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6,12-Diphenyldibenzo[*b,f*][1,5]diazocine as an Electron-Capture Agent: Efficient Mechanistic Probe for SET Processes and Reagent for the Oxidative Dimerization of Benzylic Organometallics[‡]

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In the present study, 6,12-diphenyldibenzo[*b,f*]diazocine, which X-ray diffraction measurements have now shown to possess a tub-shaped, eight-membered central ring, has been treated with sodium or lithium metal at 25 °C in THF, in an attempt to form the planar, Hückel-aromatic dianion by the addition of two electrons to the central diazocine. Hydrolysis of such an aromatic dianion should have led to the isomeric 5,12- or 5,6-dihydro derivative of the original diazocine. In actuality, the only product obtained quantitatively upon hydrolytic workup was the interesting quadricyclic transannular reduction product, 4b,9b-diphenyl-4b,5,9b,10-tetrahydroindolo[3,2-*b*]indole, whose 3D structure has now been confirmed by X-ray crystallography and ^{13}C NMR spectroscopy. Preferential SET transannular reduction of the diazocine to yield the quadricyclic indolo[3,2-*b*]indole dianion, rather than the planar, Hückel-aromatic anion, is ascribed to the transannular electronic stabilization operative in the tub-shaped diazocine radical-anion. The quantitative generation of the indolo[3,2-*b*]indole dianion can be employed for the oxidative dimerization of the organic groups in benzylic lithium reagents. Thus treating one equivalent of the diazocine with two equivalents of benzyllithium, benzhydryllithium, or trityllithium yields quantitatively bibenzyl, 1,1,2,2-tetraphenylethane, or (4-benzhydrylphenyl)triphenylmethane, respectively. This oxidative dimerization is potentially of practical preparative scope, since the hydrolysis byproduct, the indolo[3,2-*b*]indole, is conveniently reconverted into the starting diazocine reagent by oxidation with chromium trioxide in acetic acid. The formation of the indolo[3,2-*b*]indole as a byproduct in the carbometalation of the diazocine by various RLi and Grignard reagents offers a clue as to the SET mechanism of carbometalation.

Introduction

Our interest in nitrogen analogs of cyclooctatetraene has stemmed from our reinvestigation of the preparation of the purported 3,4,7,8-tetraphenyl-1,2,5,6-tetraazocine. We determined that no such structure was isolated but that the putative substance is actually 2,4,5-triphenylimidazole.[1] In an extension of our studies we then undertook the electron-transfer reduction of the authentic, tub-shaped 6,7-diphenyldibenzo[*e,g*][1,4]diazocine (**1**) in the hope of generating the Hückel-aromatic, necessarily planar dianion **2**. However, after treatment with a sodium metal suspension in THF and subsequent hydrolysis, the product was not the diamine **3** but a *Z*- and *E*-isomeric mixture of enamines **4a** and **4b**, both of which isomers were separated and their individual structures determined by X-ray crystallography.[2] Clearly, the profound rearrangement of diazocine **1**

upon reduction with sodium must have involved transannular bonding in the transition state between the asterisked N and C sites in **1** (Scheme 1). Because of the tub-shape of **1**, reaching such a transition state apparently requires less energy than attaining the necessary planarity for Hückel aromaticity.[3a]
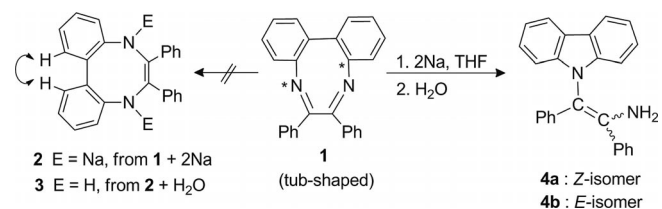
Scheme 1.

In order to avoid the destabilizing *ortho* H repulsions in **2**, we now have examined the electron-transfer reduction of an isomer of **1**, namely, 6,12-diphenyldibenzo[*b,f*][1,5]diazocine (**5**) (Scheme 2).[4] Although the validity of structure **5** was assured both by its logical synthesis via the bimolecular dehydration of 2-aminobenzophenone and by its spectroscopic data,[4] its 3D stereochemistry was not. Our electron-transfer investigations now envisaged two possible and worthwhile outcomes: either the generation of a planar, aromatic dianion of diazocine **5**, lacking the steric barriers in-
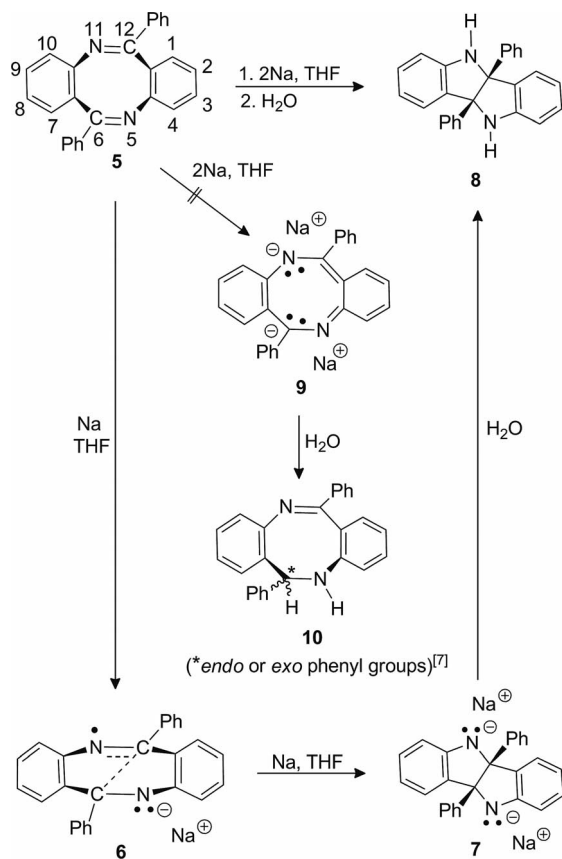
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herent in **2** or **3**, or further insight into transannular electronic delocalization operative in such [1,5]diazocines as **5**. The findings reported here have far exceeded our expectations.

Scheme 2.

5   **8**

Figure 1. Thermal ellipsoid (30%) diagrams for 6,12-diphenyldibenzo[*b,f*][1,5]diazocine (**5**) and 4b,9b-diphenyl-4b,5,9b,10-tetrahydroindolo[3,2-*b*]indole (**8**). Selected bond lengths (atom separations) [Å] and bond angle: **5** (colorless block, m.p. 191–193 °C): N1–C25 1.284(1), N1–C13 1.419(1), [N1···N2 3.294(3)], [C25···C26 3.000(2)], [N1···C26 2.879(2)], [N2···C25 2.877(2)], N2–C26 1.284(1), N2–C12 1.417(1), C1–C6 1.394(2), C1–C2 1.394(2), C1–C25 1.482(2), C25–N1–C13, 118.10(9), C26–N2–C12 118.99(9), C6–C1–C2, 119.00(10), C6–C1–C25 119.57(10), C2–C1–C25 121.36(10), C3–C2–C10 120.26(10); **8** (colorless block, m.p. 207–208 °C): N1–C14 1.396(2), N1–C2 1.477(1), N2–C8 1.405(2), N2–C1 1.480(1), C1–C15 1.524(2), C1–C2 1.609(2), C1–C9 1.524(2), C2–C21 1.524(2), C14–N1–C2 108.25(9), C8–N2–C1 107.83(9), N2–C1–C15 111.31(9), N2–C1–C9 113.85(9), C15–C1–C9 112.05(9), N2–C1–C2 103.81(9).

Results and Discussion

X-ray Diffraction Study of [1,5]Diazocine 5

The single-crystal X-ray diffraction study of **5** has now shown that it possesses a nonplanar, tub-like structure, similar to **1** (structure **5**, Scheme 2 and Figure 1). Noteworthy is the coplanarity of the transannular C=N and N=C groups, with the cross-ring N1 and N2 atom separations of 3.294(3) Å and the C25–C26, N1–C26, and N2=C25 atom separations of 3.000(2), 2.879(2), and 2.877(2) Å, respectively. The cross-ring proximity of these atoms raises the probability of transannular electronic delocalization and thus bonding in radical-anionic (i.e., **6**) and dianionic (i.e., **7**) intermediates by SET processes (Scheme 2).

The SET Reduction of [1,5]Diazocine 5 with Sodium or Lithium in THF

Experimental support for these interatomic proximities was obtained by the treatment of **5** in THF with sodium or lithium metal suspensions at 25 °C and subsequent hydro-
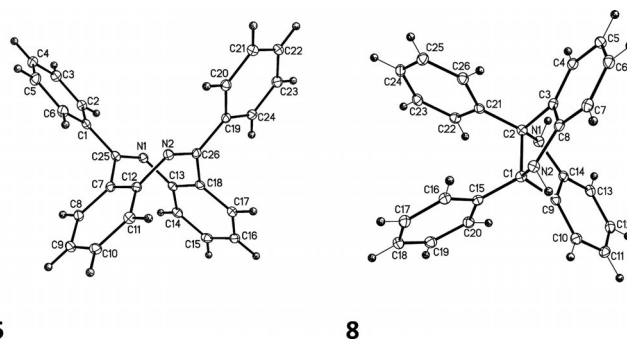
lytic workup. No matter what ratio of alkali metal to **5** was employed, the only product isolated in every run was 4b,9b-diphenyl-4b,5,9b,10-tetrahydroindolo[3,2-*b*]indole (**8**, or succinctly, indolo-indole **8**) as an *R,S* racemate. Its spectroscopic and X-ray diffraction study (Scheme 2 and Figure 1) revealed that this product has the compact quadricyclic structure shown in **8** with *syn*-neighboring phenyl groups. Although a partial structure for **8** had been previously proposed for the electrochemical reduction product of **5** on the basis of limited analytical, IR, and ^{1}H NMR spectroscopic data,[5] a correct connectivity and stereochemistry of the product could not be unambiguously established or even corroborated. The structure previously proposed for **8**[5] was based upon analogous evidence to that obtained by the Sternbach group for a dihydro derivative obtained by the chemical reduction of the 2,8-dichloro derivative of **5** by H$_2$ with a platinum catalyst or by zinc with acetic acid.[6] Again in this study, a definitive X-ray diffraction determination or even corroboration by ^{13}C NMR spectroscopy was lacking. The present X-ray diffraction study of **8** therefore represents the first confirming evidence for the tub-shaped 3D structure of **8** with its interesting strained quadricyclic ring connectivity, whose central sp^3-hybridized C–C bond is unusually long at 1.602(2) Å. The number of distinct ^{13}C singlets in the decoupled NMR spectrum [with its C_2 symmetry, 10 peaks between 110.21 and 151.01 ppm for the C(sp^2) nuclei and one peak at 83.22 ppm for a C(sp^3) nucleus corroborates the 3D structure of **8** in solution.

Since the possible, isomeric **9**, having only one of the C=N groups of **5** reduced to a –CH–NH– linkage, was never observed under our range of reduction conditions,[7] we conclude that (1) the potentially planar aromatic dianionic precursor of **10**, namely, **9**, is not formed at 25 °C;

and (2) the more stable intermediate radical anion **6** is delocalized transannularily over the remaining C=N linkage (Scheme 2). The second electron adds to the second N center with full formation of a σ C–C bond, as in **7**. From these findings it is evident that the nonplanar disodium salt **7**, with its crease of the transannular sp³-hybridized C–C bond, is much more thermodynamically stable than the formally Hückel-aromatic salt **9**. As considered above, the principal destabilizing factor in **9** is the energy required to maintain planarity in the eight-membered ring.

## The SET Reduction of [1,5]Diazocine 5 with Active Organometallics

The ease with which the SET reduction of **5** to, ultimately, **8** occurs with a heterogeneous reductant like sodium or lithium in THF aroused our curiosity about the use of homogeneous SET reductants of the organolithium in THF.[8,9] Noteworthy in this regard is our previous observation that lithium reagents, such as *n*-butyllithium and *tert*-butyllithium, also promote the rearrangement of diazocine **1** into the dilithium salts of **4a** and **4b**, albeit only in moderate yields.[2] In addition, we have already demonstrated that the allyl Grignard reagents can act as a surrogate for Mg metal, especially in THF, by serving as a SET reductant with azomethine and pyridinoid substrates.[10]

In evaluating the suitability of RLi reagents (i.e., **11**) for such SET reductions with [1,5]diazocine **5**, we sought to identify those lithium or other organometallic reagents that undergo SET (path a, structure **12**, Scheme 3) in great preference to the competing carbolithiation of the C=N linkage (path b, structure **13**, Scheme 3). As will be seen, such selectivity is essential for attaining high yields of C–C coupling in homodimer **14** and the dilithium salt **12**. The formation of homodimer **14** can be viewed as oxidative dimerization of RLi and could serve as a preparation of such dimers.[11]
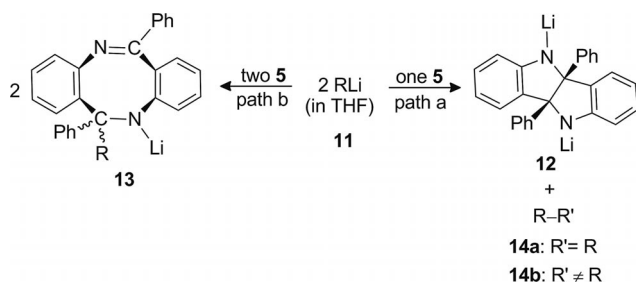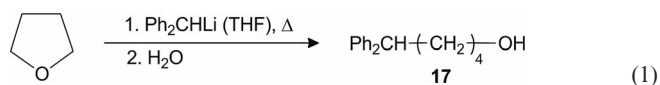

Scheme 3.

The most promising RLi reagents to consider, a priori, for preparative oxidative dimerizations were the benzyl- (**15a**), benzhydryl- (**15b**), and trityl- (**15c**) lithiums and their substituted analogs. The reason for this choice is that the donor SET character of anions **15a**–**15c** should be greater than that of an isolated alkyl carbon because benzylic carbanion **15a**–**15c** and their corresponding radicals share similar stabilizations (not the same) by π-electron delocalization (Scheme 4).
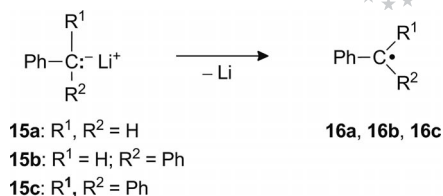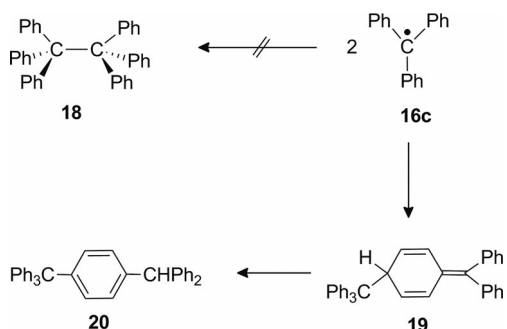

Scheme 4.

Let it be noted, in advance, that each of these three lithium reagents ultimately gave quantitative yields of indolo-indole **8** as well as of an oxidative dimer **14** under appropriate experimental conditions and subsequent hydrolysis. First and most straightforward is the behavior of benzhydryllithium (**15b**). Simply stirring diazocine **5** with two equivalents of **15b** in THF at 25 °C, followed by hydrolysis, gave only **8**, without a trace of any **13**, and one equivalent of homodimer, 1,1,2,2-tetraphenylethane [**14a**, R = (C₆H₅)₂-CH-].[12] However, when such a reaction of the same scale was conducted instead at reflux for 48 h, hydrolytic workup showed that 84% of the diazocine had been converted into **8** and **14a**. The rest of the lithium reagent **15b** (about 15%) apparently was consumed by attack on the THF by the known reaction in Equation (1) because 30% of 5,5-diphenyl-1-pentanol (**17**) was formed.[13]

$$\text{(1)}$$

Previous experimental evidence on this cleavage of THF are consistent with **15b** attacking THF, not as a nucleophile but as a donor SET reagent, just in the same manner shown in path a of Scheme 3.[14]

The reaction of diazocine **5** with two or more equivalents of tritylithium (**15c**) in THF at room temperature also occurred smoothly to give, upon hydrolysis only **8** and a molar equivalent of a heterodimer R–R′ of the trityl group. As has been long known, this dimer is not hexaphenylethane (**18**), the dimer originally sought by Gomberg, but the so-called Ullmann–Borsum hydrocarbon (**20**), formed by the trityl radical (**16c**) coupling of the central carbon of one radical with a *para*-carbon of the other radical (i.e., **19**). A

Scheme 5.

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1,5-suprafical H-migration, either thermally allowed or acid-catalyzed, yields the final, aromatized product **20** (Scheme 5).[15]

Finally, the reaction of diazocine **5** with two or more equivalents of benzyllithium in THF[16] at room temperature followed both path a and path b of Scheme 3. Hydrolytic workup gave 36% (0.08 mmol) of **8** and 0.08 mmol of bibenzyl, as well as 64% of 6-benzyl-6,12-diphenyl-5,6-dihydrodibenzo[*b,f*][1,5]diazocine [**21**; Equation (2)].[17] Of great interest is that a 1.0:1.1 molar ratio of **5** and the benzyllithium-TMEDA complex in toluene (i.e., **15a**) gave, upon warming from –78 °C to room temperature and hydrolysis, 95% of *only* **21**.

$$(2)$$
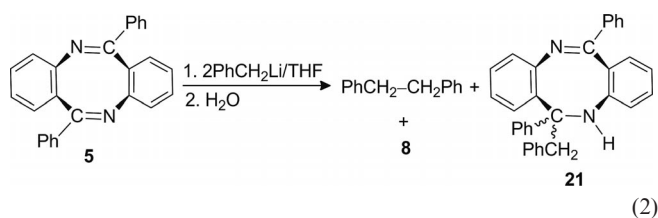
In an attempt to attain a higher ratio of **8** to **21**, benzyllithium was prepared from toluene, *n*-butyllithium, and TMEDA.[18] However, this reagent in toluene at 25 °C again consumed all of the diazocine **5**, but on hydrolysis the ratio of **8/21** was comparable to that of the reaction in THF, namely, 45:55, with 45% of bibenzyl as a side product.

In a last attempt to change the **8/21** ratio, the foregoing reaction of benzyllithium in TMEDA/toluene solution with **5** was heated for 24 h at reflux. Now upon hydrolysis the reaction mixture yielded 100% of the indolo-indole **8** and an equivalent amount of bibenzyl but no trace of adduct **21**. Clearly from these experiments it can be concluded that the lithium salt of adduct **21**, formed at 25 °C, undergoes loss of the benzyl group at about 110 °C. The mechanistic implications of this elimination reaction will be discussed in the next section.

At this point, feasible procedures are now available for the oxidative dimerizations of (1) benzyllithiums by the interaction of the benzyllithium-TMEDA complex with **5** in refluxing toluene to yield bibenzyl; (2) benzhydryllithiums with **5** in THF at 25 °C to produce 1,1,2,2-tetraphenylethanes; and (3) trityllithiums with **5** in refluxing THF to yield dimers of the Ullmann–Borsum type (structure **20**). Enhancing the practicality of this oxidative dimerization to these respective hydrocarbons are (1) the ease of column chromatographic separation of these hydrocarbon products from the indolo[3,2-*b*]indole byproduct **8** on silica gel with a 1:10 ethyl acetate/hexane eluent and (2) the ready quantitative oxidation of byproduct **8** back into starting material **5** by chromium trioxide in acetic acid.[6] Further applications of these oxidative C–C bond couplings in synthesis are receiving ongoing study.

[1,5]Diazocine 5 as a Mechanistic Probe for SET Processes

Of great practical and especially theoretical interest is the unexpected finding that the competition depicted in Scheme 3 between carbolithiation of **5** (path b) and the SET reduction of **5** (path a) is subject to kinetic control and that path a is the thermodynamically controlled pathway. This observation and related aspects, such as the molar ratios of **5** and **15a** employed, have great relevance to the mechanisms of these processes and will be analyzed in a subsequent article, where the carbometalations by RLi and RMgX reagents, either as 1,2-additions at the C=N linkage or as 1,4-conjugate additions at the 6-phenyl-C=N system, will be shown to be almost the exclusive pathway at lower temperatures and to occur stereoselectively. At high temperatures the SET reduction of **5** then becomes dominant.[18]

Pertinent to these future mechanistic studies are preliminary observations on the competition shown in Scheme 3 for the reactions of **5** with benzylmagnesium chloride in a 1.0:2.2 molar ratio in THF. Reaction at 25 °C, followed by hydrolysis gave only about 1% of **21** (analogous to path b), whereas in refluxing THF hydrolytic workup yielded only 40% of a 1:1 mixture of **8**/bibenzyl. In an overall slower reaction the initial carbomagnesiation of **5** is the faster process, whereas the SET reduction of **5** is the thermodynamically slower process. Similar observations have been made for the reactions of **5** with allylmagnesium chloride and with *tert*-butylmagnesium chloride in THF at reflux. The detection of significant proportions of **8** upon hydrolysis of these reactions offers cogent evidence for the competition of SET processes both in the carbometalation of **5** and in the reduction of **5** into **8**.

Future searches for SET intermediates in thermal or even photochemical reactions of σ-bonded organometallics will be facilitated by utilizing the enhanced electron capture properties of dibenzo[*b,f*][1,5]diazocine derivatives. Furthermore, estimating the extent of transannular electron delocalization, as suggested in intermediates **6** and 7, will be the subject of future ESR studies in this group.[19]
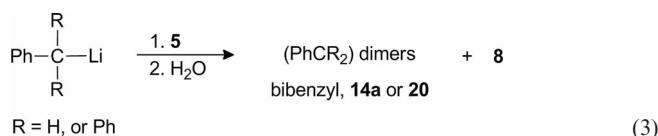
Conclusions

The present study of the reactions of 6,12-diphenyldibenzo[*b,f*][1,5]diazocine (**5**) with sodium, lithium, or benzylic derivatives of lithium (benzyl, benzhydryl, and trityl) or of magnesium in THF demonstrates that **5** is an efficient electron-capture agent. However, instead of accepting two electrons into the eight-membered, tub-shaped ring of **5** to form the Hückel-aromatic, necessarily planar dianion salt **9**, transannular bonding of the tub-shaped radical-anion **6** leads to σ-transannular bonding in dianion 7 and upon hydrolysis to indolo[3,2-*b*]indole **8**. The preferential formation of 7 over the supposedly planar Hückel-aromatic dianion **9** is interpreted to mean that the π-electron stabilization of planar, aromatic dianion **9** must be less than the energy required to maintain the planarity of the ring (estimated at 23 kcal/mol[3a]) and to overcome the bonding from transannular electron delocalization in **6** and 7.[3b]

This transannular electron delocalization in structures **6** and 7 makes **5** an efficient electron-capture agent toward

benzylic lithium reagents and makes practical the oxidative dimerization of benzyl, benzhydryl, and trityl groups in high yield and of potential widening scope [Equation (3)].

$$Ph-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-Li \quad \xrightarrow[\text{2. } H_2O]{\text{1. } \textbf{5}} \quad (PhCR_2)\text{ dimers} \quad + \quad \textbf{8}$$

bibenzyl, **14a** or **20**

R = H, or Ph
                                                                    (3)

Finally, in the foregoing SET reactions with organolithium or Grignard reagents, carbometalation has been found to be a competing process as a function of temperature. In future publications the competition exemplified in Scheme 3 will be explored with a broader array of organometallics. In addition, the stereochemistry (*exo* vs. *endo*) and the interplay of 1,2-versus 1,4-carbometalation will be explored. The ultimate goal is to establish the mechanistic relationship between the carbometalation and the SET reduction of diazocine **5**.

Experimental Section

Starting Reagents and Solvents: *n*-Butyllithium (2.5 M in hexane) was used as received from the Aldrich Chemical Company, with all transfers being made under dry, oxygen-free argon with argon-flushed gastight syringes. Likewise, the benzylic lithium reagents were prepared, as described in the following paragraphs, transferred and allowed to react under an argon atmosphere.

Benzyllithium (**15a**) was prepared as needed by two separate procedures: (1) In THF by the cleavage of benzyl methyl ether by lithium metal pieces in THF at –10 °C and then analyzed by the Gilman double titration method.[16a] (2) In toluene as the 1:1 complex with TMEDA by treatment of 1.0 equiv. of TMEDA in toluene with 1.0 equiv. of *n*-butyllithium in hexane and with subsequent analysis by adduction of an aliquot with benzophenone.[16b]

Benzhydryllithium(diphenylmethyllithium) (**15b**) was prepared by treating a solution of diphenylmethane (505 mg, 3.0 mmol, 1.0 equiv.) in THF (25 mL) with *n*-butyllithium in hexane (1.32 mL, 3.29 mmol, 1.1 equiv.) at room temperature. After 2 h the blood-red solution of **15b** was analyzed by treating an aliquot with D_2O (100 %), separating the organic layer after addition of ethyl ether, drying the organic layer, and removing volatiles and recording the ^1H NMR spectrum of the organic residue. The relative integrated intensities of the phenyl protons to the methylene protons, which had been 10.0 to 2.0 in the starting diphenylmethane, were now 10.0 to 1.2, indicating 80 % deuteration at the CH_2 group and thus an 80 % yield of **15b**. The ^1H NMR spectrum showed no trace of **17**, the product of the attack of **15b** on THF at higher temperatures [Equation (1)].

Trityllithium(triphenylmethyllithium) (**15c**) was similarly prepared by treating a solution of triphenylmethane (180 mg, 0.75 mmol, 1.0 equiv.) in THF (20 mL) with *n*-butyllithium in hexane (0.32 mL, 0.80 mmol, 1.1 equiv.) at room temperature. After 2 h an aliquot of the resulting deep-red solution was worked up with D_2O and ethyl ether, as in the foregoing procedure. The original aryl to methyne proton ratio of 15:1.0 for the starting Ph_3CH was now 15:0.55, indicating a 45 % yield of **15c**. Neither in this preparation of **15c** nor in the foregoing preparation of **15b** was there any sign of remaining *n*-butyllithium. Were any such a lithium reagent still pres-

ent in reactions with diazocine **5**, the known butylated adduct would have been formed. Thus, any *n*BuLi not consumed by lithiating Ph_2CH_2 or Ph_3CH must have been destroyed by the known attack of *n*BuLi on THF to produce ethylene and $CH_2=CHOLi$.[20]

The 6,12-diphenyldibenzo[*b,f*][1,5]diazocine (**5**), a known compound of m.p. 191–193 °C and characterized by published ^1H NMR and IR spectroscopic data, was prepared in accord with the published procedure and recrystallized from 95 % ethanol as pale yellow prisms, m.p. 197–199 °C.[4] In addition, in this work the ^{13}C NMR spectrum and the X-ray crystallographic structure of **5** have been determined. The resulting 3D structure of **5** is presented in Figure 1, along with representative bond lengths and bond angles. CCDC-868359 (for **5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

All reactions were carried out under a positive pressure of anhydrous, oxygen-free argon. All solvents employed with organometallic compounds were dried and distilled from a sodium metal-benzophenone ketyl mixture prior to use.[21]

Authentic ^1H and ^{13}C NMR spectra for comparison with those of all known compounds listed in Supplemental Information are accessible from AIST: Integrated Spectral Database System of Organic Compounds.[22]

Analytical Methods: The IR spectra were recorded with a Perkin–Elmer instrument (model 457), and samples were measured either as mineral oil mulls or as KBr films. The NMR spectra (^1H and ^{13}C) were recorded with a Bruker spectrometer (model EM-360) and tetramethylsilane (Me_4Si) was used as the internal standard. The chemical shifts reported are expressed on the δ scale in parts per million (ppm) from the Me_4Si reference signal. The GC–MS measurements and analyses were performed with a Hewlett–Packard GC 5890/Hewlett Packard 5970 mass-selective detector instrument. The gas chromatographic analyses were carried out with a Hewlett–Packard instrument (model 5880) provided with a 2-m OV-101 packed column or with a Hewlett–Packard instrument (model 4890) having a 30-m SE-30 capillary column. Melting points were determined with a Thomas-Hoover Unimelt capillary melting point apparatus.

Routinely the organometallic reaction mixtures were hydrolyzed with deoxygenated water. In cases where pieces of sodium or lithium were a reactant, residual pieces of the metal were picked out of the reaction mixture prior to hydrolysis. Ether was added to the hydrolysate, the organic layer was separated, the organic layer then dried with anhydrous Na_2SO_4, and volatile solvent was removed. ^1H and ^{13}C NMR spectra and TLC were recorded on the crude organic products. Where preparative yields were to be corroborated, column chromatographic separation of products on silica gel with a hexane/ethyl acetate eluent was carried out.

Reaction of 6,12-Diphenyldibenzo[*b,f*][1,5]-diazocine (5) with Sodium or Lithium Metal in Tetrahydrofuran: Into 30 mL of redistilled anhydrous and oxygen-free THF at room temperature magnetically stirred under an atmosphere of argon was added **5** (1.00 g, 2.78 mmol, 1 equiv.). Then the pale yellow solution was treated with freshly cut pieces of sodium metal (640 mg, 29 mmol, 10 equiv.). After 48 h of stirring, the reaction mixture turned orange and finally brown. After residual sodium pieces were removed by forceps, the reaction mixture was hydrolyzed and worked up in the standard manner. The residual organic oil showed the presence of no **5** but only 4b,9b-diphenyl-4b,5,9b,10-tetra-hydroindolo[3,2-*b*]indole (**8**). Recrystallization of the residue from

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95% ethanol yielded pure **8** (0.95 g, 95%), m.p. 200–201 °C. The ^{1}H and ^{13}C NMR spectra and the IR spectra in CHCl$_3$ and in Nujol mull have verified the identity of this solid with the previously reported compound **8**.[5] Moreover, the herein reported ^{13}C NMR spectrum in CDCl$_3$ and the XRD data on a pure, crystallized sample of **8** lend strong corroboration for the 3D structure of **8** both in the solid state and in solution. The solid-state structure of **8**, along with representative bond lengths and bond angles is presented in Figure 1. In a reaction between **5** and lithium metal pieces in THF, conducted in the same manner and on a similar scale, the yield of **8** was likewise 95%. CCDC-868360 (for **8**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The Supporting Information has reproductions of the ^{1}H and ^{13}C NMR spectra, the IR spectrum, and the 3D structure of **8**.

Reaction of 6,12-Diphenyldibenzo[*b*,*f*][1,5]diazocine (5) with Trityllithium (15c): To a deep-red solution of trityllithium (**15c**; 0.62 mmol, 2.2 equiv.) in THF (15 mL) was added a solution of **5** (100 mg, 0.28 mmol, 1.0 equiv.) in THF (5 mL). The resulting black solution was stirred at reflux for 48 h. Thereupon addition of water and usual workup gave a pale yellow product (550 mg). Analysis by ^{1}H NMR spectroscopy revealed the absence of any **5** and the presence of indolo[3,2-*b*]indole (**8**; 100 mg, 0.28 mmol) and (4-benzhydrylphenyl)triphenylmethane (**20**; 120 mg, 0.25 mmol) in a 1.0:0.90 molar ratio. In addition, only triphenylmethane was present. The components of the reaction mixture were readily separated by column chromatography on silica gel (hexane/ethyl acetate). Pure samples **8** and **20** were identified by comparing their ^{1}H and ^{13}C NMR spectra with those of authentic samples (cf. Supporting Information).

Reaction of 6,12-Diphenyldibenzo[*b*,*f*][1,5]diazocine (5) with Benzhydryllithium (15b) at a Temperature of –78 °C to Room Temperature: To an orange-red suspension of benzhydryllithium (**15b**; 2.3 mmol, 2.0 equiv.) in THF (15 mL) stirred at –78 °C was added a solution of **5** (378 mg, 1.06 mmol, 1.0 equiv.) in THF (5 mL). After 2 h at –78 °C the reaction mixture was brought to room temperature and allowed to stir for 16 h. Usual hydrolytic workup gave the crude organic product (940 mg), whose ^{1}H NMR spectroscopic analysis showed the absence of **5** and the presence of indolo[3,2-*b*]indole (**8**, 1.06 mmol) and 1,1,2,2-tetraphenylethane (**14a**) in a 1.0:0.92 ratio. Noteworthy also was the absence of 5,5-diphenyl-1-pentanol (**17**), as indicated by TLC or by ^{1}H and ^{13}C NMR analyses. Pure samples of products **8** and **14a** were compared with authentic samples by ^{1}H and ^{13}C NMR spectroscopy (cf. Supporting Information).

When the foregoing reaction of **5** with **15b** in THF was carried out with the same ratio and concentration of reactants but at reflux for 48 h, 84% of the reactants were converted into **8** and **14a** and about 30% of the THF was converted into the known 5,5-diphenyl-1-pentanol (**17**) by the balance of reagent **15b**.

Reaction of 6,12-Diphenyldibenzo[*b*,*f*][1,5]diazocine (5) with the Benzyllithium (15a)-TMEDA Complex in Toluene (Reaction Molar Ratio of 5/15a = 1.0:1.1) To a yellow suspension of the benzyllithium-TMEDA complex (1.90 mmol) in toluene/hexane (6.0 mL) at –78 °C was added a solution of **5** (620 mg, 1.70 mmol) in THF (5 mL), which generated a reddish black solution. After stirring for 2 h at –78 °C, the mixture was then allowed to come to room temperature over 12 h. Usual workup was carried out with the ethyl ether and water. Based on the ^{1}H NMR spectrum of the crude product, 95% of diazocine **5** had been converted into 6-benzyl-6,12-diphenyl-5,6-dihydrodibenzo[*b*,*f*][1,5]diazocine (**21**). Recrys-

tallization from absolute ethanol gave yellow crystals of **21**, m.p. 209–211 °C. Whether the benzyl group has been added *exo* or *endo* to the C6-position remains to be established by a future XRD study. However, the ^{1}H and ^{13}C NMR and the IR spectra are in complete accord with the structural connectivity of the structure of **21**. Finally, since compound **21** has not previously been reported, the high-resolution mass spectrum of protonated **21** has been recorded and its mass of 451.2167 compares favorably with the theoretical mass for protonated **21** of 451.2169 with a delta of –0.4 ppm and a composition of C$_{33}$H$_{27}$N$_2$. Selected IR (CHCl$_3$) absorptions: 3400 cm^{-1} (H–N) and 1635 cm^{-1} (C=N) (cf. Supporting Information).

Reaction of 6,12-Diphenyldibenzo[*b*,*f*][1,5]diazocine (5) with the Benzyllithium (15a)-TMEDA Complex in Toluene (Reaction Molar Ratio of 5/15a = 1.0:2.2) The foregoing reaction was duplicated in an identical manner and on the same scale, except that the reaction molar ratio of **5**/**15a** was 1.0:2.2. Although the purpose of this reaction had been to achieve the bis-benzyllithiation of both C=N bonds of **5**, the surprising result was that the products now consisted of a mixture of 55% (0.46 mmol) of monobenzyl adduct **21**, 45% (0.040 mmol) of indolo[3,2-*b*]indole **8**, and 0.40 mmol of bibenzyl (ratio of **8**/bibenzyl = 1.0:1.0).

When the reaction run of such a reaction at a 1.0:2.2 ratio was heated for 24 h at reflux and then worked up after hydrolysis, the starting diazocine **5** was found to have been converted quantitatively into indolo[3,2-*b*]indole **8** quantitatively (0.86 mmol). In addition, bibenzyl (0.86 mmol) was found as the byproduct.

When this reaction between **5** and **15a** in a 1.0:2.2 molar ratio in THF was repeated on the same scale and procedure at room temperature but with benzyllithium made by the Gilman method, the products were 36% of **8**, 36% of bibenzyl, and 64% of **21**. Heating at reflux yielded an uninformative mixture of **8**, **21**, and **17**, the last resulting from the attack of **15a** on THF.

Reductions of 6,12-Diphenyldibenzo[*b*,*f*][1,5]diazocine (5) to 4b,9b-Diphenyl-4b,5,9b,10-tetrahydroindolo[3,2-*b*]indole (8) by Grignard Reagents in Refluxing Tetrahydrofuran – An Exploratory Survey: The prototype for these reactions is the reaction of one equiv. of **5** with 2.2 equiv. of benzylmagnesium chloride in THF. Thus, a solution of **5** (358 mg, 1.0 mmol, 1.0 equiv.) in THF (20 mL) was treated with benzylmagnesium chloride (2.0 M in THF, 1.15 mL, 2.23 mmol, 2.2 equiv.) at room temperature. The resulting bright yellow solution was heated at reflux for 48 h and then hydrolytically worked up and the organic products analyzed by ^{1}H NMR spectroscopy. Starting **5** had been converted into **8** in 40% yield and about 1% of 6-benzyl adduct **21** had been formed. Finally, bibenzyl had also been generated, about in an equimolar amount, 0.40 mmol, to the **8** formed.

Strictly in accord with the reaction of **5** with 2.2 equiv. of the benzyl Grignard reagent, the following magnesium reagents gave the following conversions of **5** into **8** in THF: (1) Allylmagnesium chloride: 25% of **8** and 85% of 6-allyl-6,12-diphenyl-5,6-dihydrodibenzo[*b*,*f*][1,5]diazocine, having appropriate ^{1}H and ^{13}C NMR spectra, whose XRD and 3D stereochemistry is currently under investigation. (2) *tert*-Butylmagnesium chloride: 6% of **8** (lab light). (3) *tert*-Butylmagnesium chloride: 15% of **8** (75 W unfrosted light, external to the flask).

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra, DEPT-NMR spectrum, IR spectra, high-resolution mass spectrum.

Acknowledgments

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[3] a) The necessary planarity of **1** required for Hückel aromaticity faces two energy barriers. First, previous research on the barrier to inversion of the optical active derivative of **1** bearing carboxyl groups at the 3- and 10-positions has estimated the minimum repulsion energy of such *ortho* H groups in a transition of **1** to planar **3** at 20 kcal/mol (N. L. Allinger, W. Szkrybalo, M. A. DaRooge, *J. Org. Chem.* **1963**, *28*, 3007–3009). In addition, the ring strain energy of producing an all-planar eight-membered ring is assessed at about 23 kcal/mol more. (A. Streitweiser Jr., *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, **1962**, p. 283). b) Up to 81 kcal/mol, the mean bond stabilization energy for the fully formed C_{sp^3}–C_{sp^3} σ-bond between C6 and C12 in resonance structures **6** → **7** in Scheme 2, cf.: J. Waser, K. N. Trueblood, C. M. Knobler, *Chem One*, McGraw-Hill, New York, **1976**.

[4] W. Metlesics, T. Resnick, G. Silverman, R. Tavares, L. H. Sternbach, *J. Med. Chem.* **1966**, *9*, 633–634.

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[7] Such a dihydro derivative as depicted in Scheme 2 as **10** was prepared by reducing the 2,8-dichloro derivative of **5** with LiAlH$_4$ in pyridine. The product melted from 200 to 230 °C and may be a mixture of *endo*- and *exo*-6-phenyl isomers of the tub-like conformers of the central dihydro ring.

[8] For a review of SET processes occurring in organometallics, ranging from the Schlenk adducts through radical-anions involved in SET processes in additions of RLi or RMgX reagents to carbonyl or azomethine groups, cf.: J. J. Eisch, *Res. Chem. Intermed.* **1996**, *22*, 145–187.

[9] For further SET processes involving unsaturated hydrocarbons and RLi reagents, cf.: a) J. E. Mulvaney, Z. G. Garlund, S. L. Garlund, *J. Am. Chem. Soc.* **1963**, *85*, 3897–3898; b) J. J. Eisch, P. Chobe, *Advances in Chemistry Series No. 217: Polynuclear Aromatic Compounds* (Ed.: L. B. Ebert), American Chemical Society, Washington, D. C., pp. 97–105.

[10] For evidence of SET involvement also in additions of allyl Grignard reagents to azomethine groups in pyridines and quinolines, cf.: J. J. Eisch, R. L. Harrell Jr., *J. Organomet. Chem.* **1970**, *21*, 21–27; J. J. Eisch, D. R. Comfort, *J. Organomet. Chem.* **1972**, *43*, C17–C19.

[11] A similar, potentially more general method for the oxidation of RLi reagents may be the reaction between RLi and Zr(OEt)$_4$ in the following manner:

$$Zr(OEt)_4 \xrightarrow[-\,2\,LiOEt]{2\,RLi} R_2Zr(OEt)_2 \xrightarrow[-\,Zr(OEt)_2]{\Delta} R\text{–}R$$

But the yields of the dimer are often low to moderate. Further improvements are being sought, cf.: J. J. Eisch, S. Dutta, *Organometallics* **2004**, *23*, 4181–4183.

[12] The ratio of **8** to dimer **14a** in the crude reaction mixture was determined by comparing the signal due to the N–H groups (2) with the methine groups (2) in **14a**. These signals were in a 1.0:1.0 ratio within ±0.05. The quantitative course of the reaction followed from the disappearance of **5** and the absence of no other derivative of **5** (than **8**).

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[15] a) J. M. McBride, *Tetrahedron* **1974**, *30*, 2009–2012. b) For the analogy between the triphenylmethyl radical and the triphenylborane radical anion, cf.: J. J. Eisch, T. Dluzniewski, M. Behrooz, *Heteroat. Chem.* **1993**, *4*, 235–241.

[16] a) Benzyllithium in THF can be conveniently prepared by cleaving either benzyl methyl ether or benzyl ethyl ether with freshly cut lithium metal pieces in THF at –10 °C, following reproduced procedures by Professor Henry Gilman and coworkers and described in: J. J. Eisch, *Organometallic Syntheses* (Eds.: J. J. Eisch, R. B. King), Academic Press, New York, **1981**, vol. 2, pp. 94–96. b) The 1:1 benzyllithium-TMEDA adduct in toluene can be readily prepared in accord with a tested procedure described in: J. J. Eisch, *Organometallic Syntheses* (Eds.: J. J. Eisch, R. B. King), Academic Press, New York, **1981**, vol. 2, p. 95.

[17] Although the structure of **21** is consistent with available ^{1}H and ^{13}C NMR spectroscopic data, the X-ray crystal structure will be determined to learn whether the 6-benzyl group is positioned *exo* or *endo* to the tub-shaped 5,6-dihydro-dibenzo[*b,f*][1,5]diazocine ring, cf. structure **10** as cited in ref.[7]

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FULL PAPER

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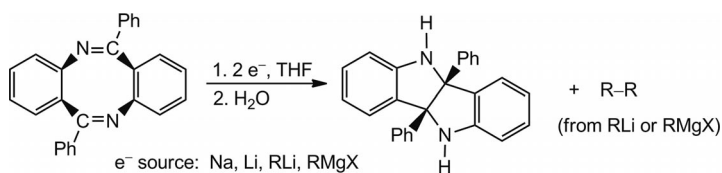
6,12-Diphenyldibenzo[*b,f*][1,5]diazocine readily undergoes transannular SET reductions with sodium, lithium, or even benzylic lithium or magnesium reagents to yield, upon hydrolysis, 4b,9b-diphenyl-4b,5,9b,10-tetra-

hydroindolo[3,2-*b*]indole. This diazocine can thereby serve as a mechanistic probe for SET processes and as a reagent for the oxidative dimerization of benzylic organometallics.

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6,12-Diphenyldibenzo[*b,f*][1,5]diazocine as an Electron-Capture Agent: Efficient Mechanistic Probe for SET Processes and Reagent for the Oxidative Dimerization of Benzylic Organometallics

Keywords: Electron transfer / Reduction / Lithium / Dimerization / Transannular reactions