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# Evidence of Reversibility in Azo-Coupling Reactions between 1,3,5-Tris(*N*,*N*-dialkylamino)benzenes and Arenediazonium Salts

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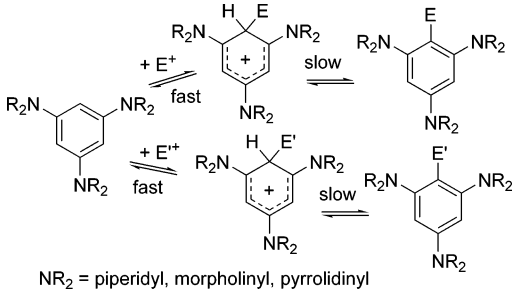



The reactions between strongly electron-rich aromatic substrates (1,3,5-tris(*N*,*N*-dialkylamino)benzenes, neutral carbon super nucleophiles) and diazonium salts produce moderately stable $\sigma$ complexes (Wheland complexes). The reactivity of Wheland complexes with electrophiles (other diazonium salts, or 4,7-dinitrobenzofuroxan) produces exchange reactions in the electrophilic part: the better electrophile replaces the less powerful electrophile. In the same way, in Wheland complexes with the 1,3,5-tris(morpholinyl)-benzene, the 1,3,5-tris(piperidinyl)benzene replaces the less powerful nucleophile 1,3,5-tris(morpholinyl)-benzene. Evidence is reported here indicating that for the title system the reaction of the attack of the electrophilic reagent producing Wheland complexes is a reversible process. The final products of the diazo-coupling reactions undergo a further attack of some diazonium salts. From the final products of the double diazo-coupling reactions (diazo compounds), we collected evidence that is a clear instance of complete reversibility of the diazo-coupling reaction.

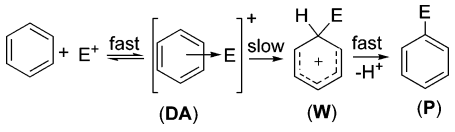
## Introduction

The usually accepted pathway[1,2] (reported also in textbooks[3]) of the electrophilic aromatic substitution reaction is shown in Scheme 1.

The first interaction between the electron-deficient reagent and an electron-rich substrate affords a donor−acceptor complex[4,5] (or $\pi$ complex, **DA**) by an equilibrium that is quickly reached. The $\pi$ complex evolves to the $\sigma$ complex (Wheland intermediate, **W**).[6]

Generally, the **W** formation is indicated to be the rate-determining step of the overall reaction. The driving force of the reaction is reported to be the re-aromatization process, which is usually proposed as a fast and hardly reversible step.[2,5]

**SCHEME 1. Generally Accepted Pathway of the $S_EAr$**




Our recent paper reports[7] a clear instance of the slow proton departure in a rate-determining step (from **W** to **P**), which follows the fast attack of the electrophilic reagent to form the **W** complex.

Even if the mechanism of this reaction has been extensively investigated,[1,8] in particular for the diazocoupling reaction[9] there are some aspects of this reaction which need further investigation, as some reported explanations are poorly supported by experimental data and are not completely convincing. Evidence of complete reversibility of the electrophilic aromatic substitution reaction concerns only a few cases as in sulfonation reactions and in nitration reactions.[10] An instance of the reversible C-azo coupling reaction is described when the reaction was carried out in the presence of *p*-toluenesulfonic acid.[11]

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In a previous paper, we reported[12] the characterization (mainly by $^1$H NMR spectroscopy) of some moderately stable Wheland intermediates obtained by the azo-coupling reaction between 1,3,5-tris(*N*,*N*-dialkylamino)benzenes and arenediazonium salts.

We now report some independent evidence on the reversibility of the reaction between 1,3,5-tris(*N*,*N*-dialkylamino)benzenes and different electrophilic reagents.

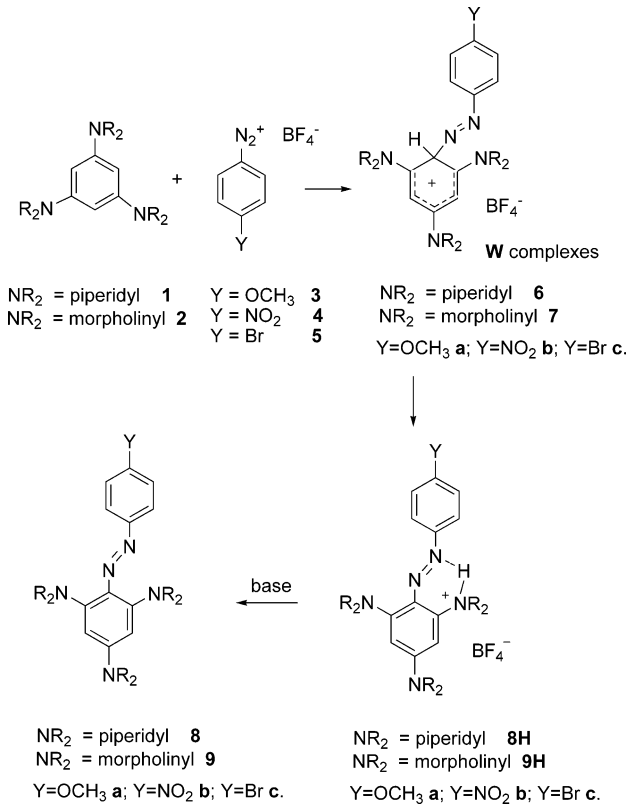
## Results and Discussion

Previously, we described[12] the reaction shown in Scheme 2 affording the **W** complexes **6** and **7**. Final diazo compounds **8H** and **9H** are spontaneously obtained from **W** complexes. Free bases **8** and **9** are obtained from **W** complexes by base catalysis and, obviously, by treatment of salts **8H** and **9H** with bases.

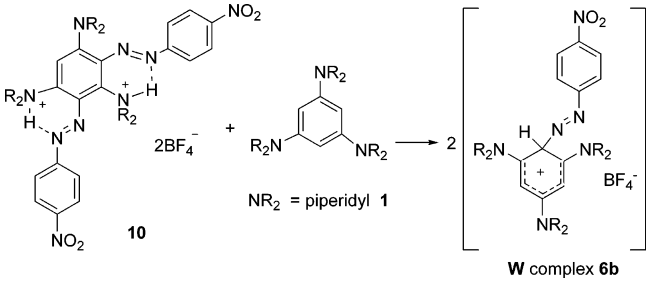
The present investigation regards some different aspects of the reaction steps reported in Scheme 1. In particular, the reversibility of each step was investigated separately by different experimental approaches which are reported in the following subheadings.

**1. Formation and Evolution of a Derivative Arising from the Double Attack of a Diazonium Salt on 1.** An interesting behavior was observed in recording $^1$H NMR spectral data of the **6b** complex. When the reaction between 1,3,5-tris(*N*,*N*-piperidinyl)benzene (**1**) and diazonium salt **4** (see Scheme 2) is carried out directly in the NMR probe tube, in $CD_3CN$ at −30 °C with reagents in equimolar amount, without waiting for the complete dissolution of **1**, the only signals recorded by $^1$H NMR spectroscopy are those related to compounds **10** (see Scheme 3) together with a very small amount (less than 5%) of the related *σ*-complex **6b**. Compound **6b** arises from a double attack of the electrophilic reagent on the substrate, which is in temporary defect, together with signals related to starting diazonium salt. Signals related to salt **10** slowly disappear as solid **1** is dissolved. After about 10 min (in this time all of **1** is dissolved) the only recorded signals where those related to **W** complex **6b**. Scheme 3 reports a reasonable explanation of the observed behavior that involves the departure from **10** of the diazonium salt **4**.

**SCHEME 2**




**SCHEME 3**




**2. Replacement of the Electrophilic Reagent Bonded to Wheland Complexes. 2.a. Exchange of Diazonium Salt.** The investigation of the diazonium moiety exchange was carried out directly in the NMR spectroscopy tube in $CD_3CN$, at −30 °C. After the time needed for the spectrum to show the disappearance of the signals of the starting materials and the complete formation of *σ*-complexes (**6a**−**c** or **7a**−**c**, obtained from mixtures of 1,3,5-tris(*N*,*N*-dialkylamino)benzenes **1** or **2** and diazonium salts **3**−**5**), the addition of another aryl diazonium tetrafluoborate, different from that used to obtain *σ*-complexes, may produce the exchange of the electrophilic reagent as represented in Scheme 4. The results are summarized in Table 1.

The reactions reported in entries 1,2, 6−8, and 12 of Table 1 clearly indicate that the more powerful electrophile expels the less powerful one. In the case of entries 3, 4, 9, and 10, the replacement of the 4-nitrobenzendiazonium salt by the 4-bromo- or 4-methoxybenzenediazonium tetrafluoroborate may be a surprising behavior, but if the formation of the **W** complex is a reversible process, the excess of the less able electrophilic reagent may produce a partial replacement.

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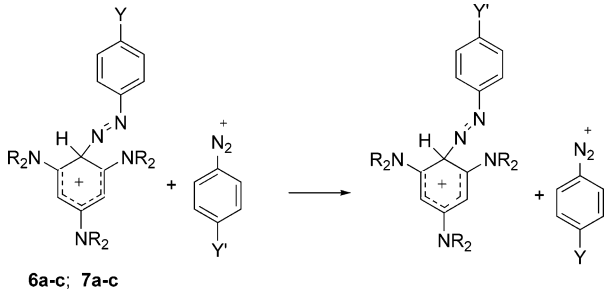
(12) Boga, C.; Del Vecchio, E.; Forlani, L. *Eur. J. Org. Chem.* **2004**, 1567−1571.

**TABLE 1. Reactions of Wheland Complexes with Diazonium Salts**

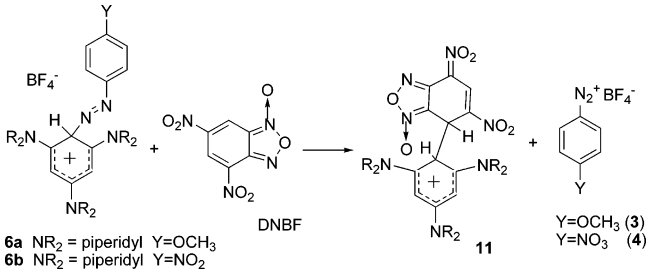
| entry | starting $\sigma$-complex (substituent) | Y′ (added diazonium salt) | obtained $\sigma$-complex | Y (diazonium salt leaving by exchange) | time,[a] min | conv, % |
|---|---|---|---|---|---|---|
| 1 | **6a** ($OCH_3$) | $NO_2$ | **6b** | $OCH_3$ | 5 | 100 |
| 2 | **6a** ($OCH_3$) | Br | **6c** | $OCH_3$ | 5 | 82 |
| 3[b] | **6b** ($NO_2$) | $OCH_3$ | **6a** | $NO_2$ | 20 | 15 |
| 4[b] | **6b** ($NO_2$) | Br | **6c** | $NO_2$ | 5 | 65 |
| 5[c] | **6c** (Br) | $OCH_3$ | **6a** | Br | 20 | 4 |
| 6 | **6c** (Br) | $NO_2$ | **6b** | Br | 5 | 67 |
| 7 | **7a** ($OCH_3$) | $NO_2$ | **7b** | $OCH_3$ | 5 | 100 |
| 8 | **7a** ($OCH_3$) | Br | **7c** | $OCH_3$ | 5 | 100 |
| 9[c] | **7b** ($NO_2$) | $OCH_3$ | **7a** | $NO_2$ | 20 | 5 |
| 10[c] | **7b** ($NO_2$) | Br | **7c** | $NO_2$ | 5 | 10 |
| 11[c] | **7c** (Br) | $OCH_3$ | no reaction | | 20 | 0 |
| 12 | **7c** (Br) | $NO_2$ | **7b** | Br | 5 | 82 |

[a] The time of conversion is affected by the stability of $\sigma$-complexes. [b] Ratio of **6b**:*p*-Y′Ar$N_2^+BF_4^-$ = 1:2. [c] Ratio of starting $\sigma$-complex:*p*-Y′Ar$N_2^+BF_4^-$ = 1:5.

**SCHEME 4**




**SCHEME 5**




**2.b. Replacement of the Diazonium Moiety with a Super Electrophilic Reagent: From a Wheland Complex to a Wheland/Meisenheimer Complex (WM).** When an equimolar amount of 4,7-dinitrobenzofuroxan (**DNBF**) was added to a solution (in $CD_3CN$, directly prepared in the NMR tube, at −30 °C) of the Wheland complex **6a** or **6b**, the signals of the product **11**, identical with those of the compound obtained by direct mixing of solutions of **DNBF** and **1**,[13] appeared together with the signals corresponding to the leaving arenediazonium (as tetrafluoroborate salt, **4)**, as reported in Scheme 5.

The reactions represented in Scheme 5 are almost quantitative and support the trend reported in the previous section 2.a, **DNBF** being, also in this case, a better electrophilic reagent than the diazonium salt **4**.

**2.c. Two Main Pathways To Explain Reactions Reported in Schemes 4 and 5.** To explain how the diazo moiety of complexes **6a**−**c** and **7a**−**c** is replaced by another electrophilic reagent, we can draw two main reaction pathways. The first one is depicted in Scheme 6 and involves the dication formation (di-**W**) which is followed by the departure of the first introduced

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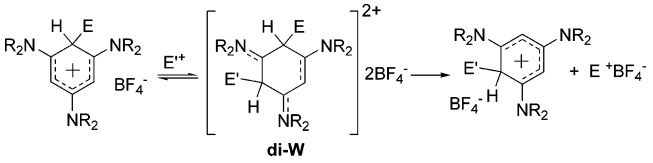
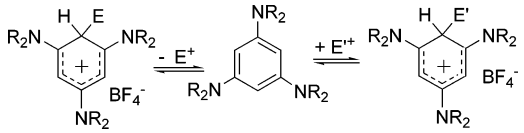
**SCHEME 6**




**SCHEME 7**



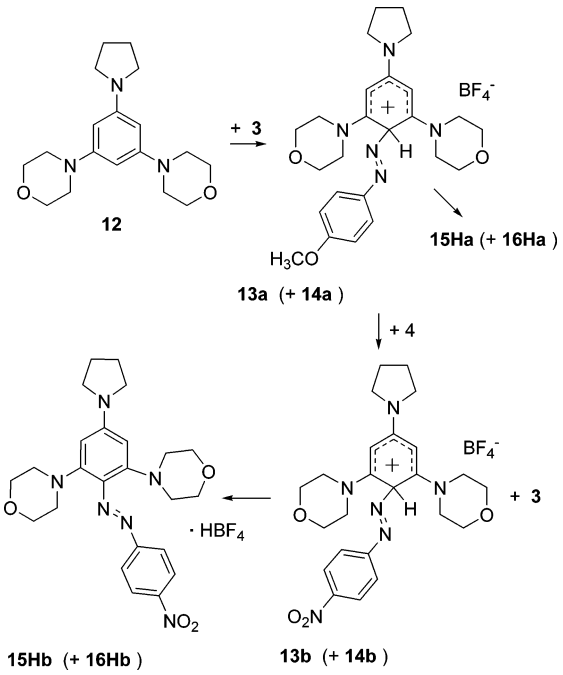
electrophilic reagent. In this case, the attack of the second electrophilic reagent occurs in a different position with respect to that occupied by the first electrophilic reagent with the formation of a complex in which the two different electrophiles are bonded to 1,3,5-tris(*N*,*N*-dialkylamino)benzene (di-**W**).

The second pathway is reported in Scheme 7. It concerns the departure of the first arenediazonium salt to return to the starting materials, followed by the addition of the second diazonium salt on the 1,3,5-tris(dialkylamino)benzene, which is in equilibrium with the Wheland complex. In this case the addition of the second electrophile might occur on the same position as the first one.

Since the three positions are equivalent in 1,3,5-tris(*N*,*N*-dialkylamino)benzenes **1** or **2**, it was not possible to discriminate between the two pathways of Schemes 6 and 7. To have more information, we synthesized the asymmetric compound **12** (4,4′-(5-pyrrolidin-1-yl-1,3-phenylene)dimorpholine) with two non-equivalent positions (Scheme 8).

A solution of diazonium salt **3** in $CD_3CN$ was then added to a solution of **12** dissolved in $CD_3CN$ at −30 °C, directly in a NMR spectroscopy tube. The main product of the reaction was the $\sigma$ complex **13a**, as tested by $^1H$ NMR spectral data (see the Experimental Section) together with a small amount of the complex bearing the arenediazonium moiety bonded in the ortho position with respect to the pyrrolidinic ring (**14a**). After complete formation of **13a**, a solution in $CD_3CN$ of diazonium salt **4** was added to the reaction mixture. The $^1H$ NMR spectrum immediately showed new signals ascribed to the complex **13b**, together with those related to the leaving arendiazonium salt **3** and, in a small percentage, with the complex bearing the electrophile **4** in the ortho position with respect to the pyrrolidinic ring (**14b**). Obviously, the same complex **13b** was also obtained by direct reaction between **12** and **4**.

**SCHEME 8**[a]




[a] Isomers **14a**, **14b**, **16Ha**, and **16Hb** were formed in low amount and they bear diazonium moiety in the ortho position with respect to the pyrrolidinic ring.

Since the second electrophilic reagent (bearing the nitro group) is bonded to the same carbon atom as the first one, we can conclude that the pathway represented in Scheme 6 is unlikely to illustrate the exchanges reported above.

A third reaction pathway should be the "ipso" exchange of the electrophilic reagent, which is supported by literature reports,[14] as represented in Scheme 9.

The "ipso" substitution pathway via the ionic reaction of Scheme 9 is unlikely because the final product of the azocoupling reaction **P** with a second electrophilic reagent does not give any exchange reaction, but a second attack (see the discussion of Scheme 11) takes place. In conclusion, our data strongly support the pathway indicated in Scheme 7 involving the starting aromatic substrate and the electrophilic reagent in an equilibrium forming the Wheland complex.

**3. Replacement of the Nucleophilic Moiety on a Wheland Complex.** On the basis of the reported results, with the aim of investigating the possible exchange of the nucleophilic part of the Wheland complexes, we prepared (in the NMR tube) a solution of the Wheland complex **7a** (by adding, at −30 °C, a solution in $CD_3CN$ of 1,3,5-tris(*N*,*N*-morpholinyl)benzene (**2**) to a solution of 4-methoxybenzenediazonium salt **3**). When the spectrum revealed complete formation of complex **7a**, a solution of 1,3,5-tris(*N*,*N*-piperidinyl)benzene (**1**) (in $CD_3CN$ at −30 °C, in an equimolar amount with **7a**) was added. The $^1H$ NMR spectrum of the obtained solution, recorded immediately after the addition of **1**, showed the disappearance of signals related to **7a** and the concomitant appearance of those related to Wheland complex **6a** together with those of 1,3,5-tris(*N*,*N*-morpholinyl)benzene (**2**).

While the reaction of Scheme 10 is complete in about 10 min, the reaction between **6a** and **2** did not produce a similar exchange: piperidinyl derivative **1** replaces morpholinyl derivative **2** because it is the more powerful electron-donor substrate,[15] but **2** is not able to replace **1**, at least under the present experimental conditions.

**4. Behavior of Compounds 8H and 9H.** The results described above, in particular the transfer of the diazonium moiety reported in Scheme 3, induced us to investigate the behavior of the final products **8Ha**−**c** and **9Ha**−**c**, in order to have information about the reversibility of the last step regarding the re-aromatization of the Wheland intermediate to the final product of the diazo-coupling reaction.

Compounds **8Ha** and **9Ha**, prepared according to the reported procedure,[12] react (in $CD_3CN$ at − 30 °C) with 1 equiv of the diazonium salts **4** or **5** affording "mixed" (unsymmetrical) disubstituted products **17**, **18**, **20**, and **21** (Scheme 11). Disubstituted compounds **10** and **17**−**21** can also be prepared and isolated, in almost quantitative yields (more than 90%), as reported in the Experimental Section. Attempts to obtain **17**, **18**, **20**, and **21** from **8Hb**,**c** or **9Hb**,**c** by adding the diazonium salt **3** failed. The attack of the second diazonium salt occurs only when this diazonium salts is activated by the presence of a substituent with high electron-withdrawing power. By reactions of Scheme 11, different aza moieties on the 1,3,5-tris(*N*,*N*-dialkylamino)benzene derivatives were introduced. It is evident that the behavior of the compounds **8Ha**−**c** and **9Ha**−**c** is different with respect to their preceding Wheland complexes **6a**−**c** and **7a**−**c**. In fact, from compounds **8Ha**−**c** and **9Ha**−**c** it was not possible to observe the exchange reaction of the electrophilic part.

When compounds **20** and **21** were dissolved in $CD_3CN$, at 25 °C, without other added substances, their $^1H$ NMR spectra showed, over a very long time, partial disappearance of the related signals, and appearance of the signals of **9Hb** and **9Hc** together with the signals of the diazonium salt **3** (50% of conversion was reached in 4 months for compound **20**, and in about 1.5 months for **21**), as depicted in Scheme 12. No signals related to diazonium salts **4** and **5** were observed: from **20** or **21** the departure of **3** (*p*-methoxydiazonium salt) is preferred to the expulsion of the more powerful electrophilic reagents **4** or **5**. Piperidyl cations **17** and **18** showed similar direct evidence of spontaneous departure of diazonium salts.

Derivatives **10** and **19** present interesting behaviors: when they are dissolved in $CD_3CN$ at −30 °C, directly in the NMR probe tube, after about 3 days, the $^1H$ NMR spectrum of the reaction mixture shows the contemporaneous presence of the salt **9Hb** and of *p*-nitrobenzenediazonium salt **4**, in a 30% ratio with starting compound **19**, as reported in Scheme 12. Compound **10** (at 25 °C) is also not stable in a solution of $CD_3CN$ and produces a complicated mixture of reaction products which are under investigation.

The protonation center of salts **8H**, **9H**, **10**, and **17**−**21** may be discussed (elucidated) on the basis of the NMR data. Protonation of 1,3,5-tris(*N*,*N*-dialkylamino)benzene derivatives is a problem deserving further investigation. $^1H$ and $^{13}C$ NMR spectral data indicate that the protons of salts reported here

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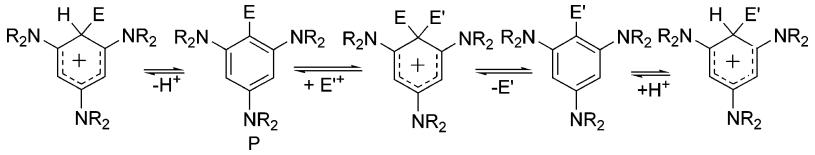
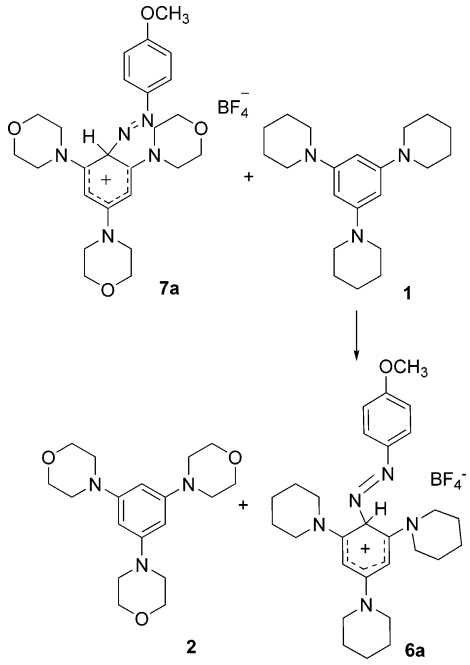
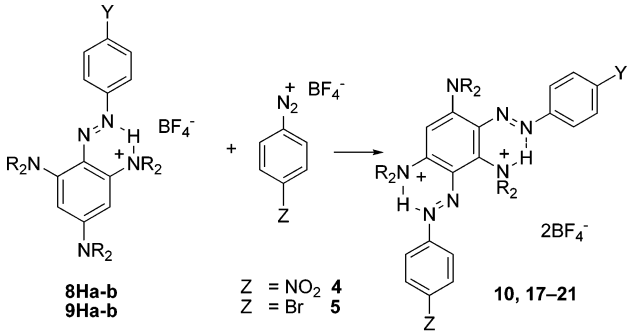
**SCHEME 9**



**SCHEME 10**

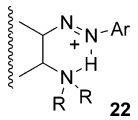


**SCHEME 11**



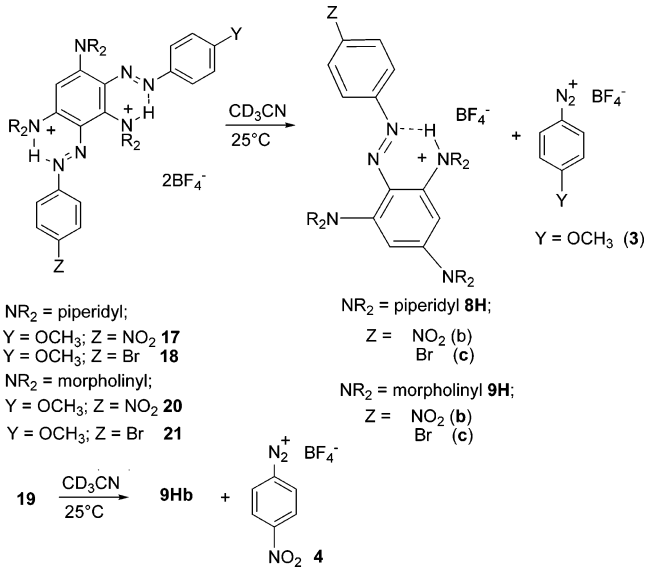
| Y | Z | Compound | Y | Z | Compound |
|---|---|---|---|---|---|
| $OCH_3$ | – | **8Ha** | $OCH_3$ | – | **9Ha** |
| $NO_2$ | – | **8Hb** | $OCH_3$ | – | **9Ha** |
| $NO_2$ | $NO_2$ | **10** | $NO_2$ | $NO_2$ | **19** |
| $OCH_3$ | $NO_2$ | **17** | $OCH_3$ | $NO_2$ | **20** |
| $OCH_3$ | Br | **18** | $OCH_3$ | Br | **21** |
| $NR_2$ = piperidyl | | | $NR_2$ = morpholinyl | | |

probably participate in a multicentered interaction between two nitrogen atoms, as represented in compound **22**.



It is possible that a proton shift from nitrogen atoms to a carbon atom of aromatic ring occurs; this possibility has already been discussed in the literature for other substrates.[15,16] In the present case this shift is the keystone of the reversibility from final products of the diazo-coupling reaction to Wheland intermediates. In fact, the return-back from compounds **17**−**21** to **8Hb**,**c** and **9Hb**,**c**, depicted in Scheme 12, implies the formation of a Wheland complex bearing both the hydrogen atom and the leaving benzendiazonium moiety on the same $sp^3$ carbon atom. Once the Wheland complex has been formed, the departure of the diazonium salt producing **8Hb**,**c** or **9Hb**,**c** is a reasonably probable process.

**SCHEME 12**



## Conclusions

It is worthy of consideration that when the reactivity of reagents is stressed as in this case (the 1,3,5-tris(*N*,*N*-dialkylamino)benzene system may be named a "carbon super nucleophilic reagent") some aspects of the studied reactions are enhanced and grow into manifest effects and behaviors which are lacking in more usual, less activated systems. And this is the case.

The main points arising from the reported data may be summarized as follows.

(i) The formation and destruction of the double attack product **10** (arising from reaction of nitrodiazonium salt **4** on tris(*N*,*N*-piperidyl)benzene **1**, see Scheme 3) and the behavior of the disubstituted compounds **19**−**21** (see Scheme 12), involving the departure of a diazonium salt from an azo compound, clearly indicates the complete reversibility of the process involving the second attack of the diazonium salt.

(ii) Scheme 12 indicates that from **20** and **21** the less powerful electrophilic reagent **3** (bearing a methoxy substituent) is more

(16) (a) Effenberger, F.; Niess, R. *Angew. Chem., Int. Ed*. **1967**, *6*, 10674. (b) Knoche, W.; Shoelle, W. W.; Schomäcker, R.; Vogel, S. *J. Am. Chem. Soc.* **1988**, *110*, 7484−7489. (c) Sachs, W.; Knoche, W.; Herrmann, C. *J. Chem. Soc., Perkin Trans. 2* **1991**, 701−710.

easily lost than the more powerful electrophilic reagents **4** and **5** (with a nitro and a bromo substituent, respectively). These findings, even if the number of electrophilic reagents is not large, suggest the possibility of drawing an "electrofugality" scale.

(iii) In agreement with the pathway depicted in Scheme 7, the data of Table 1 and the use of 4-[3-morpholino-5(1-pirrolidinyl)phenyl]morpholine (**12**) strongly indicate that the displacement of the methoxy-substituted diazonium cation by the more powerful electrophilic reagent (nitro- and bromo-substituted diazonium salt, as well as **DNFB**) occurs at the same carbon atom in two subsequent steps. Consequently, the displacement of diazonium cation from the Wheland complex is an easy process when the entering electrophile is a more powerful reagent than the leaving electrophile. In the same way, the more powerful nucleophilic reagent, 1,3,5-tris(*N*-piperidinyl)benzene (**1**), replaces the morpholino derivative **2**.

(iv) Even if the possibility of having an "ipso" attack of the second diazonium salt on the final azo coupling products (Scheme 9) cannot be completely ruled out, the lack of exchange reaction of diazonium salt from **8H** and **9H** (which react as depicted in Scheme 11) indicates this pathway as unlikely.

In conclusion, the results reported here are a clear instance of the reversibility of an electrophilic aromatic substitution reaction. Our data strongly favor the reversibility of these reactions, and we emphasize that this is the first instance of the complete reversibility of an azo-coupling reaction. The systems and the reactions reported here are a particular piece of the electrophilic aromatic substitution reaction. The attempt to generalize the observation reported here to the whole $S_EAr$ reactions may be justified. In fact, the usual experimental conditions of $S_EAr$ reactions involve several types of bases, exciting the base catalysis on the proton abstraction, which became a fast step.

## Experimental Section

Compounds **1** and **2** were prepared as reported in ref 12. Diazonium salts **3**−**5** are commercially available. Preparation and characterization data of complexes **6a**−**c**, **7a**−**c**, and **11**, as well as salts **8Ha**−**c** and **9Ha**−**c**, has been previously reported.[12,13]

**Preparation of Compounds 10 and 19.** To a magnetically stirred solution (0.092 mmol in 2 mL of $CH_3CN$) of 1,1′,1″-benzene-1,3,5-triyltripiperidine (**1**) (or 4,4′,4″-benzene-1,3,5-triyltrimorpholine, **2**), cooled at −30 °C, was added arenediazonium salt **4** (0.184 mmol). Immediately the color of the obtained solution became yellow. After 20 min a coral-red solid precipitated. After filtration compound **10** (or **19**, tile-red solid) was isolated as coral red solid in 90% yield (85% for **16**). Compounds **10** and **19** can be obtained also by addition of an equimolar amount of diazonium salt **4** to a cooled (−30 °C) solution in acetonitrile of compound **8Hb** or **9Hb**, respectively.

**1,1′-{2,4-Bis[(4-nitrophenyl)diazenyl]-5-piperidin-1-yl-1,3-phenylene}dipiperidinium ditetrafluoroborate (10):** mp 128.8−132.4 °C dec; $^1$H NMR ($CD_3NO_2$, 400 MHz, 25 °C) $\delta$ 1.50−2.80 (m, 18 H), 3.50−4.80 (m, 12 H), 6.38 (br s, 1 H), 7.50 (d, 4 H, $J$ = 9.3 Hz), 8.20 (d, 4 H, $J$ = 9.3 Hz), 10.24 (br s, 2 H); $^{13}$C NMR ($CD_3NO_2$, 100.56 MHz, −30 °C) $\delta$ 18.4 ($CH_2$), 18.9 ($CH_2$), 20.9 ($CH_2$), 22.5 ($CH_2$), 23.2 ($CH_2$), 45.4 ($CH_2$), 49.4 ($CH_2$), 55.1 ($CH_2$), 88.5 (CH), 111.6 (CH), 121.3 (CH),122.3, 139.9, 142.0, 150.8, 157.3.

**3-{3-Morpholin-4-ium-4-yl-5-morpholin-4-yl-2,6-bis[(4-nitrophenyl)diazenyl]phenyl}-1,3-oxazinan-3-ium ditetrafluoroborate (19):** mp 142.8−147.9 °C dec; $^1$H NMR ($CD_3CN$, 300 MHz, 25 °C) $\delta$ 2.02−2.42 (m, 8 H), 3.82−4.20 (m, 16 H), 6.25 (s, 1 H), 7.68 (d, 4 H, $J$ = 9.1 Hz), 8.37(d, 4 H, $J$ = 9.1 Hz), 10.22 (br s, 2 H); $^1$H NMR ($CD_3NO_2$, 400 MHz, 25 °C) $\delta$ 2.10−2.45 (m, 12 H), 3.65−4.75 (m, 12 H), 6.40 (s, 1 H), 7.60 (d, 4 H, $J$ = 9.3 Hz), 8.26 (d, 4 H, $J$ = 9.3 Hz), 10.44 (br s, 2 H); $^{13}$C NMR ($CD_3NO_2$, 150.56 MHz, −30 °C) $\delta$ 50.1 ($CH_2$), 53.8 ($CH_2$), 59.3 ($CH_2$), 66.7 ($CH_2$), 67.7 ($CH_2$), 68.0 ($CH_2$), 94.5 (CH), 117.5 (CH), 126.4, 126.8 (CH), 145.9, 147.2, 156.7, 163.3.

**Preparation of 4,4′-(5-pyrrolidin-1-yl-1,3-phenylene)dimorpholine (12).** An autoclave was charged with 1,3,5-trichlorobenzene (1.8 g, 10 mmol), pyrrolidine (2.5 mL, 30 mmol), potassium *tert*-butoxide (3.4 g, 30 mmol), and dry toluene (5 mL). The autoclave was seeled and the mixture was magnetically stirred at 120 °C. After 24 h the reaction mixture was allowed to stand, then treated with water to dissolve the salts. The organic layer was collected, then the aqueous layer was extracted with dichloromethane. The organic layers were dried over $MgSO_4$. After filtration and concentration in vacuo, **1-(3,5-dichlorophenyl)pyrrolidine** was isolated from the residue by flash chromatography (petroleum light/diethyl ether from 99/1 until 90/10) as a white solid (46% yield): mp 73.1−73.3 °C; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.98−2.02 (m, 4 H), 3.22−3.25 (m, 4 H), 6.38 (d, 2 H, $J$ = 1.7 Hz), 6.60 (t, 1 H, $J$ = 1.7 Hz); $^{13}$C NMR ($CDCl_3$, 75.56 MHz) $\delta$ 25.4, 47.6, 109.8, 114.9, 135.3, 149.1; MS (EI, *m*/*e*, %) 214 ($M^+$, 100), 187 (6), 172 (12), 159 (28), 145 (13). HRMS calcd for $C_{10}H_{11}Cl_2N$ 215.02685, found 215.02690. Anal. Calcd for $C_{10}H_{11}Cl_2N$: C, 55.58; H, 5.13. Found: C, 55.55; H, 5.15. From the reaction mixture two other new products were separated and characterized, whose structure was unequivocally assigned by Nuclear Overhauser Effect experiments. **1,1′-(4-Chloro-1,3-phenylene)dipyrrolidine**: pale yellow oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.90−1.97 (m, 4 H), 1.97−2.03 (m, 4 H), 3.22−3.30 (m, 4 H), 3.34−3.41 (m, 4 H), 6.03 (dd, 1 H, $J$ = 8.5, 2.9 Hz), 6.06 (d, 1 H, $J$ = 2.9 Hz), 7.11 (d, 1 H, $J$ = 8.5 Hz); $^{13}$C NMR ($CDCl_3$, 100.56 MHz) $\delta$ 25.0, 25.5, 47.7, 50.9, 100.5, 104.4, 110.7, 131.3, 147.3, 147.5; MS (EI, *m*/*e*, %) 250 ($M^+$, 100), 221 (6), 207 (9), 194 (11), 152 (4); HRMS calcd for $C_{14}H_{19}ClN_2$ 250.12368, found 250.12370. Anal. Calcd for $C_{14}H_{19}ClN_2$: C, 67.05; H, 7.64. Found: C, 67.09; H, 7.67. **1,1′-(2-Chloro-1,4-phenylene)dipyrrolidine:** pale yellow oil; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.89−1.95 (m, 4 H), 1.95−2.02 (m, 4 H), 3.11−3.19 (m, 4 H), 3.20−3.23 (m, 4 H), 6.41 (dd, 1 H, $J$ = 2.7, 8.6 Hz), 6.61 (d, 1 H, $J$ = 2.7 Hz), 6.95 (d, 1 H, $J$ = 8.6 Hz); $^{13}$C NMR ($CDCl_3$, 100.56 MHz) $\delta$ 24.3, 25.4, 47.9, 51.5, 110.5, 113.8, 119.4, 127.8, 136.7, 144.1; MS (EI, *m*/*e*, %) 250 ($M^+$, 100), 215 (46), 207 (12), 194 (5), 185 (15), 159 (4), 145 (6), 125 (8); HRMS calcd for $C_{14}H_{19}ClN_2$ 250.12368, found 250.12367. Anal. Calcd for $C_{14}H_{19}ClN_2$: C, 67.05; H, 7.64. Found: C, 67.06; H, 7.66.

1-(3,5-Dichlorophenyl)pyrrolidine (0.7 g, 3 mmol), morpholine (1.0 mL, 12 mmol), potassium *tert*-butoxide (1.5 g, 12 mmol), and toluene (5 mL) were introduced in an autoclave. The vessel was seeled and the mixture was magnetically stirred at 200 °C. After 72 h the reaction mixture was allowed to stand, then treated with water until the salts were dissolved. The organic layer was collected, then the aqueous layer was extracted with dichloromethane. The organic layers were dried over $MgSO_4$. After filtration and concentration in vacuo, **4,4′-(5-pyrrolidin-1-yl-1,3-phenylene)-dimorpholine** (**12**) was purified by flash chromatography (petroleum light/diethyl ether from 99/1 until 90/10) and obtained in 75% yield as a white solid: mp 247.8−248.2 °C, $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.95−2.00 (m, 4 H), 3.13−3.16 (m, 8 H), 3.26−3.30 (m, 4 H), 3.83−3.86 (m, 8 H), 5.73 (d, 2 H, $J$ = 1.9 Hz), 5.89 (t, 1 H, $J$= 1.9 Hz); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 25.4, 47.7, 50.1, 67.1, 93.1, 93.4, 149.4, 153.4; MS (EI, *m*/*e*, %) 317 ($M^+$, 100), 288 (11), 274 (10), 260 (59), 200 (14), 158 (13), 145 (6), 100 (13); HRMS calcd for $C_{18}H_{27}N_3O_2$ 317.21033, found 317.21035. Anal. Calcd for $C_{18}H_{27}N_3O_2$: C, 68.11; H, 8.57. Found: C, 68.08; H, 8.60.

**Formation and behavior of Wheland Complex 13a: General Procedure.** To a solution of compound **12** (0.010 g, 0.0315 mmol), prepared in $CD_3CN$ (0.5 mL) at −30 °C directly in a NMR tube, was added a solution containing diazonium salt **3** (0.0315 mmol in 0.5 mL of $CD_3CN$), cooled at −30 °C. The reaction mixture was monitored each 5 min, until its $^1$H NMR spectrum showed complete disappearance of signals related to compound **3**, and concomitant appearance of signals of the Wheland complex **13a**: $^1$H NMR ($CD_3CN$, 300 MHz, −30 °C) $\delta$ 1.97−2.40 (m, 4 H), 3.18−3.88 (m, 20

H), 3.89 (s, 3 H), 5.32 (s, 2 H), 6.42 (s, 1 H), 7.08 (d, 2 H, $J = 8.8$ Hz), 7.72 (d, 2 H, $J = 8.8$ Hz). Once complex **13a** was completely formed, a solution of salt **4** (0.0315 mmol in 0.5 mL of $CD_3CN$), cooled at − 30 °C, was added. Immediately, the spectrum showed disappearance of signals related to the *p*-methoxyphenyl moiety of complex **13a**, with concomitant appearance both of signals belonging to salt **3**, and to those of complex **13b**: $^1$H NMR ($CD_3CN$, 300 MHz, −30 °C) $\delta = 1.98-2.10$ (m, 8 H), 3.40−4.00 (m, 16 H), 5.35 (s, 2 H), 6.69 (s, 1 H), 7.89 (d, 2 H, $J = 8.7$ Hz), 8.40 (d, 2 H, $J = 8.7$ Hz).

The $^1$H NMR spectrum containing complex **13a** showed the presence of other signals, ascribed to complex **14a**, obtained by attack of diazonium salt **3** to **12** in the ortho-position with respect to the pyrrolidinic ring; the relative ratio of the $sp^3$ CH signals of the $\sigma$-complexes revealed the presence of complex **14a** in minor amount with respect to **13a**. Complex **14a**: $^1$H NMR ($CD_3CN$, 300 MHz, −30 °C) $\delta$ 1.95−2.40 (m, 4 H), 2.90−3.98 (m, 20 H), 3.84 (s, 3 H), 5.20 (s, 1 H), 5.49 (s, 1 H), 6.26 (s, 1 H), 7.02 (d, 2 H, $J = 8.9$ Hz), 7.42 (d, 2 H, $J = 8.9$ Hz). After addition of diazonium salt **4**, the spectrum showed the presence of both complex **13b** and complex **14b**, allowing from the analogous parallel reaction exchange on compounds **14a**. Complex **14b**: $^1$H NMR ($CD_3CN$, 300 MHz, −30 °C) $\delta$ 1.98−2.25 (m, 4 H), 2.80−4.05 (m, 20 H), 5.23 (s, 1 H), 5.53 (s, 1 H), 6.50 (s, 1 H), 7.50 (d, 2 H, $J = 8.7$ Hz), 8.29 (d, 2 H, $J = 8.7$ Hz).

Solutions of compounds **13a** (containing **14a**) and **13b** (containing **14b**) are not stable and spontaneously formed salts **15Ha** and **15Hb** (and related **16Ha** and **16Hb**), as previously reported for complexes **6a**−**c** and **7a**−**c.**[10] Compounds **15Ha** and **15Hb** can be isolated also by precipitation from their reaction mixture according to the procedure previously reported for obtaining compounds **8Ha**−**c** and **9Ha**−**c**.[12] Chemicophysical data of compounds **15Ha** and **15Hb**, together with those of the corresponding minor isomers **16Ha** and **16Hb**, are as follows:

**4,4′-{2-[(4-Methoxyphenyl)diazenyl]-5-pyrrolidin-1-yl-1,3-phenylene}dimorpholine·HBF$_4$ (15Ha):** 95% yield, red solid, impure of its isomer **16Ha**: $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) $\delta$ 1.99−2.23 (m, 4 H), 2.95−3.16 (m, 2 H), 3.19−3.36 (m, 2 H), 3.83 (s, 3 H), 3.53−4.17 (m, 16 H), 5.60 (d, 1 H, $J = 1.8$ Hz), 6.01(d, 1 H, $J = 1.8$ Hz), 6.95 (d, 2 H, $J = 9.1$ Hz), 7.28 (d, 2 H, $J = 9.1$ Hz), 12.41 (s, 1 H); $^{13}$C NMR ($CDCl_3$, 100.56 MHz, −30 °C) $\delta$ 25.0, 25.1, 47.8, 50.1, 50.9, 51.1, 51.3, 55.7, 66.4, 66.5, 66.7, 93.6, 100.1, 115.5, 117.1, 123.4, 135.1, 151.2, 157.1, 157.9, 159.3. Anal. Calcd for $C_{25}H_{34}BF_4N_5O_3$ (539.37): C, 55.67; H, 6.35. Found: C, 55.65; H, 6.37. ES+: 452. ES−: 87. **4,4′-{4-[(4-Methoxyphenyl)diazenyl]-5-pyrrolidin-1-yl-1,3-phenylene}dimorpholine·HBF$_4$ (16Ha):** $^1$H NMR ($CDCl_3$, 300 MHz, 25 °C) $\delta$ 1.99−2.23 (m, 4 H), 2.95−3.16 (m, 2 H), 3.19−3.36 (m, 4 H), 3.53−4.17 (m, 16 H), 3.83 (s, 3H), 5.55 (d, 1 H, $J = 1.9$ Hz), 6.17 (d, 1 H, $J = 1.9$ Hz), 6.95 (d, 2 H, $J = 9.1$ Hz), 7.24 (d, 2 H, $J = 8.9$ Hz), 12.73 (br s, 1 H).

**4,4′-{2-[(4-Nitrophenyl)diazenyl]-5-pyrrolidin-1-yl-1,3-phenylene}dimorpholine·HBF$_4$ (15Hb):** 95% yield, red solid, impure of its isomer **16Hb**: $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C) $\delta$ 2.02−2.11 (m, 4 H), 2.88−3.10 (m, 2 H), 3.21−3.41 (m, 2 H), 3.56−4.16 (m, 16 H), 5.66 (d, 1 H, $J = 2.0$ Hz), 5.93 (d, 1 H, $J = 2.0$ Hz), 7.54 (d, 2 H, $J = 9.0$ Hz), 8.31 (d, 2 H, $J = 9.0$ Hz), 11.87 (br s, 1 H); $^{13}$C NMR ($CD_3CN$, 100.56 MHz, −30 °C) $\delta$ 24.4, 24.6, 48.1, 50.3, 50.4, 50.6, 50.7, 65.7, 65.8, 66.3, 92.1, 99.4, 115.2, 125.7, 128.2, 143.5, 147.2, 150.9, 157.8, 158.9. Anal. Calcd for $C_{24}H_{31}BF_4N_6O_4$ (554.35): C, 52.00; H, 5.64. Found: C, 51.97; H, 5.37. ES$^+$: 467. ES$^-$: 87. **4,4′-{4-[(4-Nitrophenyl)diazenyl]-5-pyrrolidin-1-yl-1,3-phenylene}dimorpholine·HBF$_4$ (16Hb):** $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C) $\delta$ 2.02−2.11 (m, 4 H), 2.88−3.10 (m, 2 H), 3.21−3.41 (m, 2 H), 3.56−4.16 (m, 16 H), 5.58 (d, 1 H, $J = 2.4$ Hz), 6.09 (d, 1 H, $J = 2.4$ Hz), 7.53 (d, 2 H, $J = 8.8$ Hz), 8.30 (d, 2 H, $J = 8.9$ Hz), 12.28 (br s, 1 H).

**Preparation of Compounds 17, 18, 20, and 21.** To a solution of salt **8Ha** (or **9Ha**) (0.092 mmol in 2 mL of $CH_3CN$), prepared as reported in ref 12, cooled at −30 °C, was added 0.092 mmol of arenediazonium tetrafluoborate **4** or **5**. Immediately the solution assumed a yellow color. After magnetic stirring for 20 min the color turned red. After removal of the solvent in vacuo, the crude product was dissolved in 2 mL of $CH_2Cl_2$ and the compounds **17** or **18**, or **20**, or **21** were precipitated by adding $Et_2O$. The products **17** or **18**, or **20**, or **21** were isolated as solids in 80−90% yield and crystallized from $CH_2Cl_2$ and *n*-hexane.

**1,1′-{4-[(4-Methoxyphenyl)diazenyl]-2-[(4-nitrophenyl)diazenyl]-5-piperidin-1-yl-1,3-phenylene}dipiperidinium ditetrafluoroborate (17):** red solid, yield 90%, mp 135.2−148.3 °C dec; $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C) $\delta$ 1.7−2.46 (m, 18 H), 3.35−4.50 (m, 12 H), 3.87 (s, 3 H), 6.22 (s, 1 H), 7.07 (d, 2 H, $J = 9.02$ Hz), 7.51 (d, 2 H, $J = 9.02$ Hz), 7.63 (d, 2 H, $J = 9.2$ Hz), 8.33 (d, 2 H, $J = 9.2$ Hz), 9.94 (s, 1 H), 10.02 (s, 1 H); $^{13}$C NMR ($CD_3CN$, 100.56 MHz, −30 °C) $\delta$ 22.5, 22.6, 22.8, 24.6, 24.7, 26.1, 26.6 (2 signals overlapped), 26.9, 49.1, 49.5, 53.0, 53.4, 54.9, 58.1, 58.2, 91.4, 114.4, 115.3, 117.9, 121.1, 125.3, 126.6, 134.3, 143.5, 146.2, 154.8, 155.5, 157.9, 161.7. Anal. Calcd for $C_{34}H_{44}B_2F_8N_8O_3$ (786.37): C, 51.93; H, 5.64. Found: C, 51.99; H, 5.62.

**1,1′-{2-[(4-Bromophenyl)diazenyl]-4-[(4-methoxyphenyl)diazenyl]-5-piperidin-1-yl-1,3-phenylene}dipiperidinium ditetrafluoroborate (18):** red solid, yield 80%, mp 130.2−140.4 °C dec; $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C) $\delta$ 1.63−2.07 (m, 18 H), 3.63−3.97 (m, 12 H), 3.86 (s, 3 H), 6.24 (s, 1 H), 7.05 (d, 2 H, $J = 8.8$ Hz), 7.42 (d, 2 H, $J = 8.8$ Hz), 7.51 (d, 2 H, $J = 9.1$ Hz), 7.64 (d, 2 H, $J = 9.1$ Hz), 9.80 (br s, 1 H), 9.92 (br s, 1 H); $^{13}$C NMR ($CD_3CN$, 100.56 MHz, −30 °C) $\delta$ 22.1, 22.8, 22.9, 24.3 (2 signals overlapped), 26.0, 26.3, 26.4, 27.1, 48.6, 49.4, 53.1, 53.3, 55.4, 57.5, 58.3, 92.6, 114.9, 115.3, 117.9, 118.3, 118.9, 121.7, 132.5, 135.7, 140.8, 155.7, 156.0, 158.5, 162.4. Anal. Calcd for $C_{34}H_{44}B_2BrF_8N_7O$ (820.27): C, 49.78; H, 5.41. Found: C, 49.73; H, 5.40.

**4,4′-{4-[(4-Methoxyphenyl)diazenyl]-5-morpholin-4-yl-2-[(4-nitrophenyl)diazenyl]-1,3-phenylene}bismorpholin-4-ium ditetrafluoroborate (20):** tile red solid, yield 88%, mp 139.9−154.8 °C dec; $^1$H NMR ($CD_3CN$, 400 MHz, 25 °C) $\delta$ 2.1−2.4 (m, 4H), 3.40−4.16 (m, 16H), 3.95 (s, 3H), 4.21−4.77 (m, 4H), 6.24 (s, 1H), 7.10 (d, 2H, $J = 9.16$ Hz), 7.54 (d, 2H, $J = 9.16$ Hz), 7.65 (d, 2H, $J = 9.16$ Hz), 8.35 (d, 2H, $J = 9.16$ Hz), 10.15 (br s, 1H), 10.20 (br s, 1H); $^{13}$C NMR ($CD_3CN$, 100.56 MHz, −30 °C) $\delta$ 48.4, 48.7, 49.3, 49.9, 55.5, 57.4 (2 signals overlap), 66.2, 66.4, 65.7, 66.7 (2 signals overlap), 66.8, 92.9, 115.0, 116.4, 118.8, 120.9, 125.6, 126.0, 135.7, 144.7, 146.4, 156.0, 156.8, 159.0, 162.7. Anal. Calcd for $C_{31}H_{38}B_2F_8N_8O_6$ (792.29): C, 46.99; H, 4.83.Found: C, 47.02; H, 4.84.

**4,4′-{2-[(*E*)-(4-Bromophenyl)diazenyl]-4-[(*E*)-(4-methoxyphenyl)diazenyl]-5-morpholin-4-yl-1,3-phenylene}bismorpholin-4-ium ditetrafluoroborate (21):** tile red solid, yield 85%, mp 142.3−162.5 °C dec; $^1$H NMR ($CD_3CN$, 300 MHz, 25 °C) $\delta$ 2.23−2.33 (m, 4H), 3.60−4.13 (m, 16H), 3.93 (s, 3H), 4.20−4.41 (m, 4H), 6.22 (s, 1H), 7.11 (d, 2H, $J = 9.11$ Hz), 7.50 (d, 2H, $J = 9.11$ Hz), 7.61 (d, 2H, $J = 9.11$ Hz), 7.66 (d, 2H, $J = 9.11$ Hz), 10.05 (br s, 1H), 10.21 (br s, 1H); $^{13}$C NMR ($CD_3CN$, 75.56 MHz, −30 °C) $\delta$ 47.5, 47.8, 50.0, 52.1, 55.0, 57.0, 57.2, 65.1, 65.3, 65.8, 66.1(2 signals overlap), 66.4, 91.8, 114.4, 116.4, 117.9, 118.1, 120.7, 122.9, 132.3, 134.2, 140.3, 155.7, 156.1, 158.1, 162.4. Anal. Calcd for $C_{31}H_{38}B_2BrF_8N_7O_4$ (826.19): C, 45.07; H, 4.64. Found: C, 46.00; H, 4.63.

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**Supporting Information Available:** General experimental details and copies of $^1$H and $^{13}$C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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