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Metal–Halogen Exchange between Hydrazine Polyanions and α,α'-Dibromo-*o*-xylene

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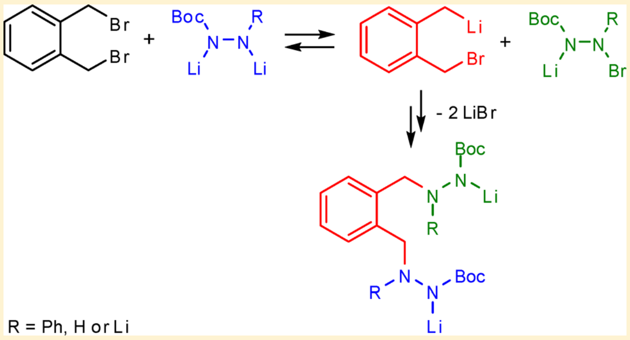
Ⓢ *Supporting Information*

ABSTRACT: Aromatic-bridged bis(hydrazines) were found to be the main products in the reaction of hydrazine polyanions with α,α'-dibromo-*o*-xylene. It was confirmed that the reaction is driven by a metal–halogen exchange process. A three-step reaction mechanism is suggested.



INTRODUCTION

Hydrazine derivatives are currently of great importance, finding application as dyes, pesticides, drugs, and building blocks in organic synthesis. Some of them have been proven to be active against tuberculosis, hypertension, and Parkinson's disease.[1] In addition, certain hydrazines show remarkable neuroprotective activity and are used for the treatment of psychiatric disorders. Many of the hydrazine-based antidepressants are molecules where a hydrazine moiety is bonded to an aromatic core through one or several methylene groups: e.g., phenelzine (Figure 1).[2]

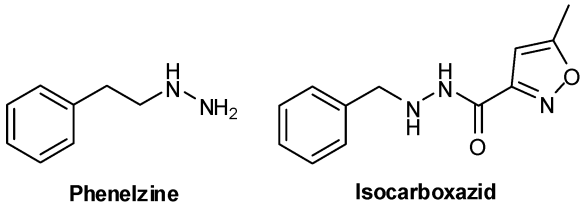
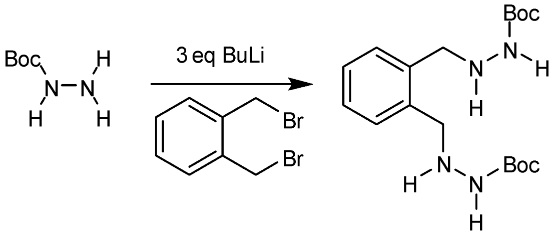


Figure 1. Hydrazine-based antidepressants phenelzine and isocarboxazid.

Previously we reported that the reaction of $BocNHNH_2$ treated with 3 equiv of BuLi and α,α'-dibromo-*o*-xylene unexpectedly afforded a product with two hydrazine fragments attached to the aromatic ring (Scheme 1).[3] Such aromatic-bridged bis(hydrazines) may be considered as close analogues of phenelzine; however, only a limited number of examples have been synthesized so far. Similar compounds with a carbonyl group have been prepared by the reaction of hydrazines with aromatic esters or acyl halides.[4]

A surprising result inspired us to start searching for an explanation of the phenomenon, because generally alkylation of monosubstituted hydrazines with dihalides leads to the corresponding heterocycles.[3] In our case steric hindrance cannot be a reason for the formation of the noncyclic product, as even bulkier heterocycles have been prepared utilizing similar aromatic dihalides.[5] In the obtained compound two methylene groups are bonded to equivalent nitrogens, but of different hydrazine molecules. Understanding that there is not an objective reason for this behavior of α,α'-dibromo-*o*-xylene, we assumed that the reaction pathway should include the formation of an intermediate bearing two different substituents on the aromatic ring. According to the proposed mechanism the trianion **1a** and α,α'-dibromo-*o*-xylene (**6**) generate the intermediates **2a** and **3** via metal–halogen exchange (Scheme 2). In the next step **3** may interact with the trianion **1a**, affording the intermediate **4a** which, in turn, can react either with the intermediate **2a** or its azo form **5a**, finally completing the structure. In the current work we present an experimental confirmation of our hypothesis that the reaction is driven by a metal–halogen exchange process.[6]

Scheme 1. Synthesis of an Aromatic-Bridged Bis(hydrazine)



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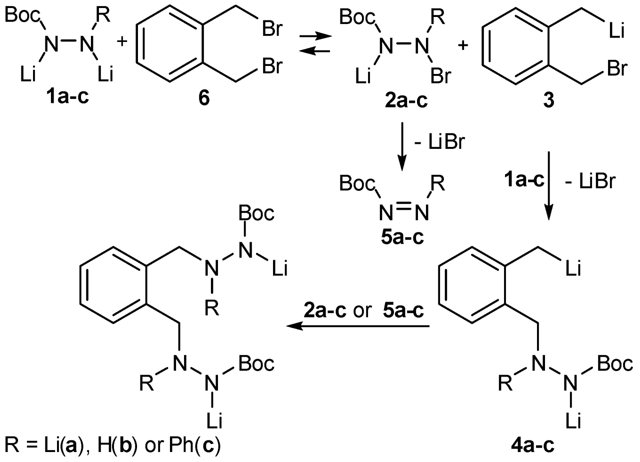
Scheme 2. Proposed Reaction Pathway



■ RESULTS AND DISCUSSION

We started with screening the hydrazine dianions in the reaction with the dibromide **6**. The dianions **1b**,**c** were generated from the corresponding hydrazines by treatment with 2 equiv of BuLi in THF at −78 °C prior to the addition of the dihalide. In compliance with the proposed mechanism, hydrazine dianions may be able to react similarly to the trianion. Indeed, it was found that $BocNHNH_2$ dianion furnished the same product **9** (Figure 2) with no impact on the yield and the reaction time (Table 1, entry 2). The dianion generated from PhNHNHBoc reacted in the same manner, giving the noncyclic bis(hydrazine) **11** in good yield (entry 3). These experiments confirmed that the method has a broader scope and is not limited to monosubstituted hydrazines. Nevertheless, the experiment with BocNHNHBoc dianion revealed that the presence of two strongly electron withdrawing groups on both nitrogens totally blocks the metal−halogen interconversion (entry 13).

To prove the metal−halogen exchange process, similar reactions have been carried out with 2,2′-bis(bromomethyl)-1,1′-biphenyl (**7**). This halide is similar to **6**, and it is expected to give the analogue of the intermediate **3** if the metal−halogen exchange is taking place. However, the intermediate **3′** generated from **7** was supposed to undergo self-cyclization via fast intramolecular alkylation to build a favorable six-membered-ring system; this is in contrast to its analogue **3** obtained from the dihalide **6**, for which this way is undesirable, as it would produce a strained four-membered cycle (Scheme 3). The desired carbocycle **12** was found in both reactions with $BocNHNH_2$ and PhNHNHBoc (entries 4 and 5). Some similar examples of a bromine−lithium interconversion with subsequent intramolecular cyclization may be also found in the literature.[7]

The next step of our work was to confirm that hydrazine polyanions act as metal donors in the process. The measured pK_a values of mono- and disubstituted hydrazines indicate that the existence of the corresponding dianions is definitely possible.[8] In our recent works we assumed that the trianion may be likewise obtained by the treatment of $BocNHNH_2$ with 3 equiv of BuLi and used for selective alkylation.[3,9] Despite the successful results obtained, full deprotonation of $BocNHNH_2$ has not been proven so far, thus making the existence of the trianion still questionable.

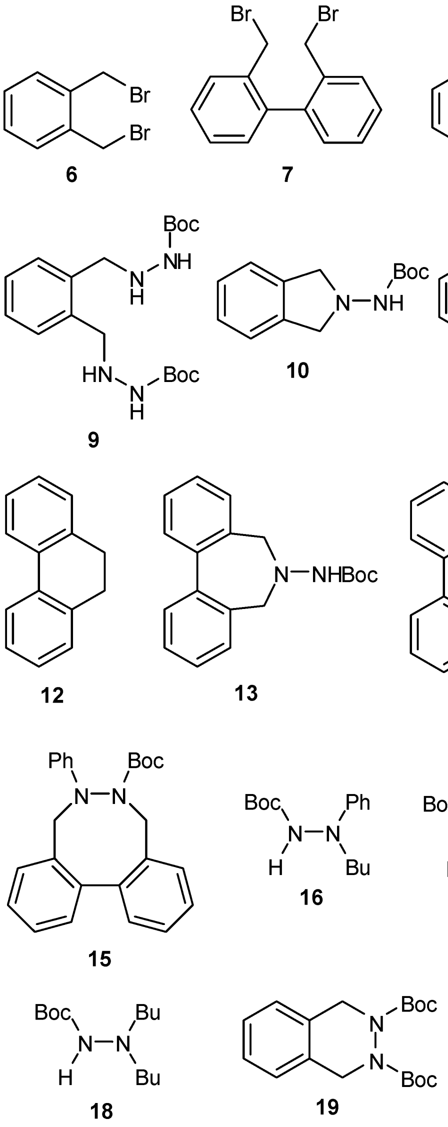


Figure 2. Compounds **6**−**19**.

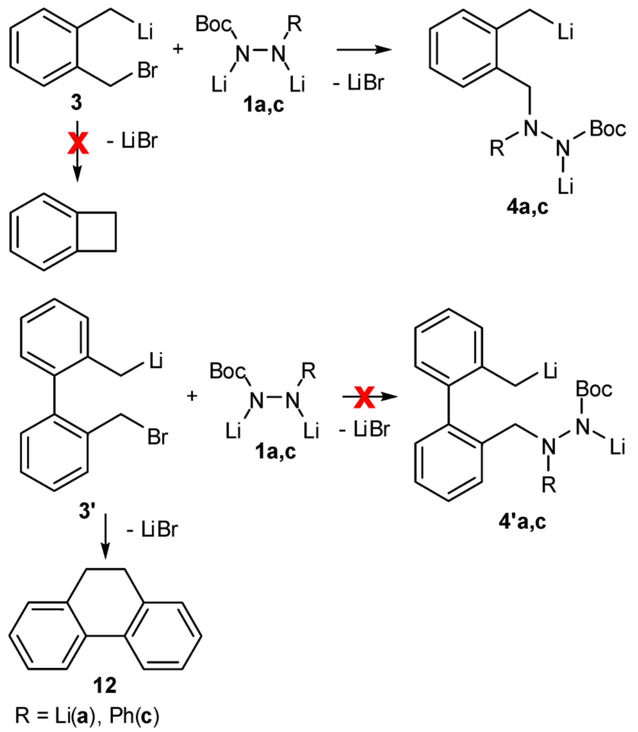
Our idea was to demonstrate the absence of free BuLi in the reaction mixture after 3 equiv of BuLi is added to $BocNHNH_2$ and the possibility to trap the excess BuLi if a greater amount was employed. At first we designed a model system adding 3 equiv of BuLi to PhNHNHBoc to produce the dianion **1c** with a fixed excess of BuLi. There are two theoretical possibilities for further metal−halogen exchange with the dihalides **6** or **7**. The first option is participation of the dianion **1c**, which should afford the intermediate **2c** or its azo analogue **5c**, which would likely react with BuLi. Alternatively, the process may take place between BuLi and the dihalide, providing BuBr, which can alkylate the dianion. This means that in both cases the hydrazine derivative **16** is expected to form (Scheme 4). This hypothesis was successfully confirmed (entries 6 and 7). As may be seen from Table 1, the yield of **16** is higher if the dihalide **7** is employed. This result is consistent with the inference that the intermediate **3′** is being constantly removed from the reaction mixture via self-cyclization, thus suppressing possible side reactions with BuLi or BuBr. The analogous experiments with $BocNHNH_2$ and 3 equiv of BuLi revealed no *N*-butyl derivatives, pointing out full deprotonation of the starting material (entries 1 and 4). In contrast, the use of 4

Table 1. Summarized Results of the Experiments

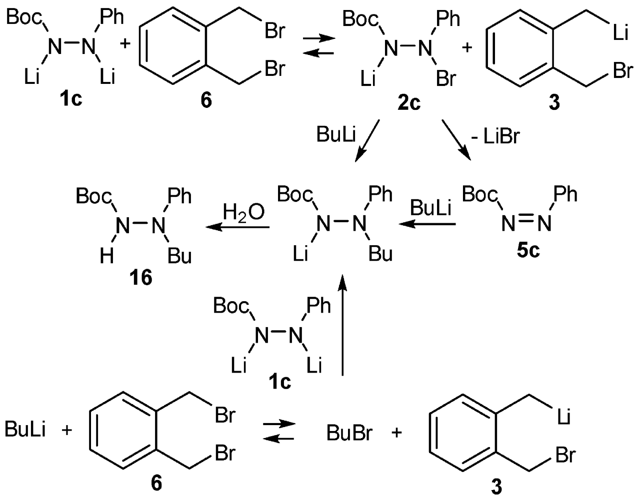
entry	starting material	conditions	reaction time	isolated products (yield, %)
1	$BocNHNH_2$	3 equiv of BuLi, 1 equiv of **6**	10 min	**9** (44), **10** (4)
2	$BocNHNH_2$	2 equiv of BuLi, 1 equiv of **6**	10 min	**9** (42), **10** (4)
3	PhNHNHBoc	2 equiv of BuLi, 1 equiv of **6**	30 min	**11** (65)
4[a]	$BocNHNH_2$	3 equiv of BuLi, 1 equiv of **7**	1 h	**12** (58), **13** (30)
5	PhNHNHBoc	2 equiv of BuLi, 1 equiv of **7**	1 day	**12** (26), **14** (34), **15** (17)
6	PhNHNHBoc	3 equiv of BuLi, 1 equiv of **6**	1 day	**11** (18), **16** (27)
7[a]	PhNHNHBoc	3 equiv of BuLi, 1 equiv of **7**	1 h	**12** (61), **16** (52)
8[a]	$BocNHNH_2$	4 equiv of BuLi, 1 equiv of **6**	2 h	**17** (18),[b] **18** (21)[b]
9[a]	$BocNHNH_2$	3 equiv of BuLi, 0.5 equiv of **6**	1 day	complex mixture
10[c]	$BocNHNH_2$	3 equiv of BuLi, 2 equiv of **6**	10 min	**9** (40)
11	$BocNHNH_2$	2 equiv of BuLi, 0.5 equiv of **6**	10 min	**9** (62)
12	PhNHNHBoc	2 equiv of BuLi, 0.5 equiv of **6**	2 h	**11** (60)
13[a]	BocNHNHBoc	2 equiv of BuLi, 1 equiv of **6**	2 days	**19** (60)
14[a]	$BocNHNH_2$	3 equiv of BuLi, 1 equiv of **8**	1 day	**9** (8), **10** (30)
15	PhNHNHBoc	2 equiv of BuLi, 1 equiv of **8**	1 h	**11** (70)

[a]Full conversion of the starting material was not observed. [b]The yield is based on the excess of BuLi. [c]0.76 equiv of **6** was recovered.

Scheme 3. Illustration of the Different Behavior of the Intermediates 3 and 3′ Generated from the Dihalides 6 and 7



Scheme 4. Two Possible Ways of the Formation of 16 in Entry 6 of Table 1



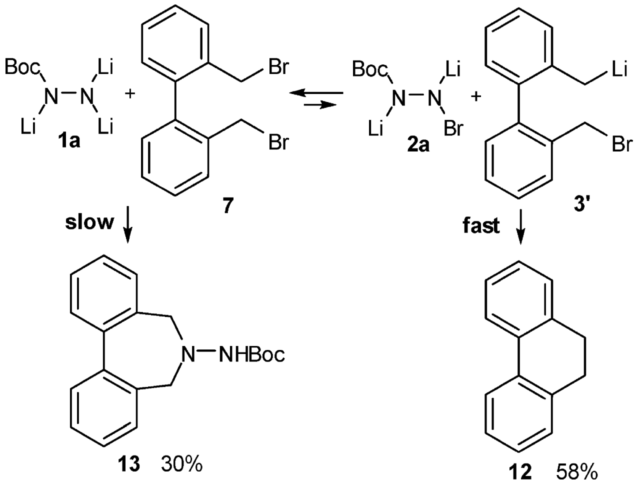
equiv of BuLi and **6** as a halide afforded the desired species **17** and **18** in 39% total yield, whereas the formation of **9** was totally suppressed (entry 8). This experiment finally verified that free BuLi is observed only if more than 3 equiv is added to $BocNHNH_2$.

Next we studied the reactions of hydrazine polyanions with 0.5 equiv of *α*,*α*′-dibromo-*o*-xylene, which is the stoichiometric quantity for **9** and **11**. As we know from previous experience, $BocNHNH_2$ trianion failed the test to yield the desired product **9** at these conditions (entry 9). Amazingly, $BocNHNH_2$ dianion afforded **9** in 62% yield which is the best known result for this compound (entry 11). The reason for such different actions for these two species is still unclear. Probably, $BocNHNH_2$ trianion has some specific feature requiring dihalide in 2-fold stoichiometric quantity. However, it was demonstrated that there is no positive impact on the yield of **9** if more than 1 equiv of **6** is added to the trianion, as the additional quantity of the dihalide remains unconsumed (entry 10). PhNHNHBoc dianion was proven to have almost no difference reacting with either 0.5 or 1 equiv of **6**, as very similar yield values for **11** were found (entry 12).

Finally we tested the reactions of hydrazine polyanions with *α*,*α*′-dichloro-*o*-xylene (**8**). It is known that the rates of metal interconversion in chlorides are significantly lower in comparison with bromides.[10] Indeed, the experiment with $BocNHNH_2$ trianion afforded the bis(hydrazine) **9** only in 8% yield, whereas the main isolated component was the heterocyclic product **10** as a result of competing direct alkylation of the trianion (entry 14). The reaction of PhNHNHBoc dianion with the dichloride **8** required significantly more time than the analogous reaction with the dibromide **6**; however, it was surprisingly discovered that the yield of **11** was almost the same (entry 15).

The obtained results encouraged us to make additional suggestions regarding the mechanism of the reaction. As has been shown, the first step of the reaction was proven to be metal−halogen exchange between a dianion or the trianion and *α*,*α*′-dibromo-*o*-xylene. We anticipate that it is an equilibrium process shifted to the left. We propose that if the equilibrium were shifted to the intermediates **2** and **3**, these species would likely interact with each other, giving heterocycles as main products. Nevertheless, **10** was isolated as only a minor component in entries 1 and 2. Our hypothesis is also supported by entry 4, where two competing reactions—intramolecular cyclization of the aromatic intermediate 3′ and intermolecular alkylation of the trianion—are taking place. Though the intramolecular process is much faster, there is still a comparable amount of the heterocycle **13** formed (Scheme 5).

Scheme 5. Formation of 12 and 13 in Entry 4 of Table 1



An equilibrium of metal−halogen exchange may be imagined as a reflective measure of relative anion stability.[11] If the equilibrium is shifted to the left, it may be suggested that $BocNHNH_2$ trianion is a weaker base than the intermediate **3**, which is an analogue of benzyllithium. Understanding that the pK_a value of toluene is at least several units lower than the pK_a value of butane,[12] it is obvious that BuLi should fully deprotonate $BocNHNH_2$, which has been experimentally confirmed.

In the case of PhNHNHBoc dianion the equilibrium has to be shifted to the left even more strongly than in the case of $BocNHNH_2$ trianion. Analogously with the previous situation described above, it was also confirmed by an experiment with the dihalide **7**. It was found that the total yield of the products of dianion alkylation with the dihalide **7** is twice as high as the yield of the carbocycle **12**, despite the fact that the latter species is expected to form much more quickly (entry 5). A special case is BocNHNHBoc dianion, where the equilibrium is shifted to the left so strongly that the metal−halogen interconversion is not actually taking place (entry 13). Obviously, the strong electron-withdrawing properties of the Boc group make the N−Li bond more covalent, eliminating the possibility for interchange of the metal.

The second step of the mechanism includes an interaction between the intermediate **3** and the polyanion **1**. Our confidence is based on a comparison of the reactions of $BocNHNH_2$ trianion **1a** with the dihalides **6** and **7** (entries 1 and 4). The only difference in actions of these two dihalides lies in the failure of **7** to provide the intermediate **3′** in sufficient quantity, as it is rapidly converting to the carbocycle **12** (Scheme 3). As can be observed, knocking out this intermediate is sufficient to terminate the process of the formation of the bis(hydrazine) at step 1, hence giving a green light for direct alkylation of the trianion **1a** (Scheme 5). This allows us to conclude that the next step of the formation of the bis(hydrazine) **9** has to include the interaction of **3** with a hydrazine derivative. Among all three candidates present in the reaction mixture, the intermediates **2a** and **5a** are inappropriate, as they would more likely afford the heterocycle **10**, which was found only as a minor component. Therefore, the most probable step is the interaction of the intermediate **3** with the trianion **1a**, furnishing the trianion **4a**.

Considering the structure of **9**, the third step of the mechanism should include the reaction of the intermediate **4** with either **2** or **5**, as the polyanion **1** is not able to contribute due to the absence of possible reaction centers. It is still unknown whether **2** is stable enough to function itself or transforms to the azo form **5**; therefore, we consider both options. An absolutely analogous reaction of unsymmetrical azo compounds with alkyllithium reagents under very similar conditions has been previously reported by our research group, and it was confirmed to be a very fast and selective process.[13] Apparently, the selectivity of the alkylation of $BocN{=}NR^1$ with R^2Li is achieved due to the greater stability of the anion $BocN^-{-}NR^1R^2$, thus being controlled thermodynamically.

The stability of the key intermediates **3** and **5a**−**c** is an important point that shall be discussed. We suppose that the intermediate **3** is a stable molecule which does not undergo intramolecular ring closure at low temperatures. Our expectations are in good accord with Parham's report, where a very similar intermediate has been described.[14] The stability of the intermediates $RN{=}NBoc$ (**5a**−**c**) strongly depends on the nature of the R group. If R has an aromatic origin, the stability of **5** is assured, as such compounds are well-known synthetic reagents.[13] The diazene $HN{=}NBoc$ is still an unknown substance; however, a similar analogue has been recently described to be a stable intermediate even at 70 °C.[15] Diazene anions, like $LiN{=}NBoc$ that is thought to be generated in the reaction of $BocNHNH_2$ trianion, are also known from the literature to be trapped as intermediates.[16]

■ CONCLUSION

In conclusion, we have confirmed that the reaction of hydrazine polyanions with *α*,*α*′-dibromo-*o*-xylene goes through a metal−halogen exchange, which is the first step of the proposed mechanism. Lithium−halogen interconversion is a known reaction; however, to the best of our knowledge we are the first to report the process at a nitrogen atom. Our method is a good synthetic tool, giving access to aromatic-bridged bis(hydrazines) in one step.

■ EXPERIMENTAL SECTION

General Considerations. All reactions were performed under an argon atmosphere in oven-dried glassware. THF was freshly distilled from Na/benzophenone. PhNHNHBoc and BocNHNHBoc were prepared by known methods.[17] All other reagents were obtained from commercial sources and used without further purification. TLC was performed using Macherey-Nagel silica gel TLC plates (Alugram SIL G/UV 254). Spots were visualized by UV light at 254 nm or by a ∼1% ethanolic solution of phosphomolybdic acid with subsequent heating. Column chromatography was carried out on 70−230 mesh Merck Kieselgel. ^1H and ^{13}C spectra were recorded at 200 and 50 MHz, respectively, on an AVANCE II 200 spectrometer (Spektrospin AG, Switzerland). Deuteroform was used as a solvent. The chemical shifts are reported on the ppm scale relative to the singlet (7.26 ppm for ^1H) and triplet (77.0 ppm for ^{13}C). Coupling constants are reported in Hz. IR spectra were measured on a PerkinElmer Spectrum BXII FTIR spectrometer using the ATR technique with ZnSe. Melting points were determined on a Stuart SMP10 melting point apparatus. HRMS spectra were acquired using direct nano-ESI infusion on a Q Exactive mass spectrometer (Thermo Fischer Scientific).

Typical Procedure for Alkylation of BocNHNH$_2$ Trianion with 1 Equiv of Dihalide. An oven-dried flask was charged with BocNHNH$_2$ (2.00 mmol, 264 mg), evacuated, and back-filled with argon. Thereafter THF (12 mL) was added to dissolve the solid. The reaction mixture was cooled to −78 °C, and a 1.6 M BuLi solution in hexane (6.00 mmol, 3.75 mL) was added dropwise. The reaction mixture was warmed to −45 °C for 15 min, and a solution of α,α'-dibromo-*o*-xylene (2.00 mmol, 528 mg) in THF (2 mL) was added. The reaction progress was monitored by TLC (petroleum ether/EtOAc 1/1). After 10 min the reaction was complete. The reaction mixture was quenched by addition of 0.1 mL of H_2O, and the solvent was evaporated under reduced pressure. To the residue were added 15 mL of chloroform and anhydrous $MgSO_4$. The mixture was filtered, and $MgSO_4$ was washed with chloroform (3 × 2 mL). The volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica (petroleum ether/EtOAc 1/1), resulting in **9** (161 mg, 44%) as a yellowish solid and **10** (21 mg, 4%) as a white solid.

Typical Procedure for Alkylation of BocNHNH$_2$ Dianion with 1 Equiv of Dihalide. An oven-dried flask was charged with BocNHNH$_2$ (2.00 mmol, 264 mg), evacuated, and back-filled with argon. Thereafter THF (12 mL) was added to dissolve the solid. The reaction mixture was cooled to −78 °C, and a 1.6 M BuLi solution in hexane (4.00 mmol, 2.50 mL) was added dropwise. The reaction mixture was warmed to −45 °C for 15 min, and a solution of α,α'-dibromo-*o*-xylene (2.00 mmol, 528 mg) in THF (2 mL) was added. The reaction progress was monitored by TLC (petroleum ether/EtOAc 1/1). After 10 min the reaction was complete. The reaction mixture was quenched by addition of 0.1 mL of H_2O, and the solvent was evaporated under reduced pressure. To the residue were added 15 mL of chloroform and anhydrous $MgSO_4$. The mixture was filtered, and $MgSO_4$ was washed with chloroform (3 × 2 mL). The volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica (petroleum ether/EtOAc 1/1), resulting in **9** (146 mg, 42%) as a yellowish solid and **10** (20 mg, 4%) as a white solid.

Typical Procedure for Alkylation of PhNHNHBoc Dianion with 1 Equiv of Dihalide. An oven-dried flask was charged with PhNHNHBoc (1.00 mmol, 208 mg), evacuated, and back-filled with argon. Thereafter THF (5 mL) was added to dissolve the solid. The reaction mixture was cooled to −78 °C, and a 1.6 M BuLi solution in hexane (2.08 mmol, 1.30 mL) was added dropwise (a lemon yellow solution of the dianion was obtained). The reaction mixture was warmed to −45 °C for 15 min, and a solution of α,α'-dibromo-*o*-xylene (1.00 mmol, 264 mg) in THF (1 mL) was added. The reaction progress was monitored by TLC (petroleum ether/EtOAc 5/1). After 30 min the reaction was complete. The reaction mixture was quenched by addition of 0.1 mL of H_2O, and the volatiles were evaporated under reduced pressure. The residue was purified by column chromatography on silica (petroleum ether/EtOAc 5/1), resulting in **11** (168 mg, 65%) as a white solid.

Typical Procedure for Alkylation of BocNHNHBoc Dianion with 1 Equiv of Dihalide. An oven-dried flask was charged with BocNHNHBoc (1.00 mmol, 232 mg), evacuated, and back-filled with argon. Thereafter THF (5 mL) was added to dissolve the solid. The reaction mixture was cooled to −78 °C, and a 1.6 M BuLi solution in hexane (2.08 mmol, 1.30 mL) was added dropwise. The reaction mixture was warmed to −45 °C for 15 min, and a solution of α,α'-dibromo-*o*-xylene (1.00 mmol, 264 mg) in THF (1 mL) was added. The reaction mixture was warmed to room temperature for 1 h and stirred at room temperature for 2 days. The reaction progress was monitored by TLC (petroleum ether/EtOAc 5/1). The reaction mixture was quenched by addition of 0.1 mL of H_2O, and the volatiles were evaporated under reduced pressure. The residue was purified by column chromatography on silica (petroleum ether/EtOAc 10/1 → 5/1), resulting in **19** (199 mg, 60%) as a white solid.

Compound Characterization Data. *tert-Butyl 2,2′-(1,2-Phenylenebis(methylene))bis(hydrazinecarboxylate) (**9**).*[3] Yellowish solid. Mp: 120−122 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.35−6.90 (m/broad s, 6H), 4.92 (broad s, 2H), 4.09 (s, 4H), 1.48 (s, 18H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 156.6, 136.6, 131.3, 128.0, 80.2, 54.2, 28.3. FTIR ν (cm^{-1}): 3336, 3307, 3226, 2977, 2934, 2867, 1698, 1552, 1482, 1454, 1367, 1271, 1251, 1152, 1007, 854, 844, 739.

*tert-Butyl Isoindolin-2-ylcarbamate (**10**).* White solid. Mp: 79−81 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.25−7.16 (m, 4H), 6.26 (broad s, 1H), 4.35 (s, 4H), 1.52/1.50 (s/s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.9, 138.0, 126.9, 122.2, 80.2, 60.0, 28.3. FTIR ν (cm^{-1}): 3253, 3046, 3027, 2977, 2930, 1700, 1520, 1477, 1463, 1391, 1366, 1274, 1250, 1157, 1049, 910, 738. HRMS (ESI): *m/z* calcd for $C_{13}H_{18}N_2O_2$ (MH$^+$) 235.1441, found 235.1443.

*tert-Butyl 2,2′-(1,2-Phenylenebis(methylene))bis(2-phenylhydrazinecarboxylate) (**11**).* White solid. Mp: 178−179 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.41−7.10 (m, 8H), 6.90−6.80 (m, 7H), 6.46/6.21 (broad s/broad s, 1H), 4.69 (s, 4H), 1.37 (s, 18H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.0, 149.6, 135.4, 130.9, 129.0, 127.8, 120.0, 113.8, 80.5, 54.0, 28.2. FTIR ν (cm^{-1}): 3294, 3062, 3029, 2978, 2930, 1700, 1598, 1497, 1456, 1391, 1366, 1248, 1155, 1050, 736, 690. HRMS (ESI): *m/z* calcd for $C_{30}H_{38}N_4O_4$ (MH$^+$) 519.2966, found 519.2969.

*9,10-Dihydrophenanthrene (**12**).*[18] Colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.3 Hz, 2H), 7.45−7.30 (m, 6H), 2.99−2.97 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 137.4, 134.5, 128.1, 127.4, 126.9, 123.7, 29.0. FTIR ν (cm^{-1}): 3064, 3016, 2931, 2891, 2834, 1485, 1454, 1443, 771, 743, 725.

*tert-Butyl 5H-Dibenzo[c,e]azepin-6(7H)-ylcarbamate (**13**).* Yellowish oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.52−7.36 (m, 8H), 5.70 (broad s, 1H), 3.65 (s, 4H), 1.49/1.45 (s/s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.4, 141.0, 133.2, 132.8, 128.6, 127.9, 127.8, 80.2, 58.8, 28.3. FTIR ν (cm^{-1}): 3242, 3062, 2976, 2933, 1725, 1492, 1481, 1451, 1391, 1366, 1244, 1159, 1098, 1051, 910, 753, 731. HRMS (ESI): *m/z* calcd for $C_{19}H_{22}N_2O_2$ (MH$^+$) 311.1754, found 311.1755.

*tert-Butyl 2,2′-(Biphenyl-2,2′-diylbis(methylene))bis(2-phenylhydrazinecarboxylate) (**14**).* White solid. Mp: 76−77 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.60−7.26 (m, 8H), 7.16 (t, *J* = 7.8 Hz, 4H), 6.81 (t, *J* = 7.1 Hz, 2H), 6.57 (d, *J* = 7.0 Hz, 4H), 6.02/5.76 (broad s/broad s, 2H), 4.47 (s, 4H), 1.48/1.31 (s/s, 18H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.5, 148.9, 140.4, 135.4, 129.8, 129.3, 129.0, 127.7, 127.4, 119.2, 112.5, 80.8, 54.9, 28.2. FTIR ν (cm^{-1}): 3318, 3060, 3023, 2977, 2929, 1703, 1598, 1498, 1476, 1454, 1391, 1366, 1246, 1155, 1050, 1008, 909, 747, 729, 690. HRMS (ESI): *m/z* calcd for $C_{36}H_{42}N_4O_4$ (MH$^+$) 595.3279, found 595.3281.

*tert-Butyl 7-Phenyl-7,8-dihydrodibenzo[d,f][1,2]diazocine-6(5H)-carboxylate (**15**).* Colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.43−7.12 (m, 10H), 6.76 (t, *J* = 6.8 Hz, 1H), 6.63−6.56 (m, 2H), 4.78−4.28 (m, 4H), 1.31/1.25 (s/s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.1, 148.3, 142.1, 141.6, 134.2, 130.4, 129.7, 129.4, 129.3, 129.1, 128.9, 128.5, 127.8, 127.7, 127.5, 118.3, 111.2, 80.4, 55.5, 53.2, 28.2. FTIR ν (cm^{-1}): 3062, 2973, 2931, 2870, 1700, 1597, 1498, 1479, 1454, 1384, 1365, 1320, 1167, 1136, 1089, 910, 747, 691. HRMS (ESI): *m/z* calcd for $C_{25}H_{26}N_2O_2$ (MH$^+$) 387.2067, found 387.2065.

*tert-Butyl 2-Butyl-2-phenylhydrazinecarboxylate (**16**).* Yellowish oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.28−7.20 (m, 2H), 6.84−6.78 (m, 3H), 6.35/6.15 (broad s/broad s, 1H), 3.50−3.43 (m, 2H), 1.64 (quin, *J* = 7.4 Hz, 2H), 1.50−1.26 (m, 11H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.9, 149.3, 129.1, 119.0, 112.7, 80.7, 52.3, 28.5, 28.0, 20.3, 13.9. FTIR ν (cm^{-1}): 3292, 3062, 3027, 2959, 2931, 2871, 1704, 1599, 1499, 1455, 1391, 1366, 1248, 1162, 1140, 1058, 747, 691. HRMS (ESI): *m/z* calcd for $C_{15}H_{24}N_2O_2$ (MH$^+$) 265.1911, found 265.1911.

*tert-Butyl 2-Butylhydrazinecarboxylate (**17**).* Brownish oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.93/4.57 (broad s/broad s, 2H), 2.80 (t, *J* = 7.0 Hz, 2H), 1.46−1.33 (m, 13H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 156.7, 80.3, 51.7, 29.8, 28.3, 20.2, 13.9. FTIR ν(cm^{-1}): 3306, 2960, 2932, 2871, 1704, 1476, 1456, 1392, 1366, 1280, 1253, 1165, 1045, 1019. HRMS (ESI): *m/z* calcd for $C_9H_{20}N_2O_2$ (MH$^+$) 189.1598, found 189.1598.

*tert-Butyl 2,2-Dibutylhydrazinecarboxylate (**18**).* White solid. Mp: 53−55 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.45/4.90 (broad s/broad s, 1H), 2.69 (broad s, 4H), 1.50–1.25 (m, 17H), 0.89 (t, J = 7.1 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 79.9, 58.1, 29.9, 28.1, 20.3, 13.9. FTIR ν (cm^{-1}): 3278, 2957, 2932, 2870, 1713, 1697, 1492, 1457, 1390, 1366, 1247, 1171, 1114, 1080, 1044, 1014. HRMS (ESI): m/z calcd for $C_{13}H_{28}N_2O_2$ (MH^+) 245.2224, found 245.2222.

*Di-tert-butyl Phthalazine-2,3(1H,4H)-dicarboxylate (**19**).*[19] White solid. Mp: 112–113 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.26–7.11 (m, 4H), 5.12–4.87 (m, 2H), 4.60–4.32 (m, 2H), 1.53/1.51 (s/s, 18H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.3, 131.7, 126.7, 126.3, 81.1, 44.9, 28.2. FTIR ν (cm^{-1}): 3068, 2977, 2931, 2854, 1704, 1477, 1454, 1391, 1366, 1294, 1280, 1236, 1223, 1164, 1148, 1122, 1111, 1043, 1027, 857, 747, 729.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving ^{1}H and ^{13}C NMR spectra for all isolated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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