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Photosubstitution-Photoreduction Mechanistic Duality in the SET Photoreactions of Nitrophenyl Ethers with Amines. The Role of the Steps that follow the ET.

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Abstract : Nitrophenyl ethers are photoreduced by primary amines in water through a mechanism initiated by single electron transfer that is in direct competition with the single electron transfer photosubstitution mechanism (S_NAr^*-SET). Our results indicate that the preferred pathway does not depend on the electron donor or proton donor ability of the amine. The key factor that determines the progress of the photoreaction is the structure of the carbon skeleton of the amine, particularly the type of hydrogens on the carbon α to the amino group. A mechanistic rationale that includes hydrogen atom transfer as a key step is discussed.

Keywords : Electron transfer; nitro compounds; photochemistry; reduction.

INTRODUCTION

Nucleophilic aromatic photosubstitutions in nitroaromatic compounds have been the object of intense research since their discovery in 1956.[1] A mechanistic borderline between polar S_N2Ar^* [2] and S_NAr^*-SET (reactions that take place through single electron transfer from the nucleophile to the excited nitroaromatic substrate) has been well established.[3,4] However, there is a much less explored borderline between the S_NAr^*-SET process and the electron transfer initiated photoreduction of the nitro group.

In Schemes 1 and 2 the two mechanisms proposed in the literature for photoreductions of aromatic nitrocompounds in isopropanol are shown in a simplified manner. The mechanism of Scheme 1 (direct hydrogen atom transfer to the nitroaromatic excited state)[5] would ideally correspond to the photoreduction of nitroaromatics without electron donor substituents (n-π* excited state), in solvents capable of transferring hydrogen atoms, and in the absence of electron transfer reducing agents. On the other hand, the mechanism of Scheme 2 would correspond to the photoreduction of nitroaromatics substituted by electron donor groups in protic solvents (π-π* excited state), in the presence of electron transfer reducing species (D^-).[6] The nature of the excited state involved (normally a triplet excited state) is crucial for the observed photoreactivity. Thus, nitroaromatic compounds with a lower excited state of the n-π* type tend to react through an

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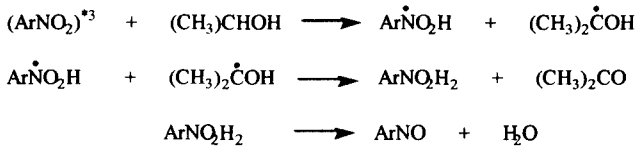
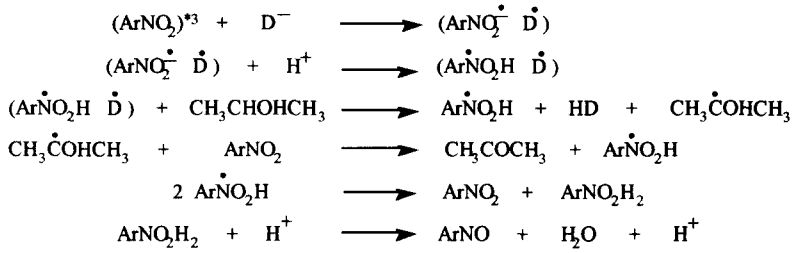
hydrogen atom abstraction mechanism.[7] On the other hand, the ones with a lower excited state of the π-π* type are not active in hydrogen atom abstraction reactions, and in these cases photosubstitutions, or photoreductions through the electron transfer mechanism are predominantly observed.[1-4] Two factors govern the relative energy of the n-π* and π-π* excited states in nitroaromatics: the substitution in the aromatic ring (electron donor substituents stabilise the π-π* states *vs.* the n-π*),[8] and the nature of the solvent (π-π* states are stabilised by hydrogen bond formation with the solvent).[9]

Amines photoreduce aromatic compounds through an electron transfer mechanism.[10] Dopp *et al.*[11] studied the photoreduction of nitroaromatic compounds with amines for which they also proposed an electron transfer type mechanism. Interestingly, these photoreductions were only observed when the amine was used as a solvent. When mixtures of water/amine are used, only photosubstitution products are generally observed.[4,5a,12]



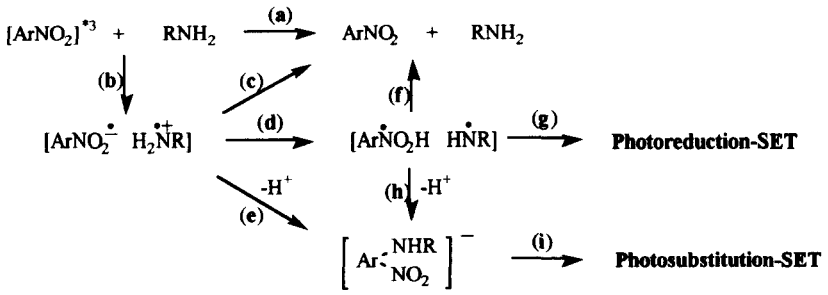
Scheme 1



Scheme 2

Nitrophenyl ethers react photochemically with amines in aqueous solutions giving rise predominantly to photosubstitution products[12] in spite of the fact (Scheme 3) that in several well established cases the photosubstitution follows an electron transfer mechanism (SNAr*-SET).[3,4] It is known[9] that the n-π* and the π-π* triplet excited states of nitrophenyl ethers are rather close in energy, being populated according to the Boltzmann distribution. However, the π-π* state is generally the one with lower energy in polar protic solvents such as water, thus justifying the observed photoreactivity.

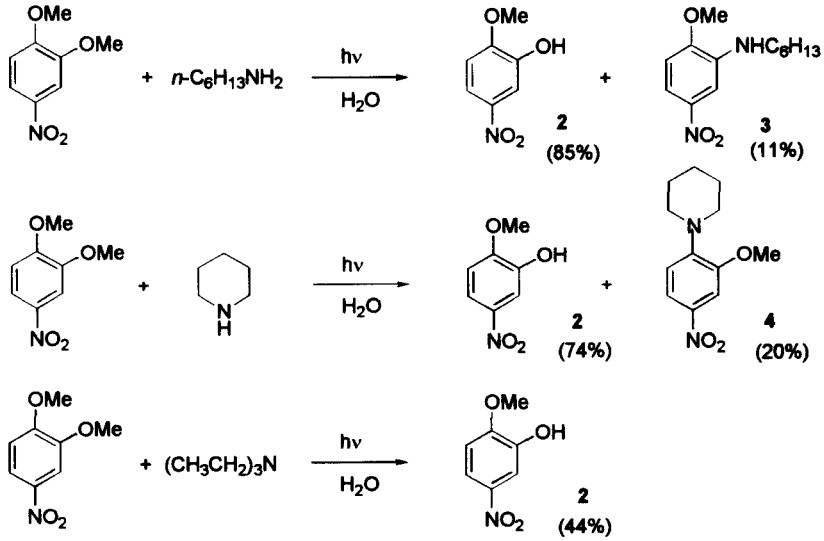
In connection with our photochemical studies in organised media,[13] we were interested in determining the factors that govern the progress of the nitroaromatic radical anion once formed, to photosubstitution or to photoreduction products, in the absence of solvent participation (Scheme 3) and at which level the discrimination occurs, radical-ionic pair [step (**d**) vs. (**e**), in scheme 3] or radical pair [step (**g**) vs. (**h**), in scheme 3]. Therefore, we present here a mechanistic study on the borderline S_NAr^*-SET / photoreduction-SET in the photoreactions of nitrophenyl ethers with amines in pure water, a solvent not capable of transferring hydrogen atoms.



Scheme 3

RESULTS

First, we decided to test the effect of the ability of the amine, as electron donor, in the photoreaction with 4-nitroveratrole (NVT, **1**) as a typical nitrophenyl ether. In Scheme 4, the photoreactions of NVT with three amines of rather different ionisation potential[4c] (*n*-hexylamine, piperidine, and triethylamine) in pure water as solvent are shown. We have previously reported the corresponding photoreactions in mixtures of methanol-water[4a] or acetonitrile-water.[4c] A common feature in this set of amines is the fact that the hydrogens next to the amino group are all of them of the simple methylene typ, and therefore (leaving aside entropic effects) the ability of the amines as hydrogen atom donors should be similar.



Scheme 4

The photoreaction of NVT, **1**, with excess *n*-hexylamine in water (Scheme 4) gave rise to 2-methoxy-5-nitrophenol, **2** (85% yield), and *N*-hexyl-2-methoxy-5-nitroaniline, **3** (11% yield). Both photoproducts come from the photosubstitution on NVT by the nucleophiles present in the reaction mixture, and the

observed regioselectivity suggests the operation of a S_N2Ar^* (polar) mechanism.[4] In contrast to what it is observed in mixtures water-organic solvent,[4a] no photosubstitution in the *para* position with respect to the nitro group (S_NAr^*-SET mechanism) was observed in water.

The photoreaction of NVT, **1**, with excess piperidine in water (Scheme 4) led to 74% yield of 2-methoxy-5-nitrophenol, **2**, and 20% yield of 2-piperidino-5-nitroanisole, **4**. The observed regioselectivity in the photosubstitution of NVT by piperidine (substitution of the methoxy group in the *para* position with respect to the nitro group)[4a,c] suggests the operation of a S_NAr^*-SET mechanism for this photosubstitution.

The photoreaction of NVT, **1**, in the presence of excess of triethylamine led exclusively to 2-methoxy-5-nitrophenol, **2** (44%) and the recovery of starting material (Scheme 4).

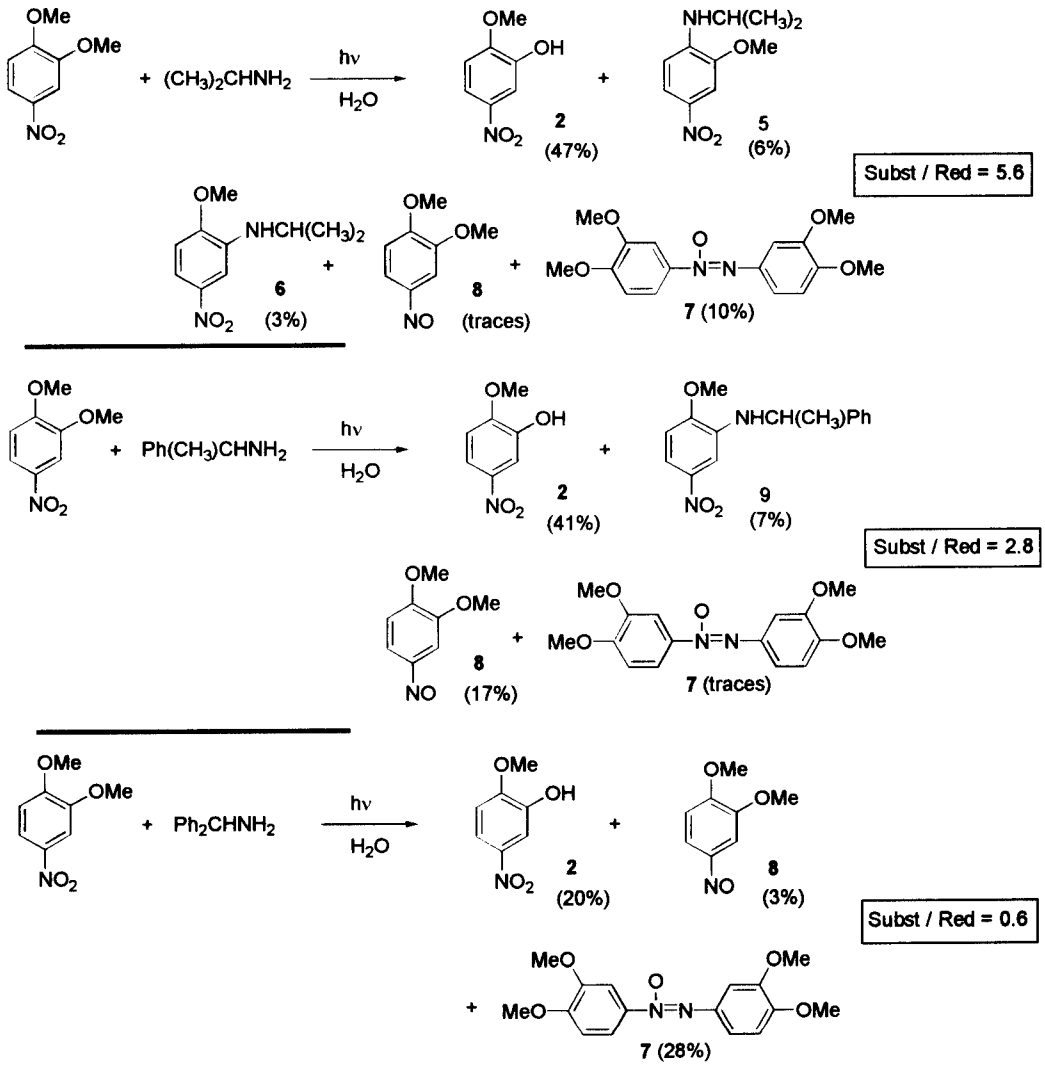
From the results reported in Scheme 4 it becomes evident that in spite of the different abilities of the amines used as electron donors and the fact that the S_NAr^*-SET photoreaction is produced in pure water if the amine is soft enough (piperidine) no photoreduction of the nitro group is observed at all.

Once it had been demonstrated that the electron donor ability of the amine had little effect on the photosubstitution-photoreduction ratio, we turned our attention to the properties of the hydrogen atoms bonded to the carbon next to the amine group. Thus, the photoreactions of NVT, **1**, in the presence of several primary amines such as 2-propylamine, 1-phenylethylamine, and benzhydrylamine were studied (Scheme 5). The main difference among the amines is now their hydrogen atom donor ability, which is much larger in benzylic amines.

The photoreaction of NVT, **1**, with excess of 2-propylamine in water gave rise to 2-methoxy-5-nitrophenol, **2** (47% yield); *N*-methylethyl-2-methoxy-4-nitroaniline, **5** (6%); *N*-methylethyl-2-methoxy-5-nitroaniline, **6** (3% yield); 3,3',4,4'-tetramethoxyazoxybenzene, **7** (10% yield); and traces of 4-nitrosoveratrole, **8**. The products **5** and **6** correspond to the substitution of NVT by 2-propylamine, and the observed regioselectivities suggest[4a,c] they are formed through the S_NAr^*-SET and S_N2Ar^* mechanisms respectively. Products **7** and **8** are photoreduction products, and the ratio photosubstitution/photoreduction is approximately 5.6.

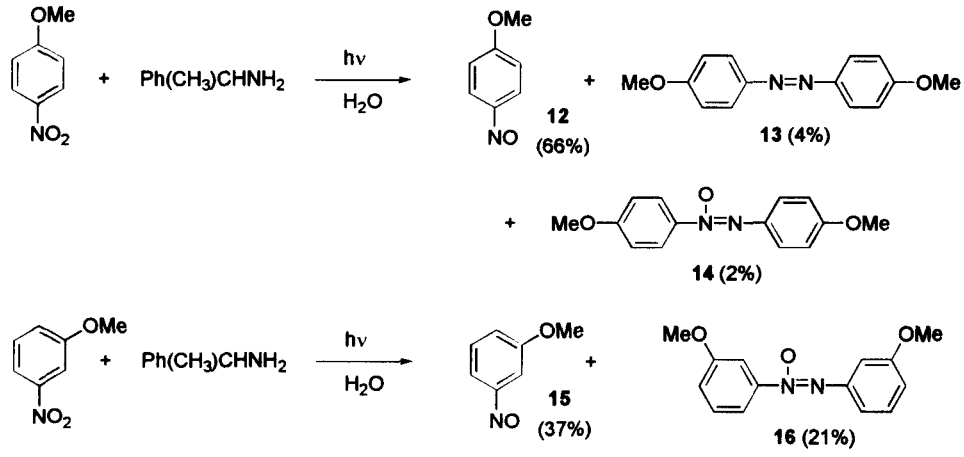
The photoreaction of NVT, **1**, with an excess of a benzylic amine such as 1-phenylethylamine in water (Scheme 5) produced 2-methoxy-5-nitrophenol, **2** (41% yield); *N*-(1-phenylethyl)-2-methoxy-5-nitroaniline, **9** (7% yield); 4-nitrosoveratrole, **8** (17% yield); and 3,3',4,4'-tetramethoxyazoxybenzene, **7** (traces). In this case the ratio photosubstitution/photoreduction is aprox. 2.8. Acetophenone, a product of oxidation of the amineand subsequent hydrolysis, was also obtained. The regioselectivity of the photosubstitution by amine (presence of product **9** and absence of the corresponding product of photosubstitution of the methoxy group in the *para* position with respect to the nitro group) was established by NOE experiments. Thus, irradiation of the methyl group of the photosubstitution product (δ 3.9) produced 19% NOE effect on the hydrogen bonded to the C-3 in the phenyl ring (δ 6.7). Interestingly enough, no S_NAr^*-SET photosubstitution product (substitution of the methoxy group in the *para* position) was observed in this photoreaction.

The photoreaction of NVT, **1**, with an excess of benzhydrylamine in water (Scheme 5) gave rise to 2-methoxy-5-nitrophenol, **2** (20% yield); 3,3',4,4'-tetramethoxyazoxybenzene, **7** (28% yield); and 4-nitrosoveratrole, **8** (3% yield). Benzophenone, a product derived from oxidation of the amine and subsequent hydrolysis was also obtained. In this photoreaction, no photosubstitution products by the amine were detected, and the general ratio photosubstitution/photoreduction is now approximately 0.6.



Scheme 5

We have reported[12b] that 4-nitroanisole (4-NA, **10**) reacts photochemically with primary amines in mixtures of water and organic solvents leading to photosubstitution products. Nitro group substitution is observed when primary amines with high ionisation potential are used (S_N2Ar^* mechanism). On the other hand, methoxy group substitution is observed in the presence of primary amines with lower ionisation potential (S_NAr^*-SET mechanism).[4b] It is also known that 3-nitroanisole (3-NA, **11**) photoreacts with primary amines in mixtures of water and organic solvent leading to photosubstitution products.[14] From the results described for NVT (Schemes 4 and 5) it was clear that the borderline between photosubstitution and photoreduction was mainly governed by the properties of the hydrogen atoms on carbon α to the amino group. Therefore, we decided to test the photoreactions of 2-NA and 3-NA in the presence of a benzylic amine such as 1-phenylethylamine (Scheme 6).



Scheme 6

The photoreaction of 4-NA, **10**, in the presence of an excess of 1-phenylethylamine in water (Scheme 6) produced 4-nitrosoanisole, **12** (66% yield); 4,4'-dimethoxyazobenzene, **13** (4% yield); and 4,4'-dimethoxyazoxybenzene, **14** (2% yield). Similarly, the photoreaction of 3-NA, **11**, in the same conditions gave rise to 3-nitrosoanisole, **15** (37% yield), and 3,3'-dimethoxyazoxybenzene, **16** (21% yield). In both cases, all the products detected were of photoreduction origin. In addition, acetophenone was also obtained.

There are a few reports in the literature concerning the possibility of benzylic amines acting as photoreducing agents for nitroaromatic compounds through the hydrogen atom transfer mechanism (Scheme 1). Thus, Takami *et al.* postulate that *N*-phenylbenzylamine photoreduces *m*-chloronitrobenzene in benzene through a hydrogen atom transfer mechanism.[15] It was therefore necessary to establish which mechanism, hydrogen atom transfer (Scheme 1) or electron transfer (Scheme 2), was operating in our photoreductions with 1-phenylethylamine.

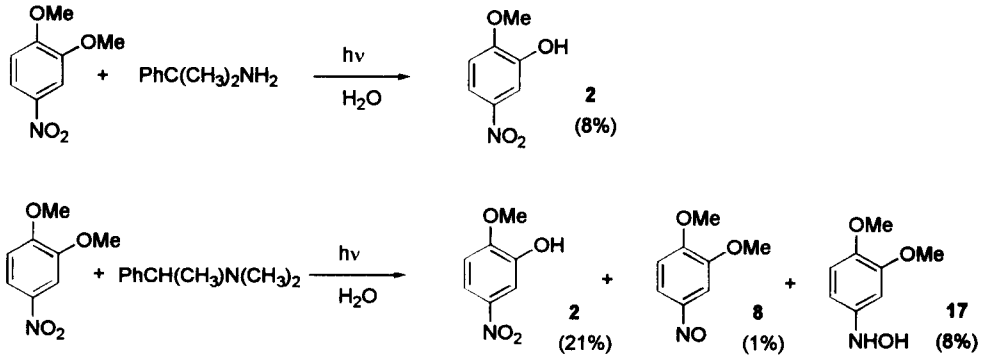
First of all, the ability as a photoreducing agent for NVT of 1-phenylethanol was tested. The hydrogen atom transfer ability of 1-phenylethylamine and of 1-phenylethanol must be similar, but their electron transfer properties are completely different. It is very unlikely that the electron transfer mechanism could be initiated by 1-phenylethanol. The irradiation of NVT, **1**, in the presence of excess 1-phenylethanol in water, in the conditions used for the photoreaction with 1-phenylethylamine, led to the complete recovery of the starting material.

The operation of the electron transfer mechanism in the photoreaction in the presence of 1-phenylethylamine was confirmed by carrying out the photoreaction in the presence of *m*-dinitrobenzene (quencher of electron transfer processes). In this case, no photoreduction products were observed.

From these experiments we conclude that, in agreement with the majority of the related literature precedents, the mechanism of the photoreduction of our nitrophenyl ethers in the presence of 1-phenylethylamine was initiated by single electron transfer from the amine to the excited state of the nitroaromatic substrate.

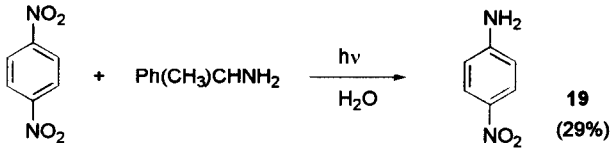
In order to confirm the importance of the hydrogen atom on the carbon-α with respect to the amino group, and to know if the amine hydrogens are necessary for the reduction to occur in water, the

photoreactions of NVT, **1**, with 1-methyl-1-phenylethylamine and with *N,N*-dimethyl-1-diphenylethylamine were studied and the results are summarised in Scheme 7. Interestingly, a significant amount of photoreduction products were detected in the second case, in spite of the steric hindrance associated with the amino group, but no photoreduction products were produced at all in the first case. These results confirm that the electron transfer initiated photoreduction is governed mainly by the transfer of the benzylic hydrogen and that the amine hydrogens are not essential for the photoreduction to occur in a proton donor solvent such as water.



Scheme 7

For the sake of comparison, the photoreaction between a nitroaromatic compound with electron withdrawing substituents, such as *p*-dinitrobenzene (*p*-DNB, **18**), and 1-phenylethylamine in water gave *p*-nitroaniline, **19**, in 29% yield (Scheme 8). The comparison between this result and those described in Scheme 6 indicates a lower efficiency for the photoreduction process in this case, in agreement with other reports in the literature that show that nitroaromatic compounds with electron withdrawing substituents are not photoreduced by the electron transfer mechanism.[7,8]



Scheme 8

DISCUSSION

In the photoreactions of NVT, **1**, with *n*-hexylamine, piperidine, and triethylamine in water, no photoreduction products are obtained even though in the piperidine case, a photosubstitution product of electron transfer origin (S_NAr^*-SET), the 2-piperidino-5-nitroanisole, **4**, is produced.

In the photoreactions of NVT, **1**, with 2-propylamine, 1-phenylethylamine, and benzhydrylamine, substitution products appear, but in these cases photoreduction products are also observed. The proportion of photoreduction products increases following this sequence. Comparison of the results of irradiation

experiments of NVT with 1-phenylethanol and 1-phenylethylamine, in the absence and in the presence of *m*-dinitrobenzene indicate that the first step of the photoreduction mechanism is the single electron transfer from the amine to the nitrophenyl ether. However, our results indicate that the electron donating ability of the amine does not have a decisive influence on its activity as a reducing agent for nitroaromatic compounds. On the other hand, they also suggest that the structure of the amine, and particularly the type of hydrogens on the α-carbon govern the outcome of the photochemical reaction. The fact that photoreduction products are obtained when NVT, **1**, is irradiated in the presence of *N,N*-dimethyl-1-phenylethylamine, but not when it is irradiated in the presence of 1-methyl-1-phenylethylamine strongly support this conclusion, indicating that the amino group hydrogens are not essential for the photoreduction to occur in water.

These results have been extended to other nitrophenyl ethers such as 4-nitroanisole and 3-nitroanisole.

The most studied photoreduction reactions with amines correspond to the photoreductions of alkenes and carbonyl compounds with tertiary amines.[10,16] In these cases, the transfer of a proton from the α-carbon follows the electron transfer step, and in the case of the carbonyl compounds it seems that this is a very fast process.

When primary or secondary amines are used, the step that follows the electron transfer is also a proton transfer, but now the proton can come from the α-carbon or from the nitrogen depending on their relative acidity. Fessenden and Neta have reported that for the isopropylaminium radical cation, the most acidic proton is the one on the nitrogen (pK_a *ca.* 6.5).[17] For carbonyl compounds, Cohen *et al.*[18] propose that the lower efficiency in their photoreduction when primary or secondary amines are used, when compared with tertiary amines, is due to the fact that the proton is transferred from the aminium radical cation nitrogen and that the resulting alkylaminyl radical has a high tendency to regenerate the starting reagents through hydrogen abstraction.

In the case of alkenes, Lewis *et al.*[16] have reported that in the photoreaction between secondary amines and stilbenes, the resulting photoproducts come exclusively from intermediates formed by proton transfer from the amine N-H.

The corresponding processes of nitroaromatic compounds have been much less studied. The cases described assume (without carrying out specific studies) the general mechanistic scheme proposed for the photoreduction of carbonyl compounds and alkenes by tertiary amines, electron transfer followed by proton transfer from the amine α-carbon.[11,19] However, our results for the photoreductions carried out in water suggest a different mechanism, more close to what it is known about the photoreactivity of amines in the presence of alkenes and carbonyl compounds.

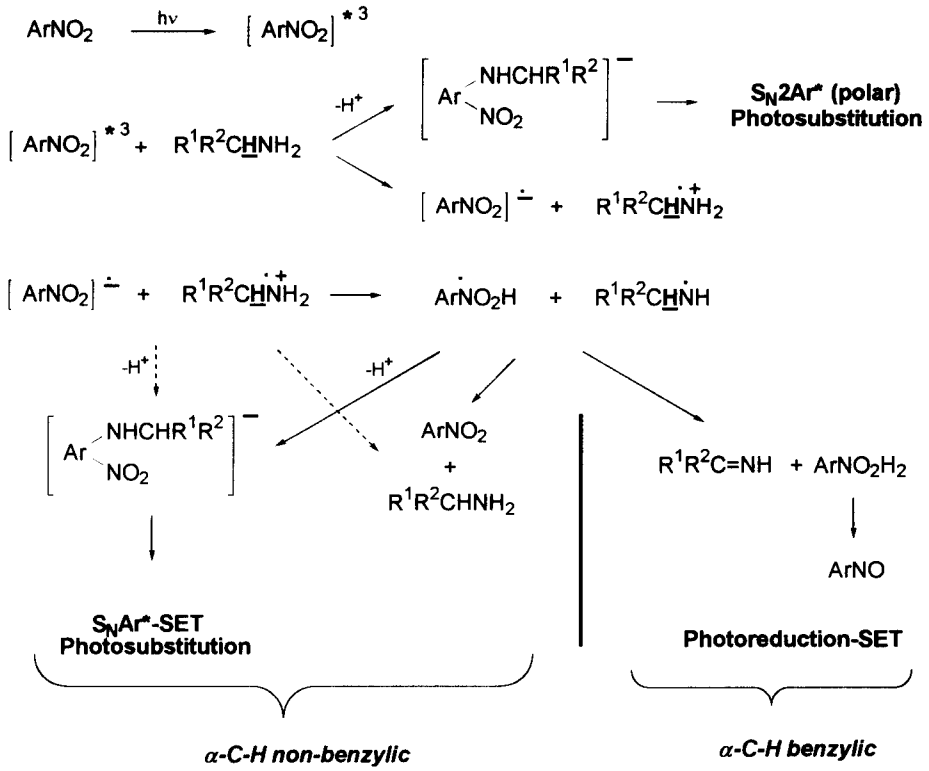
The first interesting fact is that the photoreduction processes of nitroaromatic compounds, initiated by an electron transfer step, are more efficient with substrates bearing electron donor substituents (more negative reduction potentials). This is related to the non-dependence of the outcome of our photoreactions on the electron donor ability of the amines used (Schemes 4 and 5). These results indicate that the key step that governs the borderline photosubstitution-photoreduction in the photoreactions of nitroaromatic derivatives with amines is not the electron transfer step.

Substrates bearing electron-donor substituents show a π-π* low energy excited state that is stabilised by hydrogen bond formation with the solvent or with the amine N-H.[9] Therefore, proton transfer after electron transfer will be probably a very fast process in all the cases studied (the results reported in Scheme 7 indicate that the amino N-H hydrogens are not essential for the photoreduction to occur).

The borderline between photosubstitution and photoreduction in water is clearly observed when the

photoreactivity of non-benzylic and benzylic amines is compared (Scheme 5). The ratio substitution/reduction depends on the hydrogen donor ability of the amine, and the benzylic hydrogen is essential for the photoreduction (Scheme 7).

In Scheme 9, a mechanistic proposal is shown that agrees with the reported facts.



Scheme 9

For substrates bearing electron withdrawing substituents (Scheme 8), the electron transfer mechanism of photoreduction (Scheme 9) is less efficient for several reasons: 1) These compounds show normally n-p* low energy excited states[8] that do not form hydrogen bonds.[9] 2) The radical anions are less basic than the ones of nitroaromatic compounds with electron-donor substituents (the pK_a values in water for the protonated radical anions of *p*-dinitrobenzene and *p*-nitrophenol are 1.6 and 3.6 respectively).[20] Back electron transfer can be a prevalent process in these cases. 3) The spin density in the nitro group of the corresponding radical anions and probably in the conjugate acids is significantly lower when the nitroaromatic compound bears electron withdrawing substituents than when it has electron donor ones (*i.e.* 4-nitroanisole,[21] $a_N(G)$ = 14.6, *p*-dinitrobenzene,[22] $a_N(G)$ = 1.74). This would translate in a reduced tendency to abstract hydrogen atoms. According to that, all the steps that follow the electron transfer are less efficient for substrates with electron withdrawing substituents. Therefore, the electron transfer mechanism (Scheme 9) is less efficient, and alternative mechanisms (direct hydrogen atom transfer to the nitroaromatic excited state)[5,7] can operate in the proper conditions.

EXPERIMENTAL PART

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 250 MHz and ^{13}C NMR spectra at 62.5 MHz. 1-Methyl-1-phenylethylamine[23] and *N,N*-dimethyl-1-phenylethylamine[24] were prepared according to literature methods. 4-Nitroveratrole, **1**, 4-nitroanisole, **10**, 3-nitroanisole, **11**, and *p*-dinitrobenzene, **18**, and the rest of the amines used were commercially available.

General procedure for the photoreactions of nitroaromatic compounds (1, 10, 11, and 18) with amines (Schemes 4-8). In a 600 mL photochemical reactor, 1 mmol of nitroaromatic substrate, and 10 mmol of the corresponding amine dissolved in 600 mL of water were introduced. The solution was irradiated through a pyrex filter with a 400 W medium-pressure Hg lamp at room temperature for 1 h. Then the reaction mixture was extracted between chloroform and water, and the aqueous phase acidified with HCl (1M) and extracted again with chloroform. The two organic layers were dried and the solvent evaporated. Phenol **2** was obtained directly from the acid medium extraction. All other reaction products were obtained from the residue of the initial extraction after column chromatography through silica gel using mixtures of chloroform/hexane as eluent. In the different reactions described in Schemes 4-8 the following products were obtained with the yields indicated in the Schemes:

2-Methoxy-5-nitrophenol, **2**: mp 102-103 °C (lit.[1] mp 105 °C).

N-Hexyl-2-methoxy-5-nitroaniline, **3**: mp 34-35 °C (lit.[4a] mp 34-36 °C).

2-Piperidino-5-nitroanisole, **4**: mp 70-73 °C (lit.[4a] mp 74-75 °C).

Products **2**, **3**, and **4** were identified by comparison with authentic samples.[4a]

N-Methylethyl-2-methoxy-4-nitroaniline, **5**: mp 56-57 °C; IR (film): 3390, 2968, 2923, 1595, 1533, 1319, 1287, 1226, 1095 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (d, J = 6.3 Hz, 6H), 3.71 (sept., J = 6.3 Hz, 1H), 3.90 (s, 3H), 4.88 (broad, 1H), 6.46 (d, J = 9.1 Hz, 1H), 7.58 (d, J = 2.2 Hz, 1H), 7.88 (dd, J = 9.1, 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.6, 43.8, 55.8, 104.7, 106.6, 120.5, 136.4, 143.4, 144.8; MS *m/e* (relative intensity) 211 (4), 210 (M^+, 31), 196 (11), 195 (100), 149 (31), 91 (5), 78 (10), 51 (8); Calculated for $C_{10}H_{14}N_2O_3$: C, 57.13; H, 6.71; N, 13.32. Found: C, 57.33; H, 6.45; N, 13.01.

N-Methylethyl-2-methoxy-5-nitroaniline, **6**: mp 70-72 °C; IR (film) 3409, 2969, 1585, 1523, 1464, 1367, 1336, 1262, 1231, 1174, 1089, 1023, 744 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (d, J = 6.5 Hz, 6H), 3.65 (sept., J = 6.5 Hz, 1H), 3.91 (s, 3H), 4.25 (broad, 1H), 6.71 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 2.6 Hz, 1H), 7.56 (dd, J = 8.8, 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.6, 43.8, 55.9, 103.8, 107.8, 112.4, 137.5, 142.5, 151.4; ; MS *m/e* (relative intensity) 211 (3), 210 (M^+, 24), 196 (10), 195 (100), 149 (32), 79 (15), 52 (10), 51 (12), 43 (10), 41 (13); Calculated for $C_{10}H_{14}N_2O_3$: C, 57.13; H, 6.71; N, 13.32. Found: C, 57.48; H, 6.61; N, 12.96.

3,3',4,4'-Tetramethoxyazoxybenzene, **7**: mp 187-190 °C (lit.[25] mp 185-192 °C); IR (KBr) 2982, 2951, 1596, 1453, 1415, 1334, 1278, 1232, 1140, 1123 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.9 (s, 12H), 6.90 (d, J = 8.9 Hz, 1H), 6.92 (d, J = 8.9 Hz, 1H), 7.83 (d, J = 2.4 Hz, 1H), 7.90 (dd, J = 8.9, 2.5 Hz, 1H), 7.93 (dd, J = 8.9, 2.5 Hz, 1H), 7.99 (d, J = 2.4 Hz, 1H); MS *m/e* (relative intensity) 318 (M^+, 15), 302 (20), 275 (10), 151 (13), 149(18), 137(61), 79 (22), 71 (22), 57 (25), 55 (19), 44 (100).

4-Nitrosoveratrole, **8**: mp 50-53 °C (lit.[25] mp 52.5-55.5 °C); ^{1}H NMR ($CDCl_3$) δ 3.8 (s, 3H), 4.10 (s, 3H), 6.60 (d, J = 2.0 Hz, 1H), 7.20 (d, J = 8.8 Hz, 1H), 8.50 (dd, J = 8.8, 2.5 Hz, 1H); MS *m/e* (relative intensity) 167 (M^+, 100), 153 (34), 138 (37), 137 (47), 122 (12), 110 (21), 107 (20), 94 (15), 92 (17), 79 (34), 77 (24), 51 (19).

N-(1-Phenylethyl)-2-methoxy-5-nitroaniline, **9**: mp 86-89 °C; IR (film) 3427, 2969, 1585, 1524, 1447,

1369, 1338, 1262, 1234, 1143, 1089, 1018, 855, 814, 749, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56 (d, J = 6.6 Hz, 3H), 3.92 (s, 3H), 4.53 (m, J = 6.6 Hz, 1H), 4.85 (broad, 1H), 6.68 (d, J = 8.8 Hz, 1H), 7.16 (d, J = 2.8 Hz, 1H) 7.2-7.4 (m, 5H), 7.52 (dd, J = 8.8,2.8 Hz, 1H), irradiation at δ 3.9 (OCH_3) gives NOE enhancement (19%) at δ 6.7; ^{13}C NMR ($CDCl_3$) δ 24.5, 52.9, 55.9, 104.7, 107.8, 113.0, 125.7, 128.7, 137.1, 142.2, 143.9, 151.3; MS *m/e* (relative intensity) 272 (M^+,31), 257 (41), 168 (34), 105 (100), 79 (25), 77 (19), 44 (22);); Calculated for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92; N, 10.29. Found: C, 66.28; H, 5.98; N, 10.25.

4-Nitrosoanisole, **12**: mp 25-28 °C (lit.[26] mp 23 °C, lit[27] mp 35 °C); ^1H NMR ($CDCl_3$) δ 3.9 (s,3H), 7.0 (d, J = 9.0 Hz, 2H), 7.9 (d, J = 9.0 Hz, 2H); MS *m/e* (relative intensity) 137 (M^+, 91), 123 (16), 108 (29), 107 (40), 92 (81), 80 (21), 77 (100), 64 (68), 63 (56), 53 (17), 52 (18), 51 (22), 50 (31).

4,4'-Dimethoxyazobenzene, **13**: mp 160-163 °C (lit.[5a] mp 162-164 °C); ^1H NMR ($CDCl_3$) δ 3.9 (s, 6H), 7.00 (d, J = 10.0 Hz, 4H), 7.90 (d, J = 10.0 Hz, 4H); MS *m/e* (relative intensity) 242 (M^+, 100), 135 (53), 108 (16), 107 (99), 92 (40), 77 (57), 64 (23).

4,4'-Dimethoxyazoxybenzene, **14**: mp 113-116 °C (lit.[5a] mp 117-118 °C), ^1H NMR ($CDCl_3$) δ 3.90 (s, 6H), 7.10 (dd, J = 10.3, J = 3.0, 4H), 8.30 (dd, J = 10.3 Hz, J = 3.0 Hz, 4H); MS *m/e* (relative intensity) 258 (M^+, 61), 242 (15), 135 (28), 121 (49), 107 (100), 106 (21), 92 (47), 80 (21), 78 (31), 77 (70), 64 (38), 63 (20).

3-Nitrosoanisole, **15**: mp 45-47 °C (lit.[27] mp 48 °C) ^1H NMR ($CDCl_3$) δ 3.90 (s, 3H), 6.90 (m, 1H), 7.27 (m, 1H), 7.58 (t, J = 8.1 Hz, 1H), 8.01 (m, 1H). MS *m/e* (relative intensity) 137 (M^+, 72), 123 (35), 107 (34), 95 (12), 94 (21), 93 (27), 92 (75), 80 (19), 77 (100), 65 (21), 64 (64), 63 (48), 62 (20).

3,3'-Dimethoxyazoxybenzene, **16**: mp 50-52 °C (lit.[5a] mp 51-52 °C); ^1H NMR ($CDCl_3$) δ 3.83 (s, 3H) 3.87 (s, 3H), 6.95 (dd, J = 8.0 Hz, J = 2.6 Hz, 1H), 7.36 (dd, J = 8.0 Hz, J = 4.0 Hz, 1H), 7.38 (dd, J = 8.0 Hz, J = 4.0 Hz, 1H), 7.70 (m, 1H), 7.79 (m, 2H), 7.86 (m, 1H); MS *m/e* (relative intensity) 258 (M^+, 19), 242 (14), 187 (10), 123 (20), 107 (100), 106 (42), 95 (26), 92 (64), 78 (24), 77 (73), 64 (46), 51 (28).

N-Hydroxy-3,4-dimethoxyaniline, **17**: It was impossible to obtain this product in a pure state, but it was tentatively identified from its spectra; ^1H NMR ($CDCl_3$) δ 3.90 (s, 3H), 3.96 (s, 3H), 6.96 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 1.8 Hz, 1H), 7.44 (dd, J = 8.0 Hz, J = 1.8 Hz, 1H); MS *m/e* (relative intensity) 168 (M^+-1, 1), 167 (10), 166 (100), 165 (60), 151 (15), 95 (38), 79 (21), 77 (29), 65 (13), 51 (22).

4-Nitroaniline, **19**: mp 149-151 °C, was identified by comparison with a commercial sample.

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REFERENCES

1. Cornelisse, J.; Havinga, E. *Chem. Rev.* **1975**, *75*, 353 and references therein.
2. Van Riel, H.C.H.A.; Lodder, G.; Havinga, E. *J. Am. Chem. Soc.* **1981**, *103*, 7257.
3. a) Mutai, K.; Kobayashi, K.; Yokoyama, K. *Tetrahedron* **1984**, *40*, 1755. b) Bunce, N.J.; Cater, S.R.; Scaiano, J.C.; Johnston, L.J. *J. Org. Chem.* **1987**, *52*, 4214.
4. a) Cantos, A.; Marquet, J.; Moreno-Mañas, M.; Castelló, A.. *Tetrahedron* **1988**, *44*, 2607. b) Cantos, A.; Marquet, J.; Moreno-Mañas, M.; González-Lafont, A.; Lluch, J.M.; Bertrán, J. *J. Org. Chem.* **1990**, *55*, 3303. c) Van Eijk, A.M.J.; Huizer, A.H.; Varma, C.A.G.O.; Marquet, J. *J. Am. Chem. Soc.* **1989**, *111*, 88.
5. a) Barltrop, J.A.; Bunce, N.J. *J.C.S. Chem. Commun.* **1968**, 1467. b) Levy, N.; Cohen, M.D. *J.C.S.*

Perkin Trans 2 **1979**, 553.

6. Cu, A.; Testa, A.C. *J. Am. Chem. Soc.* **1974**, *96*, 6698.
7. Trotter, W; Testa, A.C. *J. Am. Chem. Soc.* **1968**, *90*, 7044.
8. a) Petersen, W.C.; Letzinger, R.L. *Tetrahedron Lett.* **1971**, 2197. b) Levy, N.; Cohen, M.D. *Mol. Photochem.* **1977**, *8*, 155.
9. a) Varma, C.A.G.O.; Plantenga, F.L.; Huizer, A.H.; Zwart, J.P.; Bergwerf, Ph.; van de Ploeg, J.P.M. *J. Photochem.* **1984**, *24*, 133. b) Van Zeijl, P.H.M.; van Eijk, A.M.J.; Varma, C.A.G.O. *J. Photochem.* **1985**, *29*, 415. c) Wubbels, G.G.; Susens, D.P.; Coughlin, E.B. *J. Am. Chem. Soc.* **1988**, *110*, 2538.
10. Cohen, S.G.; Parola, A.; Parsons, G.H. *Chem. Rev.* **1973**, *73*, 141.
11. a) Döpp, D. *Topics in Curr. Chem.* **1975**, *59*, 33. b) Döpp, D.; Müller, D. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 297.
12. a) Pleixats, R.; Marquet, J. *Tetrahedron* **1990**, *46*, 1343. b) Cantos, A.; Marquet, J.; Moreno-Mañas, M. *Tetrahedron Lett.* **1989**, *30*, 2423.
13. a) Mir, M.; Marquet, J., Cayón, E. *Tetrahedron Lett.* **1992**, *33*, 7053. b) Mir, M.; Wilkinson, F.; Worral, D.R.; Bourdelande, J.L.; Marquet, J. *J. Photochem and Photobiol. A: Chem.* **1997**, *111*, 241.
14. a) van Vliet, A.; Kronenberg, M.E.; Cornelisse, J.; Havinga, E. *Tetrahedron* **1970**, *26*, 1061. b) Havinga, E.; de Jongh, R.O. *Bull. Soc. Chim. Belg.* **1962**, *71*, 803.
15. Takami, M.; Matsuura, T.; Saito, I. *Tetrahedron Lett.* **1974**, 661.
16. Lewis, F.D. *Acc. Chem. Res.* **1986**, *19*, 401.
17. Fessenden, R.W.; Neta, P. *J. Phys. Chem.* **1972**, *76*, 2857.
18. Inbar, S.; Linschitz, H.; Cohen, S. *J. Am. Chem. Soc.* **1981**, *103*, 1048.
19. Sundarajan, K.; Ramakrishnan, V.; Kuriakose, J.C. *Indian J. Chem., Sect. B*, **1983**, *22B*, 257.
20. Hayon, E.; Simic, M. *Acc. Chem. Res.* **1974**, *7*, 114.
21. Van Eijk, A.; Huizer, A.H.; Varma, C.A.G.O. *J. Photochem. Photobiol., A: Chem.* **1991**, *56*, 183.
22. Shein, S.M.; Bryukhovetskaya, L.V.; Pishchugin, F.V.; StarichenKo, V.F.; Panfilov, V.N.; Voevodski, V.V.; *J. Struct. Chem.* **1970**, *11*, 228.
23. Kornblum, N.; Fifolt, M. *Tetrahedron* **1989**, *45*, 1311.
24. Chaloner, P.A., Langadianou, E.; Renuka Perera, S.A. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2731.
25. Mustill, R.A.; Rees, A.H. *J. Org. Chem.* **1983**, *48*, 5042.
26. Havinga, E.; Miljs, W.J.; Hoekstra, S.E.; Ulmann, R.M. *Rec. Trav. Chim. Pays-Bas* **1958**, *77*, 746.
27. Brown, E.V.; Kipp, W.H. *J. Org. Chem.* **1971**, *36*, 170.