Boric Acid-Catalyzed Direct Condensation of Carboxylic Acids with Benzene-1,2-diamine into Benzimidazoles

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The applicability of boric acid catalysis for the direct condensation of carboxylic acids with benzene-1,2-diamine to give 2-substituted benzimidazoles was investigated. It was found that catalytic amounts (5–10 mol-%) of boric acid efficiently promote the cyclocondensation of aliphatic carboxylic acids in refluxing toluene. In addition, the relatively neutral conditions allow the use of acid-sensitive substrates and give rise to specific transformations and selectivities that are not observed with some classical methods. Benzoic acids were found to be less reactive than aliphatic acids and thus require refluxing xylene for better efficiency. Phenylboronic acid was found to be inactive as a catalyst due to its rapid consumption by condensation with benzene-1,2-diamine to give a 2-phenylbenzodiazaborole.

Introduction. – The boric acid ($B(OH)_3$)-catalyzed condensation of carboxylic acids with amines and anilines is an elegant solution for the synthesis of amides; it avoids the use of expensive coupling reagents or the intermediacy of acid chlorides. The exceptional chemoselectivity and the applicability of this condensation has been demonstrated on a wide spectrum of substrates (aliphatic or aromatic carboxylic acids, primary and secondary amines, anilines, *etc.* [1]; $B(OH)_3$-catalyzed esterifications were also reported [2]). In most cases, 5 mol-% of $B(OH)_3$ and the azeotropic removal of H_2O, employing toluene as the carrier, is efficient, although the less nucleophilic anilines can require a larger amount of the catalyst. Arylboronic acids have been found to generally catalyze this and related types of condensations even more efficiently [3]. Their catalytic activity was thought to be based on the carboxylic acid-activation mechanism relying on the intermediate formation of a mixed carboxylic–boric acid anhydride. The ability of boric acids to activate carboxylic acids, therefore, also seems ideal for their cyclocondensation reactions, and it was thus the first option that we considered in an attempt to prepare certain benzimidazoles directly from acid-sensitive carboxylic acids.

The methods for the preparation of 2-substituted benzimidazoles based on direct cyclocondensations of carboxylic acids with benzene-1,2-diamines are otherwise well known [4], but nearly all of them require harsh conditions, consisting of either very high temperatures or highly acidic media. Many carboxylic acids undergo condensation with benzene-1,2-diamine at temperatures of *ca.* 200°, although some, like HCOOH, for example, react at steam-bath temperatures [5]. Probably the most familiar method is that developed by *Phillips*, which consists of refluxing the reactants in 4M aqueous HCl [6]. In cases where this method fails, as is commonly the case when employing benzoic

acids, heating the reactants with polyphosphoric acid or other strongly dehydrating acid reagents can give good results [7]. Even $B(OH)_3$ at high temperatures (180–200°) has been employed as a dehydrating medium [8]. But a literature search provided us with only one report in which the use of $B(OH)_3$ as an additive (catalyst) is briefly mentioned, *i.e.*, the condensation of three cholic acid derivatives with arene-1,2-diamines in refluxing xylenes [9]. Long reaction times and *ca.* 70–80 mol-% of $B(OH)_3$ were used to give products in moderate-to-excellent yields. On the other side, a related cyclocondensation of carboxylic acids with 2-aminophenols to give benzoxazoles was much more thoroughly studied earlier [10], but the use of 1 equiv. of $B(OH)_3$ in refluxing xylenes was proposed for the best results.

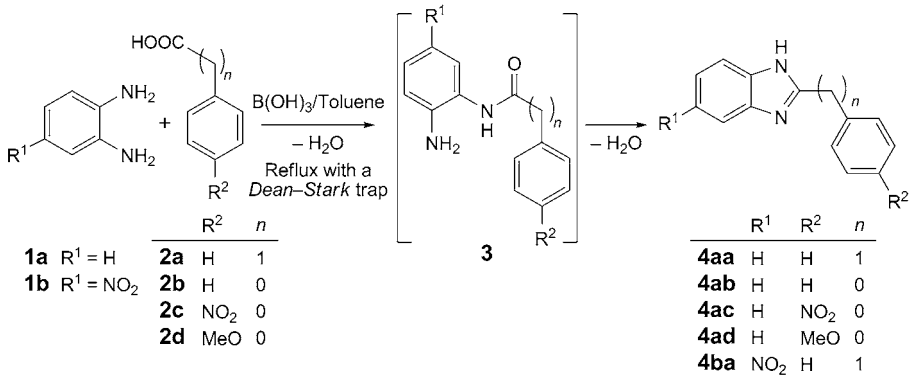
Since there was so little related information in the literature, we decided to study the $B(OH)_3$-catalyzed synthesis of 2-substituted benzimidazoles in order to better understand the applicability of this method. This was deemed to be interesting, particularly because of the importance of benzimidazoles in medicinal chemistry [4e] and as ligands for coordination compounds [11].

Results and Discussion. – As the model reaction, we selected the condensation of benzene-1,2-diamine (**1a**) and 2-phenylacetic acid (**2a**) to 2-benzylbenzimidazole (**4aa**). The product **4aa** is otherwise an active pharmaceutical ingredient due to its vasodilator and spasmolytic activity, industrially produced under the name of *Dibazol* or *Bendazol*. A stoichiometric mixture of **1a** and **2a** with 5 mol-% of $B(OH)_3$ was heated in toluene under reflux conditions, and a *Dean–Stark* trap was used for the azeotropic removal of H_2O. Such a treatment led to a nearly quantitative conversion to **4aa** after 20 h, and the product was isolated in a 90% yield after recrystallization (*Table 1*, *Entry 1*). No *N*-monoacyl intermediate **3** could be observed when analyzing the mixture with NMR spectroscopy at an intermediate reaction time. This is consistent with the published observation that 2-aminoacetanilides are indeed intermediates in the direct condensation of benzene-1,2-diamines with carboxylic acids, but that these intermediates also readily cyclize to benzimidazoles upon heating in xylene, even in the absence of a catalyst [12]. It has been reported that this cyclization occurs far below the boiling point of xylene or slowly by heating neat at 50–60°. Furthermore, acids greatly enhance the rate of the reaction [13]. This suggests that the rate-limiting step in the $B(OH)_3$-catalyzed formation of benzimidazole **4aa** is likewise the *N*-acylation to form **3aa** rather than the subsequent cyclization.

In the absence of the catalyst, in boiling toluene, the reaction also proceeded, but very slowly. After 12 h, *ca.* 35% of the theoretical amount of H_2O distilled, and the NMR spectroscopic analysis confirmed that the reaction conversion corresponds to the same value. Upon further heating to reflux, the rate of sequestration of H_2O in the *Dean–Stark* trap decreased to unpractical levels. Under the same conditions, but with 5 mol-% of $B(OH)_3$ as a catalyst, it takes less than 2 h to collect 50% of the theoretical amount of H_2O. The catalytic activity of 5 mol-% of $B(OH)_3$ in this case is rather obvious, though not exceptionally high. Additionally, doubling the amount of $B(OH)_3$ to 10 mol-% only increases the reaction rate by *ca.* 30% (*i.e.*, it is completed in 15 h instead of 20 h; *Table 1*, *Entry 3*).

Using xylene as the solvent increased the reflux temperature (b.p. 140°) and thus considerably shortened the reaction time. The reaction was complete after just 8 h of

Table 1. *Yields from the Condensations of 2-Phenylacetic Acid* (**2a**), *Benzoic Acid* (**2b**), *4-Nitrobenzoic Acid* (**2c**), *and 4-Methoxybenzoic Acid* (**2d**) *with Benzene-1,2-diamine* (**1a**) *under different reaction conditions*



1a R^1 = H
1b R^1 = NO_2

	R^2	*n*
2a	H	1
2b	H	0
2c	NO_2	0
2d	MeO	0

	R^1	R^2	*n*
4aa	H	H	1
4ab	H	H	0
4ac	H	NO_2	0
4ad	H	MeO	0
4ba	NO_2	H	1

Entry	Diamine	Carboxylic acid	Solvent[a])	Amount of $B(OH)_3$ [mol-%]	Time [h]	Product	Yield [%]
1	**1a**	**2a**	Toluene	5	20	**4aa**	90
2	**1a**	**2a**	Toluene	5	15	**4aa**	83
3	**1a**	**2a**	Toluene	10	15	**4aa**	89
4	**1a**	**2a**	Xylene	5	8	**4aa**	90
5	**1a**	**2b**	Toluene	10	72	**4ab**	71
6	**1a**	**2c**	Toluene	10	120[b])	**4ac**	40
7	**1a**	**2c**	Xylene	10	24	**4ac**	62
8	**1a**	**2d**	Xylene	10	72	**4ad**	60
9	**1b**	**2a**	Toluene	10	120[b])	**4ba**	61

[a]) Reactions were conducted in boiling solvents using the *Dean–Stark* trap for the removal of H_2O. [b]) Reaction was discontinued and worked up before reaching complete conversion.

reflux (*Table 1*, *Entry 4*). Deciding between longer reaction times and higher reaction temperatures, we preferred to continue using toluene, as our goal was to develop a method that is efficient under milder conditions so as to be suitable for sensitive substrates.

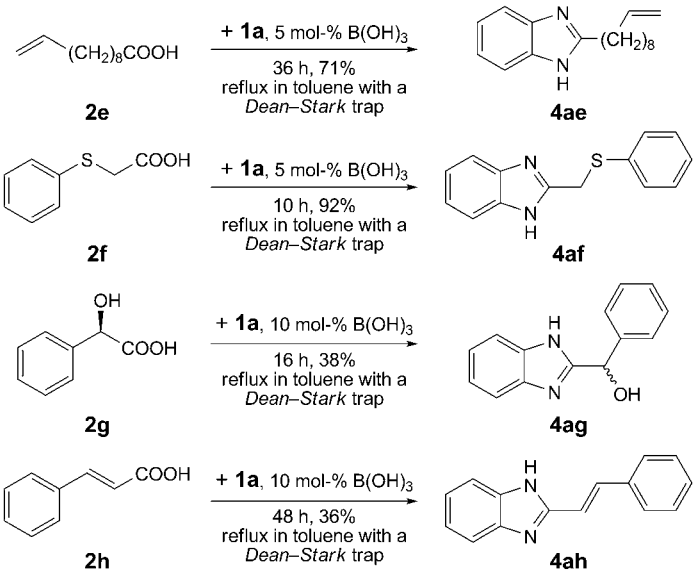
The condensation of **1a** with benzoic acid (**2b**) was very slow. It took 3 d in refluxing toluene with 10 mol-% of $B(OH)_3$ to obtain the theoretical amount of H_2O. The product, 2-phenylbenzimidazole (**4ab**), was obtained in a 71% yield after the recrystallization (*Table 1*, *Entry 5*). In an attempt with 4-nitrobenzoic acid (**2c**) under the same conditions, the reaction with **1a** proceeded even more slowly and was still incomplete after 5 d, when the mixture was worked up to give a 40% yield of 2-(4-nitrophenyl)benzimidazole (**4ac**; *Table 1*, *Entry 6*). The lower reactivity of arenecarboxylic acids has also been noted in the application of the *Phillips* method [4c][4d]. Clearly, with these aromatic acids, refluxing xylene should be used as the solvent in order to increase the reaction rate. The condensation of 4-nitrobenzoic acid (**2c**) in xylene proceeded considerably faster, and a yield of 62% was obtained after 24 h

(*Table 1*, *Entry 7*). 4-Methoxybenzoic acid (**2d**) was even less reactive and required 3 d in refluxing xylene for complete conversion. The benzimidazole **4ad** was obtained in a 60% yield after recrystallization. This indicated that the electronic properties of the *para*-substituent on benzoic acids are not uniformly related to the reaction rate, and that the reactivity in this condensation to 2-phenylbenzimidazoles is an interplay of different factors.

To evaluate the influence of the nucleophilicity and basicity of the diamine reactant, we performed a reaction with 4-nitrobenzene-1,2-diamine (**1b**) as a poorer nucleophile. Its reaction with 2-phenylacetic acid (**2a**) was extremely slow, even in the presence of 10 mol-% of $B(OH)_3$. After 5 d of reflux in toluene, there was still some unreacted starting material present, although the accumulation of H_2O in the *Dean–Stark* trap practically stopped (85% of the theoretical amount was collected). Nevertheless, the product **4ba** was isolated in a 61% yield after recrystallization (*Table 1*, *Entry 9*).

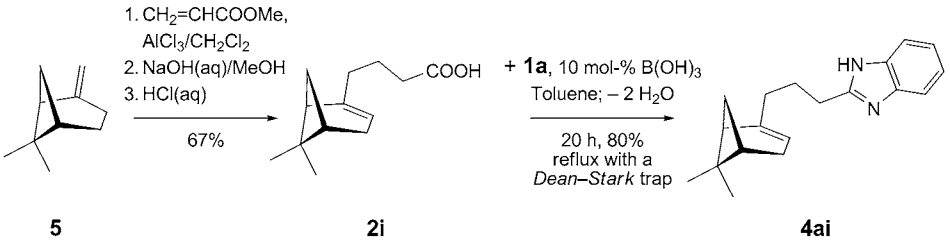
The cyclocondensation of **1a** with undec-10-enoic acid (**2e**) gave a 71% yield of **4ae** when using 10 mol-% of $B(OH)_3$ after 36 h (*Scheme 1*). 2-(Phenylsulfanyl)acetic acid (**2f**) reacted more rapidly and gave benzimidazole **4af** in a 92% yield after 10 h of reflux. On the other hand, even though the theoretical amount of H_2O accumulated in the *Dean–Stark* trap, the (−)-(*R*)-phenylglycolic acid (**2g**) only gave a 38% yield of **4ag** after recrystallization. It appears that a lot of the phenylglycolic acid was consumed in side reactions, yielding resinous materials. Furthermore, the product **4ag** was racemic as indicated by its optical inactivity. Similarly, the reaction with cinnamic acid **2h** gave **4ah** with a yield of only 36%, even after a long reaction time. Interestingly, in both cases the unidentified resinous side products did not disturb the purification, and the benzimidazoles could be obtained in a pure form after a single recrystallization.

Scheme 1. *Synthesis of Benzimidazoles from Various Carboxylic Acids and Benzene-1,2-diamine* (**1a**)



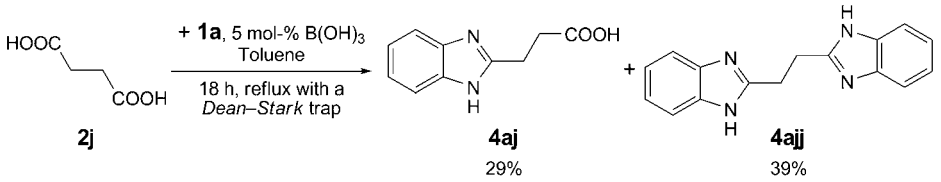
The reaction with a carboxylic acid **2i** containing the α-pinene moiety, which is otherwise known to be susceptible to the *Wagner–Meerwein* type of rearrangements in acidic media [14], also proceeded readily and without side reactions (*Scheme 2*). The product **4ai** was obtained in an 80% yield after 20 h reaction time. An attempt with a more classical approach by refluxing **1a** and **2i** in 4M aq. HCl with 1,4-dioxane as a cosolvent was not successful and led to a mixture of side products derived from **2i**. The carboxylic acid **2i** used in these reactions was prepared *via* the ene reaction between methyl acrylate and β-pinene (**5**; adapted from [15]), followed by hydrolysis.

Scheme 2. *Application of the Method to an Acid Sensitive Substrate*



Reactions with dicarboxylic acids were also considered. To determine the discrimination between a reaction with one or both COOH groups, we condensed **1a** with succinic acid (**2j**) in a 1:1 molar ratio (*Scheme 3*). This gave a mixture of 3-(benzimidazol-2-yl)propanoic acid (**4aj**) and 1,2-di(benzimidazol-2-yl)ethane (**4ajj**), which were easily separated and isolated in 29 and 39% yields, respectively (based on **1a** as the limiting reagent). This represents a 60:40 molar ratio for the isolated products **4aj**/**4ajj**. Clearly, in this case the selectivity for **4aj** is not high, regardless of the stoichiometric ratio of starting materials.

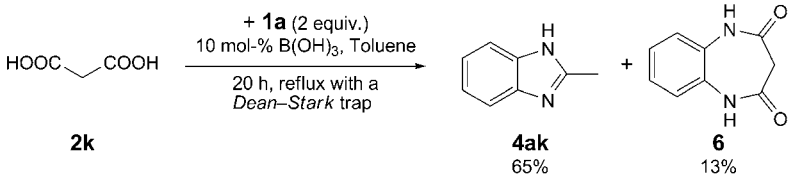
Scheme 3. *Condensations of Succinic Acid with Benzene-1,2-diamine* (**1a**)



With malonic acid (**2k**) and 2 equiv. of **1a**, 2-methylbenzimidazole (**4ak**) was obtained as the major product and 1,5-benzodiazepine **6** as the minor one (*Scheme 4*). Interestingly, the conventional condensation methods like refluxing in 4M aq. HCl are claimed, in various articles, to give as products either 1,2-di(benzimidazol-2-yl)-methane [16], or more frequently, the 1,5-benzodiazepine **6** [4a][4d][6][17]. We observed no di(benzimidazol-2-yl)methane formation among the products.

Initially, it was not clear at which stage the decarboxylation leading to **4ak** occurred, although it is well-known that malonic acid undergoes spontaneous decarboxylation at higher temperatures. At first, we considered the possibility that $B(OH)_3$ might catalyze the decarboxylation. This was checked by refluxing **2k** with 10 mol-% of $B(OH)_3$ in

Scheme 4. *Condensation of Malonic Acid with Benzene-1,2-diamine* (**1a**)

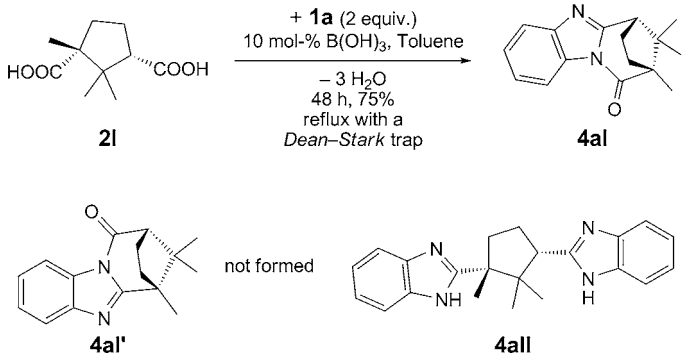


2k **4ak** 65% **6** 13%

toluene for 24 h. After this time, **2k** remained undissolved, and no AcOH could be detected by NMR spectroscopy of the mixture, thus indicating that the decarboxylation either occurs only in the presence of the basic **1a**, or it occurs at some later reaction stage. The first hypothesis that decarboxylation requires the presence of a base was checked by refluxing a mixture of **2k** in toluene with 2 equiv. of *N*,*N*-dimethylaniline as a nonreactive substitute of **1a** (in the absence of $B(OH)_3$). This indeed led to complete decarboxylation of **2k** to give AcOH in less than 3 h of reflux. A literature search revealed that huge rate enhancements of the malonic acid decarboxylation had already been observed when heating its solutions in quinoline, pyridine, *N*,*N*-dimethylaniline, aniline and *N*,*N*-dimethylnaphthalen-1-amine (rates descending in this same order) [18]. Based on these findings, we concluded that 2-methylbenzimidazole (**4ak**) must have been formed as the main product due to the rapid decarboxylation of **2k** to AcOH. The reaction was induced by the presence of **1a**, which thus acted at the same time as a catalytic *N*-base and the substrate for the subsequent condensation. The minor product **6** (*cf. Scheme 4*) is, therefore, produced by the reaction of **1a** with **2k** before all of it is consumed in the decarboxylation.

An interesting selectivity was obtained when condensing (+)-camphoric acid (**2l**) with 2 equiv. of **1a** (*Scheme 5*). This gave benzimidazole (+)-**4al** as the main product in 75% yield. Neither the dibenzimidazolyl product **4all** nor the other possible isomer **4al′**, the latter potentially resulting from a primary nucleophilic attack at the more sterically hindered COOH group, could be unambiguously identified among the minor side products in the mixture. The ^{1}H-NMR chemical shift of the CH H-atom in **4al** is

Scheme 5. *Condensation of Camphoric Acid with Benzene-1,2-diamine* (**1a**)



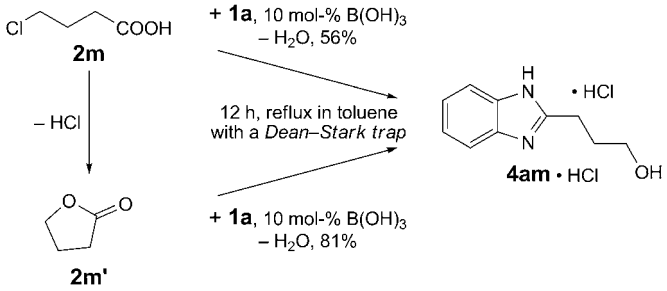
2l **4al** **4al'** **4all**

consistent with the connection to benzimidazol-2-yl rather than to the CO group, which is the case in the isomer **4al′**. The products **4al** and **4al′** were otherwise already reported to form in 45 and 33% yield, respectively, in the condensation of **2l** with **1a**, by using a zeolite catalyst under microwave heating [19].

N-Acylbenzimidazoles are generally prone to nucleophilic attack at the CO group, just like many other azolides [20]. We, therefore, checked the resistance of **4al** toward amine nucleophiles in order to better understand why it does not react further with **1a** to give the di(benzimidazolyl) product **4all**, in analogy to the product **4ajj** in the reaction with succinic acid (**2j**). Heating **4al** in a tenfold excess of morpholine in the closed vessel of a microwave reactor at temperatures up to 200° resulted in no reaction at all (for the equipment used and methodology in general, see [21]). It is thus evident that the reactivity of **4al** more closely resembles that of classical amides rather than typical azolides. The lack of reactivity, which we attributed to the steric hindrance around the CO group, thus explains the absence in the formation of a di(benzimidazolyl) product **4all**.

The reaction of 4-chlorobutanoic acid (**2m**) gave 3-(benzimidazol-2-yl)propan-1-ol hydrochloride (**4am** · HCl) in a 56% yield, and the condensation produced only 1 equiv. of H_2O in the *Dean–Stark* trap (*Scheme 6*). The hydrochloride was then transformed to the free base **4am** by treatment with aq. NaOH. The formation of an alcohol is not surprising, as the acid **2m** readily cyclizes to γ-butyrolactone (**2m′**) in the presence of bases, and this lactone should give the alcohol **4am** upon formal condensation with **1a** or its monohydrochloride (formed *in situ* from the eliminated HCl). Indeed, this was demonstrated by repeating the reaction using **2m′** and the monohydrochloride of **1a**. The reaction gave **4am** · HCl in 81% yield. However, refluxing **2m′** with the free base **1a** under the same conditions resulted in no reaction and no substantial formation of H_2O. It thus appears that the equivalent of HCl eliminated from **2m** also plays a crucial role in the reaction with the lactone. In addition, the cyclization of **2m** to **2m′** under the applied reaction conditions was confirmed by refluxing **2m** and **1a** in toluene in the absence of $B(OH)_3$. The conversion of **2m** to **2m′**, as observed by ^{1}H-NMR spectroscopy of the mixture, was found to be practically quantitative after 1 h.

Scheme 6. *Condensation of Benzene-1,2-diamine* (**1a**) *with 4-Chlorobutanoic Acid* (**2m**) *or* γ*-Butyrolactone* (**2m′**) *Leading to the Same Product*

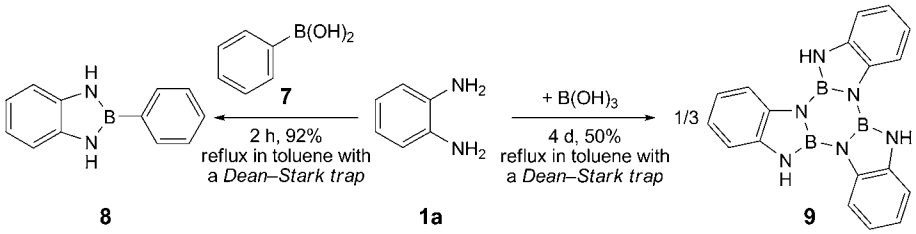


The workup was, in most cases, very simple and required no chromatographic separation. In fact, most products precipitated from the mixture in their crude form

upon cooling, and were simply filtered and recrystallized to give a pure isolated material.

Since arylboronic acids have commonly been applied as catalysts in a variety of amidations and esterifications [3], we decided to check the catalytic activity of phenylboronic acid ($PhB(OH)_2$; **7**) in the synthesis of benzimidazoles. Surprisingly, the use of 5 mol-% of **7** showed no observable catalytic activity in our model condensation reaction of **1a** with **2a** in refluxing toluene, and the reaction conversion was the same as in the control experiment with no catalyst. To explain the catalytic inactivity of phenylboronic acid, we first performed its condensation with benzene-1,2-diamine (**1a**) in refluxing toluene to obtain the benzodiazaborole **8** [22]. Compound **8** formed rapidly under these conditions and crystallized directly from the mixture in a 92% yield (*Scheme 7*). The analogous condensation of **1a** with $B(OH)_3$ was much slower and required 4 d of reflux in order to collect less than 3 equiv. of H_2O. In this reaction, H_2O formed rapidly at the beginning, and the NMR spectroscopic analysis of the mixture indicated that **1a** was being rapidly consumed, forming a mixture of products. However, after 4 d the final condensation product **9** was isolated in 50% yield after recrystallization from acetone. This trimeric diazaborole is otherwise better known to form in the reactions of **1a** with trialkyl borates, tris(dimethylamido)borane, or BCl_3 in refluxing toluene or xylene [23], but a more thorough search showed that the preparation from $B(OH)_3$ was described in a patent [24].

Scheme 7. *Condensation of Benzene-1,2-diamine* (**1a**) *with Phenylboronic Acid* (**7**) *or Boric Acid*



We then investigated the reactivity of these diazaboroles toward 2-phenylacetic acid (**2a**) and their potential catalytic activity in our model reaction. Refluxing benzodiazaborole **8** with **2a** without any catalyst resulted in no conversion to **4aa** after 3 h of reaction time (*Table 2*, *Entry 1*). The analogous experiment using 5 mol-% of **8** as a catalyst gave approximately the same conversion to **4aa** as did the control experiments using 5 mol-% of $PhB(OH)_2$ (**7**) or no catalyst (*Table 2*, *Entries 2*, *3*, and *4*, resp.). Moreover, in the reaction between **1a** and **2a** using 5 mol-% of $PhB(OH)_2$ (**7**), the formation of **8** was observed. Under the same conditions, the comparative experiment using 5 mol-% of $B(OH)_3$, instead of **7**, gave a 65% conversion to **4aa** (*Table 2*, *Entry 5*). In contrast to the $PhB(OH)_2$-condensation product **8**, the borazine **9** reacted with the 2-phenylacetic acid (**2a**) directly to give **4aa** with a 22% conversion after 3 h of reflux (*Table 2*, *Entry 6*). The low solubility of **9** in boiling toluene probably has an influence on slowing down the rate of this reaction, but the low conversion could also indicate that such a reaction pathway may not be part of the main catalytic cycle. Compound **9** was also checked for potential catalytic activity, but using a 5/3 mol-% to

compensate for its trimeric structure. It did catalyze the model reaction (*Table 2*, *Entry 6*), though with a slightly lower conversion (54%) when compared to the $B(OH)_3$-catalyzed reaction (65%). This observation also supported the possibility that the catalytically most active boron species is not necessarily **9**, but that this merely acted as a precatalyst that was slowly transformed into a common catalytically active species.

Table 2. *Conversions of 2-Phenylacetic Acid* (**2a**) *to* **4aa** *after 3 h in Refluxing Toluene under Different Reaction Conditions*

Entry	Reactants[a])	Catalyst	Conversion [%]
1	**8** + **2a**	–	–
2	**1a** + **2a**	5 mol-% of **8**	11
3	**1a** + **2a**	5 mol-% of $PhB(OH)_2$ (**5**)	10
4	**1a** + **2a**	–	10
5	**1a** + **2a**	5 mol-% of $B(OH)_3$	65
6	**9** + **2a**	–	22
7	**1a** + **2a**	5/3 mol-% of **9**	54

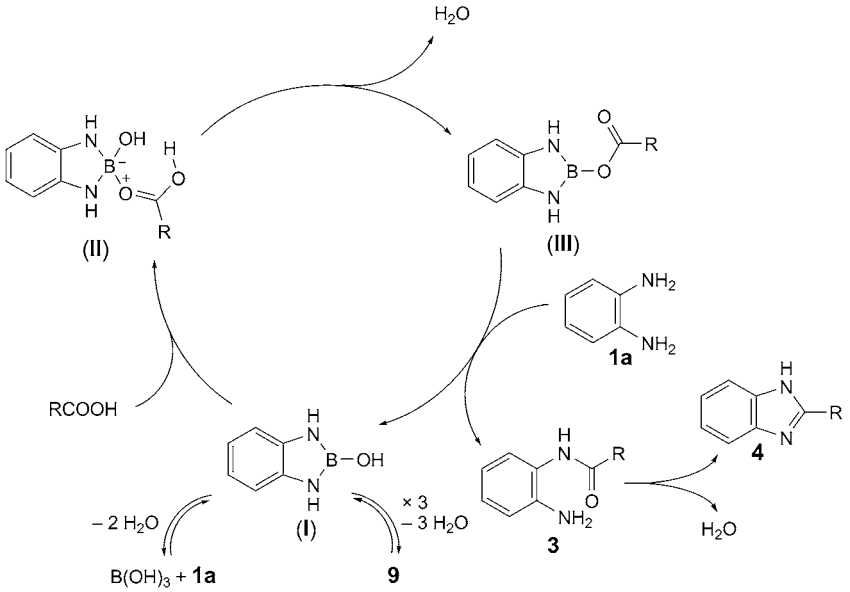
[a]) A mixture of 2 mmol of each reactant with the specified catalyst were refluxed in 5 ml of toluene for 3 h; then, a sample of the mixture was evaporated and analyzed by ^{1}H-NMR spectroscopy.

The catalytic inactivity of $PhB(OH)_2$ (**5**) thus appears to be due to its rapid consumption and the formation of the diazaborole **8**, which also lacked catalytic activity. This might be explained on the basis of the stability of the B–N bonds, which are straightened by their partial double-bond character and the resonance-based stabilization of the diazaborole system. It is conceivable that the compound **8** eventually forms ate complexes with nucleophiles [25], such as carboxylic acids or carboxylate ions. Thus, the absence of any catalytic effect additionally confirms the current opinion that such ate species cannot be considered to be active acylating reagents. Most studies on the $B(OH)_3$-catalyzed amidation indicate that the carboxylic acid is most likely activated *via* the formation of various types of acyloxyboranes, the formation of which would require an energetically unfavorable ring opening in the case of the diazaborole **8**. If so, the B–N bonds of the borazine ring in **9** must be much more prone to ring opening through a nucleophilic attack. The reaction kinetics for the hydrolyses of **8** were thoroughly studied [25]. This data could be useful as an indication of the stability of **8** toward nucleophilic ring-opening reactions. However, for the compound **9** only qualitative descriptions of its susceptibility toward hydrolysis and methanolysis have been reported [14].

Since the results obtained during the synthesis of **8** and **9** indicated that the boric acids are being rapidly consumed in condensations with benzene-1,2-diamine, we propose that the main catalytic cycle involves diazaboroles as active species (*Scheme 8*). The benzodiazaborole **I** has not been isolated, and it is reasonable to expect it to be in a hydrolytic equilibrium with $B(OH)_3$ and the trimeric **9** (similar to the trimerizations of $B(OH)_3$ to metaboric acid or arylboronic acids to boroxines [3g]). In our proposal, the benzoborazole **I** coordinates with a carboxylic acid to give the unstable ate complex **II**, which, by the elimination of H_2O, decomposes to the acyloxyborane **III**. Finally, the reaction of **III** with **1a** regenerates **I** and forms the 2-

aminoanilide **3**, which then spontaneously cyclizes to the corresponding 1*H*-benzimidazole **4**. An approach to **III** *via* a carboxylate anion reacting with **I** and subsequent elimination of a HO^- anion might be another possibility. However, considering the weak basicity of anilines and the lack of ion solvation, the concentration of carboxylate anions must be extremely low in a nonpolar solvent like toluene [18]. Also, the HO^- anion, in comparison with H_2O, is less likely to eliminate in place of the carboxylate anion from the intermediate ate complex without prior protonation, thus, in any case making **II** or another protonated ate form a most likely intermediate in the ligand-exchange process.

Scheme 8. *The Proposed Main Catalytic Cycle for the Condensation of Benzene-1,2-diamines and Carboxylic Acids*



Interestingly, it was previously observed that, for the condensation of 4-phenylbutanoic acid with $PhCH_2NH_2$, various 1,3,2-dioxaborolan-2-ols are more effective catalysts than $B(OH)_3$ itself [3h]. An analogous catalytic cycle was proposed, and 1,3,2-dioxaborolan-2-ols can be considered isosteric and isoelectronic to the 1,3,2-diazaboroles of type **I**.

One also has to consider the eventual possibility that benzimidazoles **4** might form by the initial acyl group migration within **III** onto one of the *N*-atoms, followed by further transformations toward **4**. This alternative to the intermolecular acylation of **1a** with **III** is difficult to exclude, based on the current experimental data, particularly since we found that the borazine **9** itself reacts with **2a**. In this regard, it is known that acyclic B–N bond-containing compounds like tris(dialkylamido)boranes react with carboxylic acids to give amides, but it was also demonstrated that these reactions occur through the initially formed acyloxyborane intermediates acylating the liberated amines [26].

Conclusions. – An evaluation of the $B(OH)_3$-catalyzed cyclocondensation reaction between carboxylic acids and benzene-1,2-diamine demonstrated that this method has good practical applicability and was thus used to prepare a series of 2-substituted benzimidazoles. Besides optimal atom economy, its specific advantage over the otherwise classical use of strong dehydrating acids is also in the use of non-acidic reaction conditions, allowing the application of acid-sensitive substrates (as in the case of **4ai**). These conditions gave rise to some specific transformations as well. It was thus found that the cyclocondensation with malonic acid gives 2-methyl-1*H*-benzimidazole (**4ak**) and 1,5-benzodiazepine-2,4-dione (**9**), whereas the condensation with camphoric acid gives an excellent selectivity in the formation of the azolide **4al**. The results from the three benzoic acids applied indicate that they are less reactive and thus require the use of xylene to achieve a higher reflux temperature for better conversions. Finally, we also elucidated the nature of the catalytic cycle, demonstrating that $B(OH)_3$ initially reacts with benzene-1,2-diamine, forming catalytically active diazaboroles.

Experimental Part

General. All the reagents used were commercially available, with the exception of **2i**, the preparation of which is described below. The xylene used was a commercial mixture of isomers. Reactions were monitored with TLC (SiO_2). M.p.: uncorrected; *Kofler* micro hot stage. Optical rotations: *Perkin-Elmer 241 MC Polarimeter*; concentrations in g/100 ml. NMR Spectra: at 29°; *Bruker Avance DPX 300-MHz* spectrometer with TMS as the internal standard. The coupling constants J_{AX} are given as an average distance between spectral lines (in Hz), and these distances differ from each other for *ca*. 10%. MS: *VG-Analytical AutoSpec Q* instrument. Elemental analyses (C, H, N): *Perkin Elmer 2400 CHN Analyzer*.

*4-[(1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl]butanoic Acid* (**2i**). To a stirred ice-cooled soln. of (−)-(1*S*)-*β*-pinene (**5**; 20.43 g, 150 mmol) and methyl acrylate (13.49 g, 150 mmol) in CH_2Cl_2 (60 ml) 2,6-di(*tert*-butyl)-4-methylphenol (10 mg) was added as a polymerization inhibitor, followed by the addition of anh. $AlCl_3$ (1.0 g, 5 mol-%). The clear, yellowish soln. thus obtained was left standing for 48 h at rt. Then, it was washed with H_2O (80 ml), evaporated, H_2O (50 ml) was added to the oily residue, and this mixture was again evaporated to remove the unreacted starting materials and other volatiles with H_2O vapors. MeOH (100 ml) and NaOH (12 g, 300 mmol) were then added to the residue, and the mixture was stirred on reflux for 3 h. Upon cooling, the mixture was diluted with H_2O (500 ml), acidified with conc. HCl(aq) to pH 3, and extracted with petroleum ether (PE; 300 ml). The PE extract was washed with H_2O (300 ml) and back-extracted into dil. aq. NH_3 (1%, 500 ml). An emulsion can form during extraction, but it breaks by mild heating. The aq. soln. was then washed with PE (150 ml), acidified with aq. HCl to pH 3, and again extracted with PE (250 ml); the org. extract was dried (Na_2SO_4) and evaporated *in vacuo* to give **2i** (20.90 g, 67%). Slightly yellowish oil. $[\alpha]_D^{25} = -25.2$ ($c = 4.25$, CH_2Cl_2). IR (NaCl): 1708 (br.), 1433, 1413, 1382, 1365. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.83 (*s*, 3 H); 1.13 (*d*, $J = 8.5$, 1 H); 1.27 (*s*, 3 H); 1.62–1.76 (*m*, 3 H); 1.90–2.45 (*m*, 8 H); 5.21 (br. *s*, 1 H); 11.45 (br. *s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.2; 22.2; 26.3; 31.3; 31.7; 33.7; 36.1; 37.9; 40.8; 45.7; 116.9; 147.2; 180.4. HR-ESI-MS: 209.1541 ($[M+H]^+$, $C_{13}H_{21}O_2^+$; calc. 209.1542), 191, 141.

General Procedure for the Synthesis of Benzimidazoles. A mixture of *benzene-1,2-diamine* (**1**; 100 mmol), carboxylic acid **2** (100 or 50 mmol), and $B(OH)_3$ (320 mg for 5 mol-%, or 640 mg for 10 mol-%) in toluene or xylenes (100 ml) was stirred under reflux in a reaction flask equipped with a *Dean–Stark* trap for the specified time required for the approximately theoretical amount of H_2O to accumulate in the receiver (see *Discussion*). The mixture was then worked up as described below.

*2-Benzyl-1*H*-benzimidazole* (**4aa**). To the cooled heterogeneous mixture, PE (50 ml) was added. The crude product was filtered and recrystallized from EtOH/H_2O 2:1 to give **4aa** (18.80 g, 90%). Off-

white needles. M.p. 183–186° ([27]: 187°). IR (KBr): 1536, 1401, 1456, 1426. ^{1}H-NMR (300 MHz, (D_6)DMSO): 4.17 (*s*, 2 H); 7.05–7.17 (*m*, 2 H); 7.19–7.35 (*m*, 5 H); 7.37–7.58 (*m*, 2 H); 12.26 (br. *s*, 1 H).

*2-Phenyl-1*H*-benzimidazole* (**4ab**). To the cooled heterogeneous mixture, PE (50 ml) was added, and the separated crude product was filtered off and recrystallized from EtOH/H_2O 2:1 to give **4ab** (13.70 g, 71%). Off-white crystals. M.p. 296° ([7]: 294.5–295.5°). IR (KBr): 1477, 1463, 1443, 1410, 1374. ^{1}H-NMR (300 MHz, (D_6)DMSO): 7.22 (*m*, 2 H); 7.45–7.73 (*m*, 5 H); 8.16–8.24 (*m*, 2 H); 12.91 (*s*, 1 H).

*2-(4-Nitrophenyl)-1*H*-benzimidazole* (**4ac**). The brown precipitate from the cooled mixture was filtered off, washed with PE (50 ml), 1M aq. NaOH) (100 ml), H_2O (2 × 100 ml), and MeCN/H_2O (4:1, 3 × 50 ml), and dried. This crude product was recrystallized from a minimal amount of DMF, washed with MeOH (2 × 20 ml), and dried under vacuum to give **4ac** (17.00 g, 62%). Brown crystalline powder. M.p. 321–323° ([28]: 321–322°). IR (KBr): 1636 (br.), 1606, 1515, 1435. ^{1}H-NMR (300 MHz, (D_6)DMSO): 7.21–7.35 (*m*, 2 H), 7.55–7.80 (*m*, 2 H), 8.39–8.46 (*m*, 4 H), 13.28 (br. *s*, 1 H).

*2-(4-Methoxyphenyl)-1*H*-benzimidazole* (**4ad**). The brown precipitate from the cooled mixture was filtered off, washed with PE (50 ml), 1M aq. NaOH (100 ml), and H_2O (2 × 100 ml), and the crude product was recrystallized from a mixture of EtOH/H_2O to give **4ad** (16.00 g, 61%). Brownish powder. M.p. 231–232° ([29]: 228.6–230.5°). IR (KBr) 1612, 1502, 1476, 1452, 1437, 1254. ^{1}H-NMR (300 MHz, (D_6)DMSO): 3.85 (*s*, 3 H); 7.12 (*d*, *J* = 8.7, 2 H); 7.16–7.21 (*m*, 2 H); 7.57 (*m*, 2 H); 8.14 (*d*, *J* = 8.7, 2 H); 12.74 (*s*, 1 H). ^{13}C-NMR (75 MHz, (D_6)DMSO): 55.3; 111.0; 114.3; 118.5; 121.7; 122.7; 128.0; 151.3; 160.6.

*2-Benzyl-5-nitro-1*H*-benzimidazole* (**4ba**). The precipitated crude product was filtered from the cooled mixture and dissolved in warm CH_2Cl_2 (600 ml). The red insoluble material was removed by filtration, and the filtrate was evaporated *in vacuo*. The remaining yellow solid was recrystallized from EtOH/H_2O to give **4ba** (15.35 g, 61%). Yellowish powder. M.p. 184–185° ([27]: 184°). IR (KBr): 1624, 1599, 1535, 1511, 1468, 1452, 1411, 1341. ^{1}H-NMR (300 MHz, (D_6)DMSO): 4.27 (*s*, 2 H); 7.22–7.38 (*m*, 5 H); 7.66 (*d*, *J* = 8.9, 1 H); 8.08 (*dd*, *J* = 2.2, 8.9, 1 H); 8.40 (*d*, *J* = 2.2, 1 H); 12.95 (br. *s*, 1 H).

*2-(Dec-9-en-1-yl)-1*H*-benzimidazole* (**4ae**). The cooled homogenous mixture was washed with H_2O (300 ml), sat. aq. $NaHCO_3$ (100 ml), and H_2O (300 ml), and evaporated *in vacuo* to give a viscous oil, which was crystallized from EtOH/H_2O to give **4ae** (15.10 g, 71%). Colorless needless. M.p. 106–107.5°. IR (KBr): 1641, 1621, 1591, 1541, 1452, 1422. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.16–1.42 (*m*, 10 H); 1.80–1.91 (*m*, 2 H); 1.92–2.02 (*m*, 2 H); 2.94 (*t*, *J* = 7.8, 2 H); 4.81–5.00 (*m*, 2 H); 5.69–5.83 (*m*, 1 H); 7.21, 7.54 (*AA′XX′*, J_{AX} = 3.0, 4 H); 9.85 (br. *s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 28.7; 29.0; 29.2; 29.4; 29.5; 29.5; 29.6; 33.9; 114.3; 114.7; 122.2; 138.8; 139.3; 156.0. HR-ESI-MS: 257.2030 ($[M+H]^+$, $C_{17}H_{25}N_2^+$; calc. 257.2018). Anal. calc. for $C_{17}H_{24}N_2$ (256.38): C 79.64, H 9.44, N 10.93; found: C 79.92, H 9.58, N 10.81.

*2-[(Phenylsulfanyl)methyl]-1*H*-benzimidazole* (**4af**). To the cooled heterogenous mixture, PE (50 ml) was added. The crude product was then filtered and recrystallized from EtOH/H_2O 2:1 to give **4af** (22.0 g, 92%). Off-white needles. M.p. 131–133° ([30]: 135–136°). IR (KBr): 1638, 1618, 1587, 1537, 1483, 1458, 1435. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.39 (*s*, 2 H); 7.11–7.32 (*m*, 7 H); 7.51–7.54 (*m*, 2 H); 8.80 (br. *s*, 1 H).

*(1*H*-Benzimidazol-2-yl)(phenyl)methanol* (**4ag**). To the cooled heterogenous mixture, PE (50 ml) was added. The crude product was then filtered and recrystallized from EtOH to give **4ag** (8.50 g, 38%). White crystalline powder. M.p. 206–209° ([6]: 202–203°). $[\alpha]_D^{25} = 0.0$ (*c* = 5.00, MeOH). IR (KBr): 1623br, 1455, 1435, 1292, 1276. ^{1}H-NMR (300 MHz, (D_6)DMSO): 5.92 (*d*, *J* = 4.1, 1 H); 6.49 (*d*, *J* = 4.1, 1 H); 7.08–7.16 (*m*, 2 H); 7.22–7.28 (*m*, 1 H); 7.30–7.37 (*m*, 2 H); 7.39–7.56 (*m*, 4 H); 12.35 (*s*, 1 H).

*2-[(*E*)-2-Phenylethenyl]-1*H*-benzimidazole* (**4ah**). To the cooled heterogeneous mixture, PE (50 ml) was added. The crude product was then filtered and recrystallized from EtOH/H_2O 6:1 to give **4ah** (8.00 g, 36%). Colorless crystals. M.p. 200–201° ([31]: 200–201°). IR (KBr): 1643, 1588, 1524, 1493, 1422. ^{1}H-NMR (300 MHz, (D_6)DMSO): 7.16–7.21 (*m*, 2 H); 7.24 (*d*, *J* = 16.6, 1 H); 7.33–7.39 (*m*, 1 H); 7.41–7.48 (*m*, 2 H); 7.47–7.65 (*m*, 2 H); 7.65–7.72 (*m*, 3 H); 12.63 (*s*, 1 H).

*2-{3-[(1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl]propyl}-1*H*-benzimidazole* (**4ai**). This reaction was performed on a 50-mmol scale. The mixture was washed with H_2O (2 × 100 ml) and evaporated *in vacuo*. The remaining brown resin was dissolved in AcOEt (100 ml), and 4-nitrobenzoic acid (8.4 g, 50 mmol) was added and dissolved by heating. Upon cooling, a solid precipitated, and this was vacuum-

filtered and washed with cold AcOEt (2 × 15 ml) to give **4ai** complex with 4-nitrobenzoic acid (17.95 g, 80%). Brownish powder. M.p. 118–121°. IR (KBr): 1635, 1578, 1527, 1462, 1379, 1347. Part of the product was quantitatively converted to the free base **4ai** as a brownish resin, by adding it to 1M aq. NaOH, extracting with AcOEt, washing with H_2O, and evaporating. $[\alpha]_D^{25} = 23.0$ ($c = 1.00$, CH_2Cl_2). IR (KBr): 1622, 1592, 1543, 1455, 1440, 1424. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.72 (*s*, 3 H); 1.01 (*d*, $J = 8.5$, 1 H); 1.15 (*s*, 3 H); 1.86 (*td*, $J = 5.7$, 1.2, 1 H); 1.89–2.14 (*m*, 7 H); 2.21 (*dt*, $J = 5.6$, 8.5, 1 H); 2.99 (*t*, $J = 7.2$, 2 H); 5.10 (*m*, 1 H); 7.20, 7.56 (*AA′XX′*, $J_{AX} = 3.0$, 4 H); 11.28 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.3; 26.2; 26.4; 29.3; 31.4; 31.8; 36.7; 38.0; 41.0; 45.8; 114.8; 116.9; 122.2; 138.9; 147.4; 155.9. HR-ESI-MS: 281.2025 ($[M+H]^+$, $C_{19}H_{25}N_2^+$; calc. 281.2018).

*2,2′-Ethane-1,2-diylbis[1*H*-benzimidazole]* (**4ajj**). The mixture was poured into 1M aq. NaOH (150 ml), the lumps of solids were triturated, and the mixture was left stirring for 3 h. The mixture was then vacuum-filtered, and the solid material was washed with H_2O (50 ml). The aq. layer of the filtrate was separated and kept for the isolation of **4aj**. The solid material was dried, triturated in boiling DMF (80 ml), cooled, vacuum-filtered, and washed with acetone (3 × 20 ml) to give **4ajj** (5.10 g, 39%). Slightly bluish powder. M.p. >360° ([32]: 415°). IR (KBr): 1622, 1590, 1542, 1452, 1433, 1276, 1223, 1152, 1033. HR-ESI-MS: 263.1304 ($[M+H]^+$, $C_{16}H_{15}N_4^+$; calc. 263.1297), 132. Due to poor solubility, the NMR spectra were recorded of the soluble trifluoroacetate salt, formed by adding 2 equiv. of CF_3COOH to the sample: ^{1}H-NMR (300 MHz, (D_6)DMSO): 3.81 (*s*, 4 H); 7.45, 7.77 (*AA′XX′*, $J_{AX} = 3.0$, 8 H); 12.20 (br. *s*, 4 H). DEPT135-NMR ((D_6)DMSO): 24.9 (CH_2); 114.9 (CH); 125.7 (CH).

*3-(1*H*-Benzimidazol-2-yl)propanoic acid* (**4aj**). The cooled aq. phase of the filtrate was acidified to a pH of *ca.* 5 with conc. aq. HCl, the precipitate was vacuum-filtered, washed with H_2O (2 × 30 ml), and dried under vacuum to give **4aj** (5.50 g, 29%). Colorless needles. M.p. 225–227° ([6]: 224°). IR (KBr): 1639, 1592, 1557, 1489, 1464, 1433, 1407. ^{1}H-NMR (300 MHz, (D_6)DMSO) 2.81 (*t*, $J = 7.2$, 2 H); 3.06 (*t*, $J = 7.2$, 2 H); 7.12, 7.47 (*AA′XX′*, $J_{AX} = 3.0$, 4 H); 8.00–14.00 (br. *s*, 2 H). DEPT135-NMR ((D_6)DMSO/CF_3COOH): 24.7 (CH_2); 32.2 (CH_2); 115.3 (CH); 122.0 (CH).

*1*H*-1,5-Benzodiazepine-2,4(3*H*,5*H*)-dione* (**6**). To the cooled heterogeneous mixture, PE (50 ml) was added. The crude product was filtered off, washed with PE (2 × 30 ml), suspended in warm EtOH (100 ml), and the insoluble material was filtered and washed with EtOH (3 × 15 ml) to give **6** (1.10 g, 13%). Grey powder. M.p. 349–352°, subl. ([17]: >350°, subl.). IR (KBr): 1705, 1672, 1599, 1503, 1429, 1401. ^{1}H-NMR (300 MHz, (D_6)DMSO): 3.18 (*s*, 2 H); 7.14 (*AA′BB′*, 4 H); 10.37 (*s*, 2 H). ^{13}C-NMR (75 MHz, (D_6)DMSO): 45.0; 122.2; 124.8; 129.7; 165.8.

*2-Methyl-1*H*-benzimidazole* (**4ak**). The above ethanolic filtrate was evaporated *in vacuo*, and the residue was recrystallized from H_2O to give **4ak** (4.50 g, 65%). Colorless needles. M.p. 173–175° ([7]: 177.0–177.7°). IR (KBr): 1625 (br.), 1555, 1451, 1418, 1387, 1272. ^{1}H-NMR (300 MHz, (D_6)DMSO): 2.48 (*s*, 3 H); 7.07–7.13 (*m*, 2 H); 7.42–7.46 (*m*, 2 H); 12.16 (br. *s*, 1 H).

*(6*R*,9*S*)-6,7,8,9-Tetrahydro-9,12,12-trimethyl-10*H*-[6,9]methanoazepino[1,2-*a*]benzimidazol-10-one* (**4al**). The mixture was diluted with AcOEt (100 ml), washed with 1M aq. NaOH (100 ml), H_2O (2 × 100 ml), and 1M aq. HCl (100 ml), evaporated *in vacuo*, and the residue was recrystallized from hexane to give **4al** (9.50 g, 75%). Gray crystalline powder. M.p. 92–95° ([19]: 86–88°). $[\alpha]_D^{25} = +55.0$ ($c = 1.00$, CH_2Cl_2). IR (KBr): 1724, 1616, 1562, 1475, 1453, 1440. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.84 (*s*, 3 H); 1.13 (*s*, 3 H); 1.34 (*s*, 3 H); 1.75–1.84 (*m*, 1 H); 2.04–2.10 (*m*, 2 H); 2.37–2.50 (*m*, 1 H); 3.31 (*d*, $J = 6.4$, 1 H); 7.32–7.37 (*m*, 2 H); 7.66–7.70 (*m*, 1 H); 8.15–8.19 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.9; 19.8; 23.2; 27.5; 34.2; 49.2; 49.5; 55.5; 115.2; 119.6; 124.8; 125.1; 131.3; 143.4; 159.1; 175.1. HR-ESI-MS: 255.1489 ($[M+H]^+$, $C_{16}H_{19}N_2O^+$; calc. 255.1497). Anal. calc. for $C_{16}H_{18}N_2O$ (254.33): C 75.56, H 7.13, N 11.01; found: C 75.82, H 7.27, N 11.27.

The aq. NaOH and aq. HCl washings gave no isolable products upon neutralization.

*3-(1*H*-Benzimidazol-2-yl)propan-1-ol* (**4am**). *a*) *From* **2m** *According to the General Procedure.* The solvent was decanted from the solidified mass, which was dissolved in a minimum amount of boiling EtOH. The hydrochloride that precipitated after standing for a few days in the refrigerator was filtered off and washed with acetone (4 × 30 ml) to give, after drying under vacuum, **4am** · HCl (12.00 g, 56%). White crystalline powder. M.p. 150–152.5°. IR (KBr): 1628, 1569, 1459, 1408. ^{1}H-NMR (300 MHz, (D_6)DMSO): 1.99–2.09 (*m*, 2 H); 3.20 (*t*, $J = 7.6$, 2 H); 3.51 (*t*, $J = 6.0$, 2 H); 7.51, 7.77 (*AA′XX′*, $J_{AX} = 3.0$, 4 H); 14.00 (br. *s*, 2 H).

The hydrochloride was dissolved in H_2O (100 ml) and basified with 10M aq. NaOH. The precipitated free base was vacuum-filtered, washed with H_2O (3×40 ml), and dried to give **4am** (9.10 g, 51%). White powder. M.p. 159–161° ([33] 158–160°). IR (KBr): 1634 (br.), 1592, 1534, 1452, 1440, 1420.

b) *From the Lactone* **2m′**. Compound **1a** (5.69 g, 50 mmol) was dissolved in 2M aq. HCl (55 ml, 110 mmol), the soln. was then evaporated *in vacuo*, and the residue was thoroughly dried under vacuum. The crystalline dihydrochloride was combined with a second equiv. of **1a** (5.69 g, 50 mmol), γ-butyrolactone (**2m′**; 8.69 g, 100 mmol), $B(OH)_3$ (620 mg, 10 mol-%), and toluene (100 ml). The resulting mixture was stirred on reflux for 12 h in a reaction flask equipped with a *Dean–Stark* trap and then worked up, as described above, to give **4aj** · HCl (17.20 g, 81%).

Malonic Acid Decarboxylation. A mixture of malonic acid (1.05 g, 10 mmol), *N*,*N*-dimethylaniline (2.42 g, 20 mmol), and toluene (10 ml) was stirred at reflux. At first, a biphasic liquid-liquid mixture formed, which with time and gas evolution became homogenous. After 3 h, a 0.200-ml sample of the mixture was taken for ^{1}H-NMR analysis in $CDCl_3$. Then, to this same sample was added authentic AcOH as a standard, and the sample was again analyzed to confirm the NMR signals attributed to the AcOH. The conversion of malonic acid was found to be complete.

*2,3-Dihydro-2-phenyl-1*H-*1,3,2-benzodiazaborole* (**8**). A mixture of **1a** (2.84 g, 25 mmol) and $PhB(OH)_2$ (**7**; 3.21 g, 25 mmol) in toluene (25 ml) was stirred for 2 h on reflux in a reaction flask equipped with a *Dean–Stark* trap. Upon cooling, the precipitated product was filtered and washed with PE (3×15 ml) to give **8** (4.45 g, 92%) as gray crystals. M.p. 207–208° ([34]: 206–207°). IR (KBr): 1602, 1484, 1425, 1362, 1272, 1175. ^{1}H-NMR (300 MHz, (D_6)DMSO): 6.82, 7.06 (*AA′XX′*, $J_{AX} = 3.0$, 4 H); 7.38–7.44 (*m*, 3 H); 7.87–7.93 (*m*, 2 H); 9.10 (*s*, 2 H).

*7*H,*14*H,*21*H-*Bis[1,3,2]benzodiazaborolo[1′,2′:3,4;1″,2″:5,6][1,3,5,2,4,6]triazatriborinino[1,2-*a*][1,3,2]-benzodiazaborole* (**9**). A mixture of **1a** (12.00 g, 110 mmol) and $B(OH)_3$ (6.25 g, 25 mmol) in toluene (100 ml) was stirred for 4 d on reflux in a reaction flask equipped with a *Dean–Stark* trap. Upon cooling, the precipitated crude product was filtered and recrystallized from acetone to give **9** (5.80 g, 50%). White needles. M.p. 404–406°, with crystals changing form at 310–350° ([35]: 405–407°). IR (KBr): 1611, 1543, 1510, 1481, 1460, 1282, 1254, 1022, 739. ^{1}H-NMR (300 MHz, (D_6)DMSO): 7.01–7.09 (*m*, 6 H); 7.22–7.28 (*m*, 3 H); 7.79–7.82 (*m*, 3 H); 9.23 (*s*, 3 H). ^{13}C-NMR (75 MHz, (D_6)DMSO): 111.3; 113.0; 118.6; 120.6; 134.1; 139.5.

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