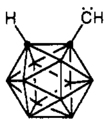

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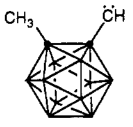

4

related to $1/r^3$, where r is the average distance between the two electrons.[5] For a carbene in which delocalization is impossible, methylene, $|D/hc| = 0.76\ \text{cm}^{-1}$.[6] For dialkylcarbenes such as diadamantylcarbene or di-*tert*-butylcarbene in which delocalization is minimal, $|D/hc| = 0.6823$ and $0.689\ \text{cm}^{-1}$, respectively.[7,8] By contrast, for arylcarbenes in which one of the nonbonding electrons is well-delocalized over one or more aromatic rings, $|D/hc|$ is much smaller.[5] Phenylcarbene, for example, shows $|D/hc| = 0.51\ \text{cm}^{-1}$.[5,9] Hutton, Roth, and Chari took their values of $|D/hc|$ to mean that there was little delocalization into the carborane cage,[4] and we see no reason to disagree with their evaluation. The nonbonding electrons of both carbenes **1** and **2** are strongly localized on the extra-cage carbon.

The other zero-field splitting parameter, $|E/hc|$, is a measure of the difference in magnetic properties along the x and y axes and will vanish for a linear molecule. Although a zero $|E/hc|$ is only consistent with a 180° angle at the divalent carbon, it has generally been taken as diagnostic for a linear species. Most simple triplet carbenes, including methylene,[6] diadamantylcarbene,[7] and phenylcarbene,[5,9] are bent, with $|E/hc| = 0.052$, 0.038, and $0.0249\ \text{cm}^{-1}$, respectively. Carbenes with cylindrical symmetry such as cyanocarbene[10] and a series of ethynylcarbenes[10] are linear ($|E/hc| \approx 0$). Although the carbon-substituted carboranylcarbenes **3** and **4** are bent ($|E/hc| = 0.0302$, $0.0293\ \text{cm}^{-1}$),[4] their boron-substituted relatives **1** and **2** are linear, as $|E/hc| < 0.002\ \text{cm}^{-1}$ in each case. Clearly, this is an important difference in the two kinds of intermediate. Equally clearly, rationalization is perilous, as very small energy differences may be involved.[12] We have calculated the structures of triplets **1** and **3** at the MNDO level. The B–C–H angle for carbene **1** is calculated to be nearly linear, 173°, whereas the related angle in **3** is only 155°. MNDO is known to overemphasize triplet linearity,[11] but the observed experimental trend is nicely reproduced.

Boron-substituted carbenes have been previously investigated computationally.[14] In H_2BCH, overlap of a filled carbene orbital with the empty 2p orbital on boron stabilizes the singlet state, but there is a competing σ effect in which the electronegativity difference between B and C acts to stabilize the triplet carbene. For H_2BCH, the two spin states emerge close in energy, with the singlet favored by 4–6 kcal/mol.[14] However, H_2BCH is not a good model for **1** and **2** as the 2p orbital that is so stabilizing to the singlet state is missing in the icosahedral species, occupied as it is in the network of three-center, two-electron bonding making up the cage frame. Perhaps better models would be silylcarbenes,[15] in which the carbene is also attached to a less electronegative atom.[16] Here, too, linear triplets are found, as $|E/hc| \approx 0$ for a series of alkylsilylcarbenes.[12,15]

In summary, the first boron-substituted carbenes are ground-state triplets and appear to be linear. It remains to verify linearity through an analysis of the ^{13}C hyperfine interactions and to examine the other possible isomers of **1** and **2**.

Acknowledgment. We thank Professors J. A. Berson, J. E. Jackson, M. S. Platz, and Dr. E. Wasserman for help, both physical and intellectual, on this project.

Supplementary Material Available: EPR spectra of **1** and **2** and Curie plot data (3 pages). Ordering information is given on any current masthead page.

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[12] A referee has quite rightly pointed out that a near-zero $|E/hc|$ value may be the result of rotational averaging in a bent structure with a very low barrier.[13] However, the carbon-substituted carbenes **3** and **4** show substantial $|E/hc|$ values,[4] not the zero values of **1** and **2**. We calculate (MNDO) a tiny 5-fold barrier to rotation about the extra-cage C–C bond of 1-methyl-*o*-carborane (ca. 0.2 kcal/mol), and there seems little chance that there would be a substantial barrier in the carbon-substituted carbenes. Accordingly, unless the carbon-substituted carbenes and the boron-substituted carbenes fortuitously find themselves in substantially different matrix sites, we think our near-zero $|E/hc|$ values are significant. We hope to resolve this point through a determination of the ^{13}C hyperfine interactions in a suitable labeled carbene.

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Direct Coupling of Aniline and Nitrobenzene: A New Example of Nucleophilic Aromatic Substitution for Hydrogen

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The majority of reactions between nucleophiles and electron-deficient aromatic compounds can be separated into two classes. The most common is nucleophilic aromatic substitution for halide and, in particular, the reaction of nucleophiles with halogenated nitroaromatics.[1] The second is nucleophilic aromatic substitution for hydrogen, which formally requires the replacement of a hydride ion. This reaction is often promoted by the addition of an external oxidant such as oxygen.[2] Both of these reactions are believed to proceed via attack of a nucleophile on the nitroarene generating an anionic σ-complex, **1**, followed by departure of the leaving group and rearomatization.[3] More recently, the removal of a proton and two electrons from σ-complexes has been shown to be facilitated in a new class of reaction referred to as vicarious nucleophilic substitution (VNS).[4] These reactions require a good leaving group, such as sulfoxonium ion,[5] halide,[6] triazole,[7] or

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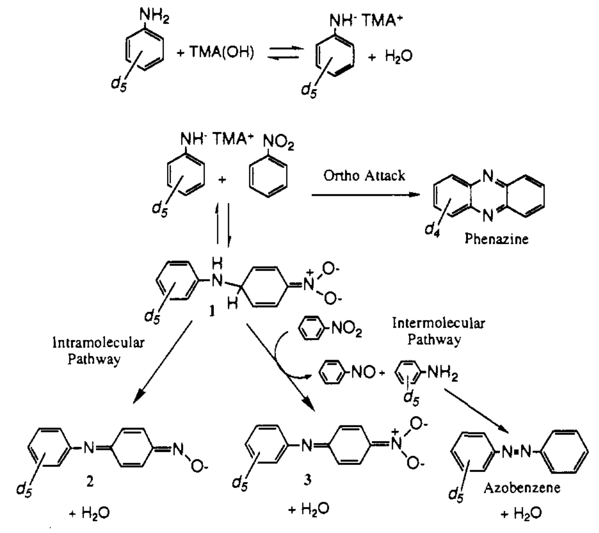
Scheme I



acetyl,[8] in a position α to the nucleophile such that decomposition of the corresponding σ-complex results in β-elimination of HX. While this class of reaction has provided useful mechanistic insight and some synthetic utility, the requirement for an auxiliary leaving group still persists. Accordingly, we now report a novel example of nucleophilic aromatic substitution for hydrogen using an amine nucleophile that proceeds in the absence of an auxiliary leaving group or external oxidant.

The dropwise addition of nitrobenzene to an aniline solution containing 2.2 equiv of tetramethylammonium hydroxide dihydrate (TMA(H)·$2H_2O$) at 50 °C under *anaerobic* conditions caused the immediate formation of a red species. Analysis of the reaction mixture by HPLC indicated that (4-nitrosophenyl)phenylamine (4-NODPA) and (4-nitrophenyl)phenylamine (4-NDPA) were generated in 89% and 4% yield, respectively. In addition, small amounts of azobenzene (3.5%) and phenazine (3.5%) were produced. This reaction was observed to proceed in a similar fashion with a variety of polar aprotic solvents such as DMSO, DMF, and *N*-methylpyrrolidinone.[9] Spectrophotometric analysis of a reaction mixture containing equal molar amounts of aniline, nitrobenzene, and TMA(H)·$2H_2O$ in DMSO revealed a single broad absorbance with $\lambda_{MAX} = 494$ nm, which is indicative of the deprotonated form of the nitroaromatic amines.[10] Thus, we conclude that the primary products of this reaction are not 4-NODPA or 4-NDPA but rather their tetramethylammonium salts **2** and **3**, respectively.

Both the amount of water present and the ratio of aniline to nitrobenzene in the reaction have been shown to play a critical role in selectivity and overall yield. The effect that varying the aniline/nitrobenzene ratio (AN/NB) has on product distributions is summarized in Table I. These results clearly demonstrate that, as AN/NB is increased, the yield of **2** increases at the expense of **3**. That water has a profound effect on product yield was demonstrated by a series of reactions that contained varying amounts of protic material. Thus, as the amount of water was increased in the reaction from 2% by weight to 14%, the combined molar yield of **2** and **3** decreased from 93% to 3%. A series of deuterium labeling experiments were performed to aid in the elucidation of the mechanism of this reaction. When aniline-d_5 was used as solvent, 4-NODPA-d_5, 4-NDPA-d_5, and azobenzene-d_5 were observed.

Table I. Effect of Varying the Aniline/Nitrobenzene Ratio on Product Distribution

mole ratio aniline/nitrobenzene	% yield[a] 3	% yield[a] 4
1.32	15	80
11.9	55	35
51.5	86	9

[a] Reversed-phase HPLC was used to analyze the reaction mixtures. The external standard method was used to quantitate reaction yields using a Vydac 210HS54 (4.6 × 250 mm) column and UV detection at 254 nm. Yields are normalized to the total moles of 4-NODPA and 4-NDPA produced at each AN/NB ratio.

A mechanism consistent with these experimental observations is shown in Scheme I. Deprotonation of aniline generates the anilide ion, which is required for nucleophilic attack on nitrobenzene forming the σ-complex **1**.[11] We interpret the inhibitory effect of water to result from its effect on the equilibrium between aniline and anilide. Formal oxidation of **1** can occur by two separate pathways: (1) an intramolecular redox process with the nitro group of **1** functioning as the oxidizing agent generating **2**, and (2) an intermolecular pathway with free nitrobenzene functioning as the oxidant producing nitrosobenzene and **3**.[12] Nitrosobenzene is not directly observed since it will condense with aniline under the reaction conditions to produce azobenzene.[13] In either pathway, a nitro group is formally reduced to a nitroso moiety by the hydride leaving group. The small amount of phenazine observed results from ortho attack on nitrobenzene followed by a similar intramolecular oxidation and ring closure of the corresponding σ-complex.[2a] This mechanism is compatible with the results contained in Table I and the deuterium labeling studies. As AN/NB decreases, the amount of free nitrobenzene (i.e., not complexed in **1**) will be higher, causing the intermolecular pathway to predominate. Furthermore, the observation that equal molar amounts of **3** and azobenzene are produced under certain reaction conditions is consistent with this mechanism.[14]

In conclusion, the formation of (4-nitrophenyl)- or (4-nitrosophenyl)phenylamine derivatives from the reaction of aniline and nitrobenzene represents a novel example of nucleophilic aromatic substitution for hydrogen. This reaction is unique in that it proceeds in high yield under mild conditions without the need for an auxiliary leaving group or oxidant and can be generally applied to other amine nucleophiles.[15] This new reaction also has significant commercial implications since it eliminates the need for halogenated aromatics, and their associated environmental concerns, in the production of substituted aromatic amines.

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(13) When DMSO is used as solvent it is possible to detect nitrosobenzene as a primary product. Furthermore, only trace amounts of azobenzene-d_{10} were observed in the deuterium labeling studies, eliminating the oxidative coupling of aniline as a major source of azobenzene. See: Jeon, J.; Sawyer, D. T. *Inorg. Chem.* **1990**, *29*, 4612.

(14) Not all reaction conditions will yield quantitative conversion of nitrosobenzene to azobenzene. The amount of water, base, and aniline present in the reaction have an effect on the yield of azobenzene.

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