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Ring contraction of 1,3-diphenylbenzo[1,2,4]triazinyl radicals to 1,2-diphenylbenzimidazoles

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Abstract

Reductive ring contraction of 1,3-diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yls (Blatter’s radicals) using zinc powder (2 equiv.) in acetic acid heated to ca. 118 °C gives 1,2-diphenylbenzimidazoles in high yield. 1,3-Diphenylbenzo[e][1,2,4]triazin-7(1H)-one and the zwitterionic tetraphenylhexaazaanthracene (TPHA) also undergo reductive ring contractions to give 1,2-diphenylbenzimidaz-6-ol and 1,2,6,7-tetraphenyl-1,7-dihydrobenzo[1,2-d:4,5-d’]diimidazole, respectively. By using less zinc, the incomplete reduction of TPHA gave the stable organic radical 1,3,7,8-tetraphenyl-4,8-dihydro-1H-imidazo[4,5-g][1,2,4]benzotriazin-1-yl. Imidazolo-, oxazolo- and thiazolo-fused 1,2,4-benzotriazinyls all undergo zinc mediated ring contractions to give imidazolo-, oxazolo- and thiazolo-fused benzimidazoles in excellent yields.
1. Introduction

1,2,4-Benzotriazinyls are stable organic radicals (e.g., Blatter’s radical 1),\textsuperscript{1} which display a range of magnetic behaviours,\textsuperscript{1f,2} and were the inspiration behind the preparation of the unusual zwitterionic bicinean tetraphenylhexaazaanthracene 2 (TPHA).\textsuperscript{3} While Blatter radical 1a (R = H) is essentially stable in its crystalline form, it can be oxidized on treatment with either MnO\textsubscript{2} or KMnO\textsubscript{4} to the useful heterocyclic scaffold, 1,3-diphenylbenzo[\textit{e}][1,2,4]triazin-7(1H)-one (3),\textsuperscript{1d,2d} which readily undergoes regiospecific addition of nucleophiles at C-6 and of electrophiles at C-8.\textsuperscript{4}

The benzotriazinone 3 also participates in a range of cyclisation reactions that led to extension of the acene core, which included the formation of new zwitterions (e.g., the quinoxalino fused 4),\textsuperscript{5} the preparation of alkaloid-like tetraazafluoranthenones 5,\textsuperscript{6} and π extended azole fused benzotriazinyls 6-8.\textsuperscript{1a,1b} Furthermore, analogues of the benzotriazinone 3, including the triazafluoranthenone 5, inhibited the formation of amyloid fibres and inhibited AChE and BChE.\textsuperscript{7} Interestingly, the 7-trifluoromethyl substituted analogue of Blatter’s radical 1e (R = F\textsubscript{3}C) was stable to oxidation\textsuperscript{2d} and along with other Blatter radicals mediated the polymersiation of styrene.\textsuperscript{8} The synthesis and chemistry of 1,2,4-triazines and their benzo derivatives have been extensively reviewed,\textsuperscript{9} while recent reviews on stable organic radicals and their potential application in organic electronics have also appeared.\textsuperscript{10}
As a continuation of our studies on 1,2,4-benzotriazines, we became interested in the reductive ring contraction of Blatter’s radical 1a reported by Barton et al.: Treatment of Blatter’s radical 1a with Zn powder (8 equiv.) and a catalytic amount of acetic acid in acetic anhydride at ca. 20 °C for 8 h gave 1,2-diphenylbenzimidazole (9a) in 39% yield (Scheme 1).

![Figure 1 Structures of important 1,2,4-benzotriazines 1-8.](image)

Scheme 1 Barton’s reductive ring contraction conditions.
The acid catalyzed zinc mediated reduction of various 1,2-diaza heteroarenes has been extensively used to effect ring contractions: 1,2,4,5-Tetrazines, cinnolines, phthalazines and pyridazines treated with zinc powder in acetic acid afford 1,2,4-triazoles, indoles, isoindoles, and pyrroles, respectively. A number of reports have also appeared on monocyclic 1,2,4-triazines which give imidazoles on chemical or electrochemical reduction, and mixtures of pyrazoles and imidazoles on photolysis.

In light of these reductive ring contractions we reinvestigated the metal mediated reductive ring contraction of benzotriazinyl radicals and identified optimum conditions for their nearly quantitative conversion into benzimidazoles.

2. Results and discussion

The reductive ring contraction of Blatter’s radical 1a in alkanoic acids was optimized with respect to the metal [In (IP 5.78 eV), Sn (7.34 eV), Ni (7.63 eV), Cu (7.72 eV), Fe (7.87 eV) and Zn (9.39 eV)], alkanoic acid (HCO₂H pKₐ 3.77, AcOH pKₐ 4.79 and F₃CCO₂H pKₐ 0.23) and reaction temperature (rt vs reflux). Initially, the effect of the alkanoic acid was investigated in the absence of any metal reducing agent: Blatter’s radical 1a in neat HCO₂H (bp 101 °C), AcOH (bp 118 °C), or F₃CCO₂H (bp 72 °C) at ca. 20 °C for 72 h was recovered unchanged, while in these solvents when heated at their respective boiling points the radical 1a slowly (ca. 30 h) degraded only in AcOH. The various metals screened were In, Sn, Ni, Cu, Fe and Zn. In general, the benzotriazinyl 1a in all (three) alkanoic acids in the presence of every metal screened was reduced to the leuco form (the benzotriazine) at rt after ca. 12 h or immediately at ca. 118 °C, which on alkali work-up gave back the radical. The radical 1a in formic or
acetic acids (24 h at ca. 118 °C) with either In or Sn powder (2 equiv.) followed by an alkali work up led to a nearly quantitative recovery of the radical. With Ni, Cu and Fe the reactivity of the radical 1a was dependant on the alkanoic acid used: The use of either Ni, Cu or Fe powder (2 equiv.) in AcOH heated at reflux gave in all cases the benzimidazole 9a in 55, 95 and 53% yields, respectively but these metals failed to give any benzimidazole in formic acid heated at reflux. When Zn powder (2 equiv.) was used in AcOH heated to ca. 118 °C, the benzotriazinyl 1a was rapidly (20 min) converted into the benzimidazole 9a, while in formic acid heated to ca. 100 °C the conversion was slow (22 h) and the benzimidazole was isolated in a lower yield (74%). Interestingly, increasing the equivalents of Zn powder (from 2 to 4 equiv.) shortened the reaction time without a drop in yield. While the use of less than 2 equiv. of Zn (1 or 1.5 equiv.) led to long reaction times (ca. 30 h), a drop in product yield and complex reaction mixtures.

The optimized conditions for the zinc powder mediated reductive ring contraction [i.e., Zn (2 equiv.), AcOH heated to ca. 118 °C] worked equally well for chloro, bromo, trifluoromethyl, phenyl and fur-2-yl C-7 substituted benzotriazinyl analogues. However, some protodeiodination was observed with the 7-iodo-substituted analogue 1d which gave a mixture of 6-iodo-1,2-diphenylbenzimidazole (9d) and 1,2-di-phenylbenzimidazole (9a). Fortunately, both compounds could be separated by silica chromatography or even by fractional recrystallisation of the crude product (Table 1).
Table 1 Reductive ring contraction of 7-substituted benzotriazinyls 1a-g into benzimidazoles 9a-g.

<table>
<thead>
<tr>
<th>R</th>
<th>Yields 9 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>9a (95)</td>
</tr>
<tr>
<td>Cl</td>
<td>9b (98)</td>
</tr>
<tr>
<td>Br</td>
<td>9c (97)</td>
</tr>
<tr>
<td>I</td>
<td>9d (60) + 9a (10)</td>
</tr>
<tr>
<td>F₂C</td>
<td>9e (96)</td>
</tr>
<tr>
<td>Ph</td>
<td>9f (99)</td>
</tr>
<tr>
<td>Fur-2-yl</td>
<td>9g (95)</td>
</tr>
</tbody>
</table>

Iodoarenes are known to undergo protodeiodination in the presence of Zn powder and AcOH.¹⁸ Not surprisingly, treating a pure sample of 6-iodo-1,2-diphenylbenzimidazole (9d) with Zn (3 equiv.) in AcOH at ca. 118 °C for 15 h gave the diphenylbenzimidazole 9a in 97% yield (Scheme 2).

Scheme 2 Zinc mediated protodeiodination of the 6-iodobenzimidazole 9d.

Interestingly, the reductive ring contraction also worked with 1,3-diphenylbenzo[e]-[1,2,4]triazin-7(1H)-one (3) but needed at least 3 equivalents of Zn powder to drive the reaction to completion and afford 1,2-diphenylbenzimidaz-6-ol (10)¹⁹ in 74% yield (Scheme 3).
Scheme 3 Reructive ring contraction of the 1,2,4-benzotriazinone 3.

Furthermore, the zwitterionic tetraphenylhexaaazaanthracene 2 (TPHA) when treated with Zn (4 equiv.) in AcOH (1 ml) for 1 h gave the anticipated 1,2,6,7-tetraphenyl-1,7-dihydro-benzo[1,2-d:4,5-d’]diimidazole (11)\textsuperscript{20} in 95% yield (Scheme 4).

Scheme 4 Reructive ring contraction of TPHA 2 using 2 or 4 equivalents of zinc powder.

However, when only 2 equivalents of zinc were used the reaction could not be driven to completion and the diimidazole 11 was obtained in only 22% yield together with the unusual imidazolo fused radical 6a in 45% yield: Radical 6a has been recently synthesized independently by our team starting from the benzotriazinone 3.\textsuperscript{1a} The radical 6a and its oxazolo- and thiazolo-fused analogues 7 (R = Ph)\textsuperscript{1a} and 8 (R = Ph)\textsuperscript{1b}.
can be reduced with Zn (2 equiv.) in AcOH to the expected imidazolo-, oxazolo- and thiazolo-fused benzimidazoles 11 (X = NPh), 12 (X = O) and 13 (X = S) in excellent yields (Scheme 5).

Scheme 5 Reductive ring contraction of imidazolo-, oxazolo- and thiazolo-fused benzotriazinyl radicals 6a, 7 (R = Ph) and 8 (R = Ph).

Mechanistic Rationale for Ring Contraction

The zinc mediated ring contraction of various 1,2-diaza heteroazines is assumed to take place via reductive cleavage of the N-N bond followed by recyclization with loss of ammonia. At least two equivalents of Zn powder were needed to consume the starting benzotriazinyl radical 1a and this is slightly above the theoretical amount needed based on the electron transfer mechanism outlined below which requires the transfer of three electrons (Scheme 6).
Scheme 6 Tentative mechanism for reductive ring contraction of benzotriazinyls.

The first reduction, affords the leuco form benzotriazine 14, which when protonated in AcOH then undergoes a second reduction to afford the radical intermediate 15, that is tentatively stabilized by several resonance charge separated forms such as 15'. Radical 15 then undergoes a ring opening to give an intermediate similar to 16 that is reduced to N-[2-(phenylamino)phenyl]benzimidamide (17). Intramolecular cyclisation affords the 2,3-dihydrobenzimidazole 18 that eliminates ammonia to give the observed 1,2-diphenylbenzimidazole 9a.

While variations of this tentative mechanism can be readily proposed, there is sufficient evidence for the chemical$^{22}$ and electrochemical$^{23}$ reduction of 1,2,4-triazines to support the proposed mechanism as far as triazinyl 14. Furthermore, while to the best of our knowledge examples of the final cyclisation step (17 to 9a) have been limited to N-(2-aminophenyl)imidamides$^{24}$ and 1-(2-aminophenyl)guanidines,$^{25}$ we note that the more closely related cyclisation of N-[2-(anilino)aryl]benzamides in hot AcOH are known to give 1,2-diarylbenzimidazoles$^{26}$ in high yield. In our hands
heating a pure sample of \(N\)-[2-(phenylamino)phenyl]benzamide (19)\(^\text{20}\) in neat AcOH for 20 min gave 1,2-diphenylbenzimidazole (9a) in 100% yield (Scheme 7).

\[
\begin{align*}
\text{Ph} & \quad \text{AcOH} \\
\text{118 °C, 20 min} & \quad \text{Ph} \\
\text{9a (100%)} & \quad \text{Ph}
\end{align*}
\]

**Scheme 7** Cyclodehydration of \(N\)-[2-(phenylamino)phenyl]benzamide (19).

3. Conclusions

To conclude, treatment of benzotriazinyl radicals with reducing metals (Zn, Cu, Fe and Ni) in alkanoic acids can lead to a reductive ring contraction to afford the \(N\)-phenylbenzimidazoles. The optimum reaction conditions that give nearly quantitative yields for the conversion are: Zn powder (2 equiv.), in AcOH heated to reflux for 20 min. Indium or tin which are milder reductants in hot alkanoic acids fail to reduce the radical beyond its leuco form, which identifies them as prospective mild and selective agents for modification of substituted benzotriazinyl radicals. While this method for the synthesis of simple benzimidazoles may not compare favourably with the many known procedures, it does nevertheless, provide an unusual route to heterole (imidazolo, oxazolo and thiazolo) fused benzimidazoles that are considerably more challenging to access.
4. Experimental Section

4.1. General methods

Anhydrous Na$_2$SO$_4$ was used for drying organic extracts, and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F$_{254}$). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography$^{27}$ was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm). Melting and decomposition points were determined using either a PolyTherm-A, Wagner & Munz, Koefler-Hotstage Microscope apparatus or a TA Instruments DSC Q1000 with samples hermetically sealed in aluminum pans under an argon atmosphere, using heating rates of 5 °C/min. Solvents used for recrystallisation are indicated after the melting point. UV spectra were obtained using a Perkin-Elmer Lambda-25 UV/vis spectrophotometer and inflections are identified by the abbreviation ‘inf’. IR spectra were recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer with a Pike Miracle Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w, respectively. $^1$H and $^{13}$C NMR spectra were recorded on a BrukerAvance 300 machine (at 300 and 75 MHz, respectively) or on a Bruker 500 MHz instrument (at 500 and 125 MHz, respectively). Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Low resolution (EI) mass spectra were recorded on a Shimadzu Q2010 GC/MS with direct inlet probe. 1,3-Diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (1a)$^{1d}$, 7-chloro-1,3-diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (1b)$^{1d}$, 7-bromo-1,3-diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (1c)$^{1d}$, 7-iodo-1,3-diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (1d)$^{1d}$, 1,3-diphenyl-7-(trifluoromethyl)-1,4-di-
hydrobenzo[e][1,2,4]triazin-4-yl (1e),

1,3,7-triphenyl-1,4-dihydrobenzo[e][1,2,4]-

triazin-4-yl (1f),

7-(fur-2-yl)-1,3-diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl

(1g), the tetraphenylhexaazaanthracene 2 (TPHA),

1,3-diphenylbenzo[e][1,2,4]-

triazin-7(1H)-one (3) and N-[2-(phenylamino)phenyl]benzamide (19) were

prepared using literature procedures.

4.2. Reaction of benzotriazines with Zn powder (2 equiv.) in hot AcOH.

4.2.1. 1,2-Diphenylbenzimidazole (9a) (Typical Procedure).

A stirred mixture of 1,4-dihydro-1,3-diphenylbenzo[e][1,2,4]triazin-4-yl (1a) (50 mg, 0.176 mmol) and Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) was heated at ca. 118 °C for 20 min. The reaction mixture was then allowed to cool to ca. 20 °C, diluted with DCM (50 ml), washed with 1 M NaOH (2 × 20 ml), dried, filtered and the volatiles removed. The residue was then dissolved in DCM (5 ml), adsorbed onto silica and chromatographed. Elution with DCM removed minor non polar side products and further elution (Et₂O/n-hexane, 1:1) gave the title compound 9a as colourless needles (45 mg, 95%), mp 109-110 °C (from n-hexane), (lit., 11 110-111 °C),

R_f (Et₂O/n-hexane, 1:1) 0.32; v_max/cm⁻¹ 3063w, 3051w and 3011w (Ar CH), 1611w, 1595w, 1584w, 1526w, 1491m, 1476m, 1456m, 1445m, 1383s, 1329w, 1279w, 1261w, 1204w, 1194w, 1182w, 1173w, 1150w, 1145w, 1109w, 1076w, 1028w, 1011w, 997w, 976w, 932w, 907w, 849w, 833w, 781m, 764s; δ_H(500 MHz, CDCl₃) 7.89 (1H, d, J 8.0, Ar H), 7.57 (2H, d, J 7.3, Ar H), 7.53-7.45 (3H, m, Ar H), 7.38-7.24 (8H, m, Ar H); δ_C(75 MHz, DMSO-d₆) 151.8 (s), 142.5 (s), 137.0 (s), 136.4 (s), 130.0 (d), 129.8 (s), 129.5 (d), 129.1 (d), 128.8 (d), 128.3 (d), 127.5 (d), 123.3 (d),
122.7 (d), 119.4 (d), 110.4 (d); m/z (EI) 270 (M$^+$, 75%), 269 (100), 166 (5), 139 (6), 135 (6), 77 (22), 63 (5), 51 (16); identical to an authentic sample.

4.2.2. 6-Chloro-1,2-diphenylbenzimidazole (9b).

Similar treatment of 7-chloro-1,3-diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (1b) (56 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) at ca. 118 °C for 20 min gave on chromatography (Et$_2$O/n-hexane, 1:1) the title compound 9b as colourless needles (53 mg, 98%), mp (DSC) onset: 132.9 °C, peak max: 134.3 °C (from n-hexane), R$_f$ (Et$_2$O/n-hexane, 1:1) 0.37; (found: C, 75.04; H, 4.22; N, 9.10. C$_{19}$H$_{13}$ClN$_2$ requires C, 74.88; H, 4.30; N, 9.19%); $\lambda_{\text{max}}$(DCM)/nm 233 (log $\varepsilon$ 3.42), 302 (3.38); $\nu_{\text{max}}$/cm$^{-1}$ 3063w (Ar CH), 1611s, 1597w, 1499m, 1460m, 1447m, 1435m, 1377m, 1331m, 1312w, 1302w, 1288w, 1273m, 1246w, 1202w, 1179w, 1157w, 1109w, 1074w, 1057m, 1028w, 988w, 978w, 937w, 922w, 854m, 841m, 824m, 812s, 775s; $\delta_{\text{H}}$(300 MHz, CDCl$_3$) 7.79 (1H, d, $J$ 9.0, Ar H), 7.40-7.48 (5H, m, Ar H), 7.40-7.27 (6H, m, Ar H), 7.23 (1H, d, $J$ 2.1, Ar H); $\delta_{\text{C}}$(75 MHz, CDCl$_3$) 153.1 (s), 141.5 (s), 137.7 (s), 136.4 (s), 130.0 (d), 129.7 (d), 129.4 (s), 129.3 (d), 129.0 (s), 128.9 (d), 128.3 (d), 127.2 (d), 123.6 (d), 120.6 (d), 110.5 (d); m/z (EI) 306 (M$^+$+2, 32%), 304 (M$^+$, 100), 268 (41), 166 (5), 164 (6), 152 (4), 139 (7), 135 (13), 77 (33), 63 (7), 51 (17).

4.2.3. 6-Bromo-1,2-diphenylbenzimidazole (9c).

Similar treatment of 7-bromo-1,3-diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (1c) (64 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) at ca. 118 °C for 20 min gave on chromatography (Et$_2$O/n-hexane, 1:1) the title compound 9c as colourless needles (59 mg, 97%), mp (DSC) onset: 154.4 °C, peak
max: 156.0 °C (from n-hexane), \( R_f \) (Et₂O/n-hexane, 1:1) 0.37; (found: C, 65.42; H, 3.68; N, 8.16. \( \text{C}_{19}\text{H}_{13}\text{BrN}_2 \) requires C, 65.35; H, 3.75; N, 8.02%); \( \lambda_{\text{max}} \)(DCM)/nm 234 (log \( \varepsilon \) 3.47), 302 (3.43); \( v_{\text{max}}\)/cm\(^{-1}\) 3049w (Ar CH), 1603w, 1593w, 1501m, 1476w, 1456m, 1445m, 1435w, 1373m, 1329m, 1312w, 1290w, 1275m, 1206w, 1182w, 1157w, 1123w, 1111w, 1072w, 1047w, 1030w, 1005w, 993w, 976w, 930w, 922w, 907w, 854w, 839m, 806s, 775s, 762m; \( \delta_{\text{H}} \)(300 MHz, CDCl\(_3\)) 7.75 (1H, d, \( J \) 8.5, Ar H), 7.59-7.48 (5H, m, Ar H), 7.44 (1H, dd, \( J \) 8.6, 1.8, Ar H), 7.40-7.28 (6H, m, Ar H);
\( \delta_{\text{C}} \)(75 MHz, CDCl\(_3\)) 153.0 (s), 141.9 (s), 138.2 (s), 136.4 (s), 130.0 (d), 129.7 (d), 129.4 (s), 129.3 (d), 128.9 (d), 128.3 (d), 127.2 (d), 126.2 (d), 121.0 (d), 116.4 (s), 113.4 (d); \( m/z \) (EI) 350 (M\(^{+2}\), 95%), 348 (M\(^+\), 100), 268 (73), 242 (3), 192 (3), 164 (9), 139 (12), 135 (38), 121 (3), 115 (3), 105 (3), 89 (4), 77 (46), 63 (15), 51 (20).

4.2.4. 6-Iodo-1,2-diphenylbenzimidazole (9d).

Similar treatment of 7-iodo-1,3-diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (1d) (72 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) at ca. 118 °C for 20 min gave on chromatography (Et₂O/n-hexane, 1:1) the title compound 9d as colourless needles (43 mg, 61%), mp (DSC) onset: 185.7 °C, peak max: 186.5 °C (from n-hexane), \( R_f \) (Et₂O/n-hexane, 1:1) 0.37; (found: C, 57.69; H, 3.24; N, 7.20. \( \text{C}_{19}\text{H}_{13}\text{IN}_2 \) requires C, 57.59; H, 3.31; N, 7.07%); \( \lambda_{\text{max}} \)(DCM)/nm 232 (log \( \varepsilon \) 3.57), 306 (3.51); \( v_{\text{max}}\)/cm\(^{-1}\) 3063w and 3048w (Ar CH), 1591w, 1501s, 1474m, 1454m, 1445m, 1431m, 1383m, 1373m, 1325m, 1312w, 1290w, 1277m, 1250w, 1204w, 1180w, 1173w, 1157w, 1124w, 1111w, 1072w, 1042w, 1030w, 1005w, 993w, 974w, 928w, 920m, 905w, 854m, 843w, 806s, 775s, 762s; \( \delta_{\text{H}} \)(300 MHz, CDCl\(_3\)) 7.66-7.59 (2H, m, Ar H), 7.59-7.55 (2H, m, Ar H), 7.55-7.47 (4H, m, Ar H), 7.40-7.27 (5H, m, Ar H); \( \delta_{\text{C}} \)(75 MHz, CDCl\(_3\)) 152.7 (s), 142.5 (s), 138.7 (s), 136.4 (s), 131.9 (d),
130.0 (d), 129.7 (d), 129.4 (d), 129.3 (s), 128.9 (d), 128.3 (d), 127.3 (d), 121.5 (d), 119.4 (d), 86.7 (s); m/z (EI) 396 (M^+, 100%), 268 (44), 166 (10), 140 (8), 139 (9), 135 (21), 77 (38), 63 (18), 51 (13). Further elution (Et_2O/n-hexane, 1:1) gave the starting 1,2-diphenylbenzimidazole (9a) as colourless needles (5 mg, 10%), mp 109-110 °C (from n-hexane), (lit., 11 110-111 °C); Rf (Et_2O/n-hexane, 1:1) 0.32; δ_H (500 MHz, CDCl_3) 7.89 (1H, d, J 8.0, Ar H), 7.57 (2H, d, J 7.3, Ar H), 7.53-7.45 (3H, m, Ar H), 7.38-7.24 (8H, m, Ar H); identical to that described above.

4.2.5. 1,2-Diphenyl-6-(trifluoromethyl)benzimidazole (9e).

Similar treatment of 1,3-diphenyl-7-(trifluoromethyl)-1,4-dihydrobenzo[e][1,2,4]-triazin-4-yl (1e) (62 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) at ca. 118 °C for 20 min gave on chromatography (Et_2O/n-hexane, 1:1) the title compound 9e as colourless prisms (57 mg, 96%), mp (DSC) onset: 144.8 °C, peak max: 146.0 °C (from n-hexane), Rf (Et_2O/n-hexane, 1:1) 0.38; (found: C, 71.12; H, 3.80; N, 8.20. C_{20}H_{13}F_{3}N_{2} requires C, 71.00; H, 3.87; N, 8.28%); λ_max(DCM)/nm 234 (log ε 3.47), 276 inf (3.34), 293 (3.39); ν_max/cm^{-1} 3067w, 3048w and 3032w (Ar CH), 1628w, 1597w, 1522w, 1499m, 1472w, 1454w, 1443w, 1387w, 1317m, 1279m, 1250m, 1202w, 1165m, 1153m, 1132m, 1115s, 1076w, 1053m, 1028w, 980w, 947w, 926w, 914w, 874m, 841m, 781m, 762m; δ_C (75 MHz, CDCl_3) 154.8 (s), 145.1 (s), 136.7 (s), 136.3 (s), 130.2 (d), 130.0 (d), 129.5 (d), 129.2 (s), 129.1 (d), 128.4 (d), 127.3 (d), 125.4 (q, ^3J_{FC} 32.4, CCF_3), 124.8 (q, ^1J_{FC} 272.0, CCF_3), 120.2 (d), 119.9 (q, ^3J_{FC} 3.5, Ar CH), 108.2 (q, ^3J_{FC} 4.2, Ar CH); m/z (EI) 338 (M^+, 65%), 337 (100), 319 (3), 317 (5), 268 (19), 159 (4), 139 (3), 77 (16), 51 (11).
4.2.6. **1,2,6-Triphenylbenzimidazole (9f).**

Similar treatment of 1,3,7-triphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (1f) (63 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) at ca. 118 °C for 20 min gave on chromatography (Et₂O/n-hexane, 1:1) the **title compound 9f** as beige needles (60 mg, 99%), mp (DSC) onset: 209.0 °C, peak max: 209.8 °C (from cyclohexane), R_f (Et₂O/n-hexane, 1:1) 0.20; (found: C, 86.74; H, 4.89; N, 8.36. C_{25}H_{18}N₂ requires C, 86.68; H, 5.24; N, 8.09%); λ_max(DCM)/nm 232 (log ε 3.52), 244 (3.54), 311 (3.55); ν\_max/cm\(^{-1}\) 3065w and 3034w (Ar CH), 1618w, 1595m, 1570w, 1501m, 1470m, 1454m, 1445m, 1431m, 1385m, 1342w, 1329w, 1310w, 1285w, 1240w, 1192w, 1179w, 1153w, 1074m, 1038w, 1028w, 1016w, 999w, 989w, 972w, 937w, 922w, 914w, 866m, 847w, 837w, 818m, 775s, 768s, 758m; δ_H (300 MHz, CDCl₃) 7.94 (1H, d, J 8.5, Ar H), 7.64-7.56 (5H, m, Ar H), 7.55-7.47 (3H, m, Ar H), 7.46-7.28 (9H, m, Ar H); δ_C (75 MHz, CDCl₃) one CH signal missing 152.9 (s), 142.5 (s), 141.7 (s), 137.8 (s), 137.1 (s), 136.9 (s), 129.92 (d), 129.88 (s), 129.5 (d), 129.4 (d), 128.7 (d), 128.6 (d), 128.3 (d), 127.4 (d), 127.0 (d), 122.9 (d), 119.9 (d), 108.9 (d); m/z (EI) 346 (M⁺, 100%), 268 (3), 241 (5), 178 (4), 173 (8), 165 (4), 151 (3), 139 (7), 121 (4), 77 (11), 51 (8).

4.2.7. **6-(Fur-2-yl)-1,2-diphenylbenzimidazole (9g).**

Similar treatment of 7-(fur-2-yl)-1,3-diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (1g) (62 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) at ca. 118 °C for 20 min gave on chromatography (Et₂O/n-hexane, 1:1) the **title compound 9g** as beige needles (56 mg, 95%), mp (DSC) onset: 183.6 °C, peak max: 185.6 °C (from cyclohexane), R_f (Et₂O/n-hexane, 1:1) 0.20; (found: C, 82.20; H, 4.86; N, 8.20. C_{23}H_{16}N₂O requires C, 82.12; H, 4.79; N, 8.33%); λ_max(DCM)/nm 232 (log ε
3.48), 251 (3.42), 307 inf (3.55), 330 (3.55); \nu_{\text{max}}/\text{cm}^{-1} 3067w and 3053w (Ar CH), 1618w, 1595w, 1582w, 1501m, 1470w, 1456m, 1437w, 1391m, 1337m, 1306w, 1296w, 1285m, 1238w, 1217w, 1180w, 1159w, 1150w, 1128w, 1111w, 1074w, 1030w, 1011m, 993w, 978w, 972w, 951w, 922w, 891m, 883w, 864m, 841w, 812m, 793m, 773s; \delta_{\text{H}}(300 \text{ MHz, CDCl}_3) 7.87 (1H, d, J 8.5, Ar H), 7.67 (1H, dd, J 8.5, 1.5, Ar H), 7.59-7.52 (6H, m, Ar H), 7.46-7.42 (1H, m, Ar H), 7.40-7.27 (5H, m, Ar H), 6.63 (1H, d, J 3.4, Ar H), 6.47 (1H, dd, J 3.4, 1.7, Ar H); \delta_{\text{C}}(75 \text{ MHz, CDCl}_3) 154.4 (s), 153.0 (s), 142.5 (s), 141.7 (d), 137.6 (s), 136.8 (s), 129.9 (d), 129.8 (s), 129.5 (d), 129.3 (d), 128.7 (d), 128.3 (d), 127.4 (d), 126.6 (s), 120.0 (d), 119.8 (d), 111.7 (d), 105.5 (d), 104.6 (d); m/z (EI) 336 (M^+, 100%), 335 (59), 307 (11), 305 (11), 204 (8), 168 (6), 153 (13), 140 (6), 102 (5), 77 (11), 51 (6).

4.2.8. 1,2-Diphenylbenzimidaz-6-ol (10).

A stirred mixture of 1,3-diphenylbenzo[e][1,2,4]triazin-7(1H)-one (3) (53 mg, 0.176 mmol) and Zn powder (34.5 mg, 0.527 mmol) in glacial AcOH (1 ml) was heated at ca. 118 °C for 1 h. The reaction mixture was allowed to cool to ca. 20 °C, diluted with DCM (50 ml), washed with sat. Na$_2$CO$_3$ (2 × 20 ml), dried, filtered and the volatiles removed. The residue was dissolved in DCM (20 ml) and column chromatographed (neutral Al$_2$O$_3$). Elution with (Et$_2$O) removed minor non polar side products and further elution (EtOH) gave the title compound 10 as beige needles (56 mg, 95%), mp (DSC) onset: 212.4 °C, peak max: 218.5 °C (from cyclohexane), (lit.,$^{19}$ 223 °C), $R_f$ (Et$_2$O) 0.59; $\lambda_{\text{max}}$(DCM)/nm 230 (log $\varepsilon$ 3.32), 256 inf (3.13), 308 (3.31); \nu_{\text{max}}/\text{cm}^{-1} 3061w, 3049w and 3042w (Ar CH), 1620m, 1595m, 1560w, 1524w, 1501m, 1483s, 1474s, 1454m, 1385s, 1337m, 1312w, 1287m, 1250s, 1211m, 1175s, 1113m, 1074m, 1030w, 1003w, 984w, 968w, 920w, 908w, 887w, 876w, 853m, 831s, 810s, 775s,
764s; δH(300 MHz, DMSO-d6) 9.39 (1H, s, OH), 7.61-7.50 (4H, m, Ar H), 7.48-7.43
(2H, m, Ar H); 7.41-7.27 (5H, m Ar H), 6.78 (1H, dd, J 8.7, 2.3, Ar H), 6.51 (1H, d, J
2.1, Ar H); δC(75 MHz, DMSO-d6) 154.6 (s), 150.3 (s), 138.0 (s), 136.8 (s), 136.0 (s),
130.1 (s), 130.0 (d), 129.1 (d), 128.8 (d), 128.7 (d), 128.3 (d), 127.4 (d), 119.9 (d),
112.6 (d), 95.4 (d); m/z (EI) 286 (M+, 94%), 285 (100), 266 (3), 255 (6), 178 (6), 165
(3), 154 (11), 143 (6), 134 (3), 127 (10), 115 (3), 104 (4), 84 (6), 77 (28), 69 (12), 63
(8), 56 (39), 51 (25); identical to an authentic sample.

4.2.9. 1,2,6,7-Tetraphenyl-1,7-dihydrobenzo[1,2-d:4,5-d']diimidazole (11).

A stirred mixture of tetraphenylhexaazaanthracene 2 (TPHA) (86 mg, 0.176 mmol)
and Zn powder (46 mg, 0.703 mmol) in glacial AcOH (1 ml) was heated at ca. 118 °C
for 20 min. The reaction mixture was allowed to cool to ca. 20 °C, diluted with DCM
(50 ml), washed with 1 M NaOH (2 x 20 ml), dried, filtered and the volatiles rem
oved. The residue was dissolved in DCM (5 ml), adsorbed onto silica and chromatographed
(Et₂O) to remove all non-polar minor side products. Further elution (THF) gave the
title compound 11 as colourless needles (77 mg, 95%), mp (DSC) onset: 281.6 °C,
peak max: 282.5 °C (from EtOH), (lit.,¹⁰ 283-285 °C), Rf (Et₂O) 0.18; (found: C,
83.22; H, 4.67; N, 12.01. C₃₂H₂₂N₄ requires C, 83.09; H, 4.79; N, 12.11%);
λmax(DCM)/nm 3063w and 3036w, (Ar CH), 2970w, 1632w, 1597m, 1522w, 1497s, 1476m,
1452w, 1445w, 1427s, 1398s, 1360m, 1327m, 1310m, 1283m, 1207m, 1177m, 1150w,
1113w, 1094w, 1076m, 1051m, 1026m, 1003w, 980w, 966w, 920w, 897m, 880w,
864w, 851m, 824m, 806w, 772s, 754m; δH(300 MHz, CDCl₃) 8.36 (1H, s, Ar H),
7.61-7.54 (4H, m, Ar H); 7.52-7.40 (6H, m, Ar H), 7.39-7.27 (10H, m, Ar H), 6.96
(1H, s, Ar H); δC(75 MHz, CDCl₃) 153.1 (s), 140.6 (s), 137.2 (s), 135.7 (s), 129.93 (s),
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129.87 (d), 129.32 (d), 129.27 (d), 128.4 (d), 128.2 (d), 127.4 (d), 109.1 (d), 90.0 (d); 
m/z (EI) 462 (M⁺, 100%), 461 (52), 384 (5), 357 (7), 231 (17), 179 (5), 165 (3), 152 
(3), 128 (5), 77 (9).

4.3. Reduction of tetraphenyhexaazaanthracene 2 (TPHA) using Zn (2 
equiv.).

4.3.1. 1,3,7,8-Tetraphenyl-4,8-dihydro-IH-imidazo[4,5-g][1,2,4]benzotriazin-1-yl 
(6).

To a stirred mixture of the tetraphenyhexaazaanthracene 2 (TPHA) (86.0 mg, 0.176 
mmol) in glacial AcOH (1 ml) at ca. 20 °C was added Zn powder (23.0 mg, 0.352 
mmol). The reaction mixture was then heated at ca. 118 °C for 20 min, then allowed 
to cool to ca. 20 °C, diluted with DCM (50 ml), washed with 1 M NaOH (2 × 20 ml), 
dried, filtered and the volatiles removed. The residue was dissolved in DCM (5 ml) 
and chromatographed on basic Al₂O₃ (DCM) to give unreacted starting material 2 as 
purple prisms (20 mg, 23%), mp 376 °C (from PhMe), (lit.,³a 376 °C), identical to an 
authentic sample. Further elution (DCM) gave the title compound 6 as dark brown 
needles (38 mg, 45%), mp (DSC) onset: 300.8 °C, peak max: 306.1 °C (decomp.) 
(from PhH) (lit.,¹a mp (DSC) onset: 300.8 °C, peak max: 306.1 °C (decomp.), Rf (Et₂O) 
0.64; (found: C, 80.52; H, 4.56; N, 14.82. C₃₂H₂₂N₅ requires C, 80.65; H, 4.65; N, 
14.70%); λmax(DCM)/nm 291 (log ε 3.61), 330 inf (3.02), 419 (3.35), 465 inf (2.63), 
540 (2.50), 624 inf (2.16); νmax/cm⁻¹ 3061w and 3044w (Ar CH), 2972w, 2918w, 
1595w, 1503w, 1489w, 1470m, 1452w, 1435m, 1402m, 1389m, 1350w, 1317w, 
1296w, 1287w, 1267w, 1236w, 1200w, 1179w, 1159w, 1096s, 1065w, 1024w, 984w,
4.4. **Reduction of imidazolo-, oxazolo- and thiazolo-fused benzotriazinyls 6-8**

4.4.1. 1,2,6,7-Tetraphenyl-1,7-dihydrobenzo[1,2-d:4,5-d']diimidazole (11).

A stirred mixture of 1,3,7,8-tetraphenyl-4,8-dihydro-1H-imidazo[4,5-g][1,2,4]benzotriazin-1-yl (6) (84 mg, 0.176 mmol) and Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) was heated at ca. 118 °C for 20 min. The reaction mixture was allowed to cool to ca. 20 °C, diluted with DCM (20 ml), washed with sat. Na₂CO₃ (2 x 20 ml), dried, filtered and the volatiles removed. The residue was dissolved in DCM (1 ml) and chromatographed on silica (t-BuOMe/n-hexane, 1:1) to give the title compound 11 as colourless needles (74 mg, 91%), mp (DSC) onset: 281.6 °C, peak max: 282.5 °C (from EtOH), (lit.,²⁰ 283-285 °C), identical to that described above.

$$\delta^H(300\text{ MHz, CDCl}_3) 8.36 (1\text{H, s, Ar } H), 7.61-7.54 (4\text{H, m, Ar } H), 7.52-7.40 (6\text{H, m, Ar } H), 7.39-7.27 (10\text{H, m, Ar } H), 6.96 (1\text{H, s, Ar } H); m/z (\text{EI}) 462 (M^+, 100\%), 461 (52), 384 (5), 357 (7), 231 (17), 179 (5), 165 (3), 152 (3), 128 (5), 77 (9);$$

4.4.2. 2,6,7-Triphenyl-7H-imidazo[4,5-f]benzoxazole (12).

Similar treatment of 1,3,7-triphenyl-1,4-dihydro[1,3]oxazolo[4,5-g][1,2,4]benzotriazin-4-yl (7) (71 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial
AcOH (1 ml) gave the *title compound* 12 as beige needles (58 mg, 85%), mp (DSC) onset: 236.7 °C, peak max: 237.7 °C (from cyclohexane), (found: C, 80.70; H, 4.60; N, 10.75. C_{26}H_{17}N_{3}O requires C, 80.60; H, 4.42; N, 10.85%); R<sub>f</sub> (t-BuOMe) 0.63; λ<sub>max</sub>(DCM)/nm 231 (log ε 3.47), 270 (3.54), 334 (3.74); ν<sub>max</sub>/cm<sup>-1</sup> 3044 w (Ar CH), 1630 w, 1597 w, 1585 w, 1560 m, 1516 w, 1501 s, 1498 m, 1477 m, 1458 w, 1447 w, 1425 s, 1387 m, 1364 s, 1333 w, 1323 w, 1310 w, 1292 m, 1283 m, 1211 w, 1198 w, 1179 w, 1153 s, 1142 w, 1097 w, 1074 s, 1057 s, 1026 w, 1001 w, 970 w, 939 w, 926 m, 920 w, 887 m, 862 w, 845 m, 839 m, 831 m, 800 w, 772 s, 737 m, 729 w; δ<sub>H</sub>(500 MHz; CDCl<sub>3</sub>) 8.32-8.21 (3H, m, Ar H), 7.62 (2H, d, J 7.3, Ar H), 7.59-7.50 (6H, m, Ar H), 7.43-7.36 (4H, m, Ar H), 7.36-7.30 (2H, m, Ar H); δ<sub>C</sub>(125 MHz; CDCl<sub>3</sub>) one CH peak missing, 163.0 (s), 153.3 (s), 148.4 (s), 140.8 (s), 139.2 (s), 136.9 (s), 136.1 (s), 131.3 (d), 130.0 (d), 129.63 (s), 129.57 (d), 129.3 (d), 128.9 (d), 128.8 (d), 128.3 (d), 127.4 (d), 127.2 (s), 109.5 (d), 91.8 (d); MALDI-TOF (m/z): 389 (MH<sup>+</sup>+1, 9%), 388 (MH<sup>+</sup>, 51), 387 (M<sup>+</sup>, 100), 169 (1), 93 (12).

4.4.3. 2,6,7-Triphenyl-7H-imidazo[4,5-f]benzothiazole (13).

Similar treatment of 1,3,7-triphenyl-1,4-dihydro[1,3]thiazolo[4,5-g][1,2,4]benzotriazin-4-yl (8) (73 mg, 0.176 mmol) with Zn powder (23 mg, 0.352 mmol) in glacial AcOH (1 ml) gave the *title compound* 13 as beige needles (68 mg, 96%), mp (DSC) onset: 245.1 °C, peak max: 245.6 °C (from cyclohexane), (found: C, 77.21; H, 4.39; N, 10.32. C_{26}H_{17}N_{3}S requires C, 77.39; H, 4.25; N, 10.41%); R<sub>f</sub> (t-BuOMe) 0.65; λ<sub>max</sub>(DCM)/nm 234 (log ε 3.55), 286 (3.76), 341 (3.70); ν<sub>max</sub>/cm<sup>-1</sup> 3049 w (Ar CH), 1595 w, 1558 w, 1518 w, 1504 m, 1487 m, 1476 s, 1443 w, 1423 s, 1373 s, 1337 s, 1308 w, 1290 w, 1283 w, 1252 w, 1194 w, 1184 w, 1152 w, 1074 w, 1028 w, 972 w, 953 m, 920 w, 885 w, 853 w, 843 w, 775 m, 766 s; δ<sub>H</sub>(500 MHz; CDCl<sub>3</sub>) 8.58 (1H, s, Ar H), 8.15-8.08
(2H, m, Ar H), 7.70 (1H, s, Ar H), 7.63 (2H, d, J 7.3, Ar H), 7.59-7.48 (6H, m, Ar H), 7.42-7.36 (3H, m, Ar H), 7.36-7.31 (2H, m, Ar H); δ_c(125 MHz; CDCl_3) one CH peak missing, 166.7 (s), 154.0 (s), 151.2 (s), 142.8 (s), 136.84 (s), 136.75 (s), 133.7 (s), 131.7 (s), 130.8 (d), 130.1 (d), 129.8 (d), 129.51 (d), 129.46 (s), 129.0 (d), 128.9 (d), 128.4 (d), 127.5 (d), 113.3 (d), 102.0 (d); MALDI-TOF (m/z): 406 (MH^+2, 2%), 405 (MH^+1, 11), 404 (MH^+, 34), 403 (M^+, 100), 402 (M^+-1, 4), 284 (1).

4.5. Conversion of 6-iodo-1,2-diphenylbenzimidazole (9d) to 1,2-diphenylbenzimidazole (9a)

A stirred mixture of 6-iodo-1,2-diphenylbenzimidazole (9d) (35 mg, 0.088 mmol) and Zn powder (17 mg, 0.264 mmol) in glacial AcOH (0.5 ml) was heated at ca. 118 °C for 15 h. The reaction mixture was then allowed to cool to ca. 20 °C, diluted with DCM (20 ml), washed with 1 M NaOH (2 × 20 ml), dried (Na_2SO_4), filtered and the volatiles removed. The residue was then dissolved in DCM (5 ml), adsorbed onto silica and chromatographed. Elution with DCM removed minor non polar side products and further elution (Et_2O/n-hexane, 1:1) gave the title compound 9a as colourless needles (23 mg, 97%), mp 109-110 °C (from n-hexane), (lit.,^{11} 110-111 °C), R_f (Et_2O/n-hexane, 1:1) 0.32; δ_H(500 MHz, CDCl_3) 7.89 (1H, d, J 8.0, Ar H), 7.57 (2H, d, J 7.3, Ar H), 7.53-7.45 (3H, m, Ar H), 7.38-7.24 (8H, m, Ar H); identical to that described above.
4.6. Conversion of \( N\)-(2-(phenylamino)phenyl)benzamide (19) to 1,2-diphenyl-benzimidazole (9a)

A stirred mixture of \( N\)-(2-(phenylamino)phenyl)benzamide (19) (51 mg, 0.176 mmol) in glacial AcOH (1 ml) was heated at \( \text{ca.} \) 118 °C for 20 min. The reaction mixture was then allowed to cool to \( \text{ca.} \) 20 °C, diluted with DCM (50 ml), washed with 1 M NaOH (2 × 20 ml), dried (\( \text{Na}_2\text{SO}_4 \)), filtered and the volatiles removed. The residue was then dissolved in DCM (5 ml), adsorbed onto silica and chromatographed. Elution (\( \text{Et}_2\text{O}/n\text{-hexane}, 1:1 \)) gave the title compound 9a as colourless needles (47 mg, 100%), mp 109-110 °C (from \( n\text{-hexane} \)), (lit.,\(^{11}\) 110-111 °C), \( R_f \) (\( \text{Et}_2\text{O}/n\text{-hexane}, 1:1 \)) 0.32; \( \delta \) (500 MHz, CDCl\(_3\)) 7.89 (1H, d, \( J \) 8.0, Ar \( H \)), 7.57 (2H, d, \( J \) 7.3, Ar \( H \)), 7.53-7.45 (3H, m, Ar \( H \)), 7.38-7.24 (8H, m, Ar \( H \)); identical to that described above.

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Supporting Information Available  $^1$H and $^{13}$C NMR spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References


Graphical Abstract

Optimized conditions for the reductive ring contraction of benzotriazinyl radicals and related analogues afford benzimidazoles in near quantitative yields.

Caption

Optimized conditions for the reductive ring contraction of benzotriazinyl radicals and related analogues afford benzimidazoles in near quantitative yields.