1,3,2-benzodiazaborolidine in 100 ml of THF, and the resulting mixture was refluxed for 120 minutes. At the end of this time, the solution was treated with 7.0 g (0.05 mol) of benzoyl chloride in 25 ml of THF. After the complete addition of the benzoyl chloride, the resulting brown mixture was refluxed for an additional 75 min and then maintained at room temperature for 12 hr with formation of a tan precipitate and a dark red solution. An nmr spectrum of an aliquot of this solution indicated the absence of the nitrogen protons: nmr (THF) $\delta$ 8.2 (m, 4, $C_6H_5$), 7.3 (m, 15, $C_6H_5$ and $C_6H_4$). The mixture was filtered to collect the tan solid which was washed with 95% ethanol resulting in very slight foaming. The solid which remained was collected, dried, and recrystallized from 1,4-dioxane and dimethylformamide (1:1) to afford 3.0 g of N,N′-dibenzoyl-*o*-phenylenediamine (**8**): mp 298–299°C; mmp with an authentic sample showed no depression. The initial THF filtrate when added to 200 ml of diethyl ether afforded an additional 1.7 g of **8** (60% overall yield). Titration of the aqueous ethanol solution indicated that no base was present.

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