THE NUCLEOPHILIC AROMATIC PHOTOSUBSTITUTIONS OF 4,5-DINITROVERATROLE WITH AMINES.
PHOTOREDUCTIONS OF AROMATIC DINITROCOMPOUNDS

JORGE MARQUET,* MARCIAL MORENO-MAÑAS, ADELINA VALLRIBERA, ALBERT VIRGILI, JOAN
BERTRAN, ANGELS GONZALEZ-LAFONT, AND JOSE Mª LLUCH*

Department of Chemistry. Universidad Autónoma de Barcelona. Campus of Bellaterra.
Barcelona. Spain

Abstract.- 4,5-Dinitroveratrole is effectively photosubstituted by amines with
relatively high ionization potential such as methylamine, n-butylamine and ethyl gly-
cinate, but is mainly photoreduced when amines with relatively low ionization poten-
tial, such as dimethyl or trimethylamine are used. The photoreduction of several aro-
matic dinitrocompounds by triethylamine gives nitroanilines. A mechanistic scheme is
proposed embracing our photosubstitutions and photoreductions, based on our experi-
mental results and on MINDO/3 calculations of the ground states and the more likely
intermediates.

INTRODUCTION

Research on biological molecules and processes has been based lately on chemical methods, among
them "photoaffinity labelling" and "photocross-linking".[1] Nucleophilic aromatic photosubstitution
reactions[2] of nitrophenyl ethers have been proposed to be potentially useful for this purpose [3]
(i.e. the amino group of lysine in proteins can act as the nucleophile). Even though this type of
reaction has been in the chemical literature for twenty years,[2] reports on amines being used as
nucleophiles are scarce. Preliminary experiments with 4-nitroveratrole as a substrate and several
simple amines as nucleophiles, led us to demonstrate the influence of the nucleophile on the regio-
selectivity.[4] Similar results have been reported independently by Mutai[5,6] and Wubbels[7] in intramo-
lecular photo-Smiles rearrangements.

We wish to report here the results obtained using 4,5-dinitroveratrole, 1, as substrate. Photo-
reactions of 1 with various amines gave rise to clean photosubstitutions or photoreductions depen-
ding on the amine.

As far as we know, there is only one report in the literature concerning the change from photo-
substitution to photoreduction of nitroaromatics upon change from primary to tertiary amines.[8] The
authors attribute this behaviour to the different hydrogen atom donating ability of the studied
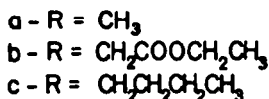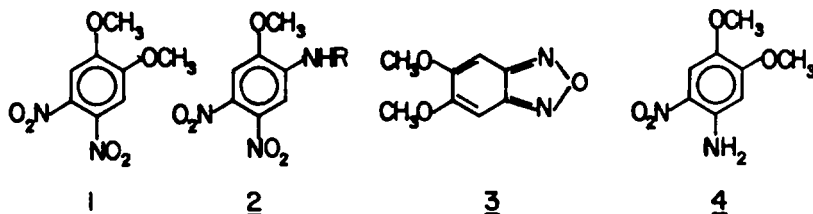amines.

Even though photoreductions of nitrobenzenes have also been in the literature for some time[9-22],
concerning photoreductions of aromatic polynitrocompounds, only that of 1,4-dinitrobenzene in iso-
propanol has been reported[23].

We report here the photoreduction of several aromatic dinitrocompounds. To gain some insight into
these processes, and to complement the experimental results, we also performed a series of cal-
culations on selected aromatic nitrocompounds. Theoretical and experimental results correlate well
to confirm that mechanistically, photosubstitutions and photoreduction of aromatic nitrocompounds
in the presence of good electron donors like amines, are two very related processes.

PHOTOREACTIONS

Photoreactions of 4,5-Dinitroveratrole with Amine Nucleophiles.

Photoreactions of 4,5-Dinitroveratrole with Amine Nucleophiles. The results obtained in the photoreactions of 1 with various amines are reported in Table I. Irradiations were maintained for 4h with a 400W medium pressure Hg lamp in a Pyrex immersion well reactor. A pH 8 buffered mixture of water and methanol or acetonitrile was used as solvent to minimize the thermal substitution of nitro group observed in some cases at uncontrolled pH. Reasonable to good yields of photosubstitution products were obtained in experiments 1, 2 and 3. Products 2a-2c, previously not reported, were characterized by their spectroscopic behaviour and elemental analyses. In experiment 3, using n-butylamine as nucleophile, a second product was isolated, namely 5,6-dimethoxybenzofurazane, 3. Due to the small amount obtained, no elemental analysis was performed on 3 but the ^{1}H NMR and ^{13}C NMR spectra indicated a very simple and symmetrical compound. It exhibited neither amino nor nitro group in its IR spectrum and the molecular ion in its mass spectrum appeared at m/e 180.   These data support the proposed structure. Product 3 is a reduction product that can arise from cyclization of the o-dinitroso compound to a benzofuroxane and further reduction of this compound to the benzofurazane, 3. An alternative would be the cyclization of an o-nitrosohydroxylamino compound.

Table I. Reactions of 4,5-Dinitroveratrole, 1, with Various Amines[a]


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a - R = CH₃
b - R = CH₂COOCH₂CH₃
c - R = CH₂CH₂CH₂CH₃
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Exper.	Amine	Products (%)[b]
1	Methylamine	2a(36)
2	Ethyl glycinate	2b(80)
3	n-Butylamine	2c(42), 3(13)
4	Dimethylamine	3(6), 4(8)[c]
5	Triethylamine	3(6), 4(6)

[a] General conditions: 400W medium pressure Hg lamp/Pyrex filter/Water-methanol, pH 8/ 4 h. In experiment 2 acetonitrile-water was used as solvent.
[b] Isolated yields, calculated with respect to reacted 1.
[c] Complex mixture of reduction (major) and substitution products.

When this experiment was repeated in the presence of benzophenone (triplet sensitizer), the ratio substitution/reduction products showed no variation.

Experiment 4, using dimethylamine as nucleophile, led to a complex mixture from which 3 and 4,5-dimethoxy-2-nitroaniline, 4, could be isolated in low yields. Experiment 5, with triethylamine gave similar results. The reaction mixture of experiment 4 was studied by CG/MS and the following products were tentatively identified, on the basis of molecular ions and fragmentations, in addition to the isolated ones (3 and 4): 2,4(or 2,5)-diamino-5(or 4)-nitroanisole, 4,5-dinitro-2--methoxyaniline, 5,6-dimethoxybenzofuroxane, 5-dimethylamino-6-methoxybenzofurazane, N,N-dimethyl--4,5-dinitro-2-methoxyaniline, N-methyl-4,5-dinitro-2-methoxyaniline. Considering these results it becomes clear that the complexity of experiments 4 and 5 compared with experiments 1, 2 and 3 is mainly due to competitive photoreduction processes. There are examples [12,17] of nitro group photoreductions carried out in isopropanol and isopropanol/HCl. When 1 was treated under these condi-

tions without added amine, no photoreduction products were detected, thus demonstrating the role of
the amines.

  Photoreductions of aromatic dinitrocompounds. In Scheme I, the results of the photoreduction of
several aromatic dinitrocompounds in the presence of triethylamine are summarized. After some ex-
perimentation with o-dinitrobenzene as a substrate, we found that for this particular case, the
presence of a photosensitizer (benzophenone), was absolutely necessary, no reaction being observed
in its absence even using quartz vessels. Therefore, we decided to use it in all the studied photo-
reductions. Isopropanol was chosen as a solvent due to the fact that the two proposed mechanisms
for photoreductions of nitroaromatic compounds,[12,17] (see scheme III in the discussion) in the pre-
sence and in the absence of good electron donors, involve hydrogen atom transfer from the solvent,
and this process is much easier from isopropanol than from methanol-water. The photoreductions of
o-, m- and p-dinitrobenzenes (5, 7 and 9) gave reasonable isolated yields of the corresponding ni-
troanilines (6, 8 and 10). Moreover, analyses of the reaction mixtures by GC/MS showed only the
presence of nitroanilines as identifiable products. Certain amounts of tars were also produced,
indicating that optimization of the reaction times might lead to improved yields. Experiment 9
(Scheme I) with 1-choro-2,4-dinitrobenzene, 11, led to the isolation, in 18% yield of the monore-
duction product, 4-chloro-3-nitroaniline, 12. A GC/MS analysis of the reaction mixture showed the
presence of another product with M^+ at m/e 172, to which the isomeric structure 2-chloro-5-nitro-
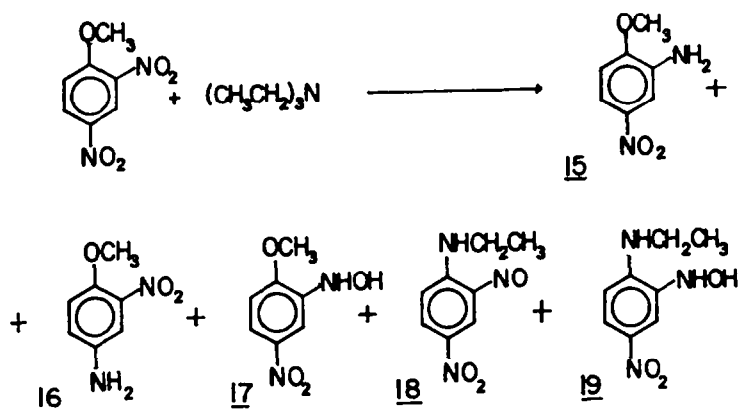aniline, 13, was assigned.
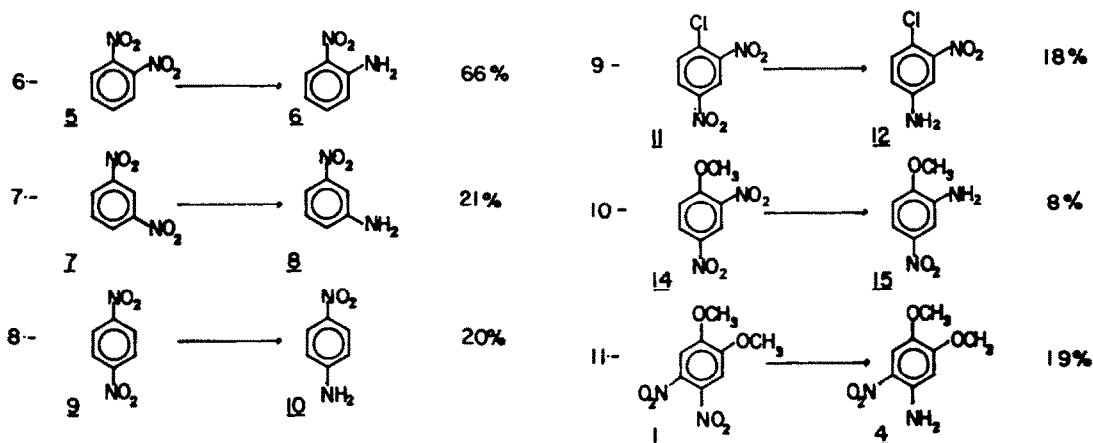
General conditions: Isopropanol/Benzophenone/Triethylamine/4ooW medium
pressure Hg lamp/Pyrex filter.

SCHEME I

  Experiment 10 with 2,4-dinitroanisole, 14, gave an 8% yield of 2-methoxy-5-nitroaniline, 15, as
the only isolatable product. The GC/MS analysis of the mixture showed it to be very complex, se-
veral chomatographic peaks being attributable, on the basis of molecular ions and fragmentations,
to 4-methoxy-3-nitroaniline (m/e 168), 16, N-hydroxy-2(or 4)-methoxy-5(or 3)-nitroaniline (m/e
184), 17, N-ethyl-4(or 2)-nitro-2(or 4)nitrosoaniline (m/e 193), 18, and N-ethyl-2(or 4)-hydroxyl-
amino-4(or 2)-nitroaniline (m/e 195), 19. Partial photoreduction and fragmentation[11] are respon-
sible for the appearence of products 17-19 (Scheme II).

  Finally, the corresponding photoreaction with 4,5-dinitroveratrole (Exp. 11, scheme I), led to
the isolation of 4,5-dimethoxy-2-nitroaniline, 4,in a 19% yield. The GC/MS analysis of the reac-
tion mixture showed the presence of another major product, tentatively identified as 2,4-diamino-5-
-nitroanisole or its isomer 2,5-diamino-4-nitroanisole (m/e 183).

  When the described experiments were repeated in the absence of irradiation, only starting mate-
rials were recovered .

General conditions: Isopropanol/Benzophenone/Triethylamine/4ooW medium
pressure Hg lamp/Pyrex filter.

SCHEME II

CALCULATIONS

The calculations presented in this work were carried out using the semiempirical MINDO/3 method[24], implemented in the MOPAC[25] program. The open shell systems were treated by means of the spin unrestricted Hartree-Fock (UHF)[26] version, HMINDO/3,[27] which uses the component with the largest value of M_s to represent each state ($M_s = 1$ and $M_s = \frac{1}{2}$ components were chosen to describe the triplet and doublet states, respectively). The ground state geometries were optimized, and the calculations of the triplet states and radical anions were performed in this initial study, keeping the geometries obtained for the corresponding ground states invariant.

Calculation results. Considering the experimental results reported in this paper, we chose three aromatic nitrocompounds with different electronic features to carry out some related theoretical calculations. The structures were o-dinitrobenzene, 5, 4,5-dinitroguaiacol, 21, as a model for 1, and o-nitroaniline, 6. Nucleophilic aromatic photosubstitutions generally go through the triplet excited state[2]. and this seems to be the situation in our reactions (experiment 3 in the presence and in the absence of benzophenone). Photoreductions of aromatic mononitrocompounds, in water-methanol and in water-acetonitrile in the presence of electron donors, are reported to take place via the triplet excited state to a radical anion and finally to reduction products.[17,22] Benzophenone was needed for experiment 6 to occur. Therefore we decided to calculate the ground and the first triplet states as well as the radical anions of 5, 21 and 6. As far as we know, no triplet excited state calculations are reported in the literature for compounds of this type except in a work by Jug on monosubstituted benzenes.[28]

In Table II the calculated frontier orbital energies are summarized. Due to spin polarization, the energies of the α-orbitals are different from those corresponding to β-orbitals in open shell systems like those of triplet and radical anions. Therefore, in these cases the given energies correspond to α-HOMO and β-LUMO spin orbitals that can bear only one electron. By contrast, for the ground states (closed shell singlets) the α and β spin orbitals are paired degenerated and their definitions are classical for HOMO and LUMO. For a better understanding, the frontier and some near to frontier spin orbital energies involved in the changes from ground states to triplet states and to radical anions are depicted in Figure 1 and listed in Table II. As expected, the frontier spin orbital energies generally increase with the electron density in the ring and therefore in the direction 5 to 21 to 6. Also of interest are the large energetic differences between the frontier spin orbitals of the triplet excited states and the corresponding radical anions. In the radical anions the unstabilization of the α-HOMO spin orbital is due to the interelectronic

Table II. Frontier Orbital Energies (eV) for Nitrocompounds 5, 21 and 6

	5		21		6	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
Ground state	-10.588	-1.145	-9.515	-1.069	-8.607	-0.130
Triplet	-8.308[a]	-3.296[b]	-7.821[a]	-2.686[b]	-6.691[a]	-1.589[b]
Radical anion	-2.335[a]	+4.320[b]	-2.354[a]	+4.028[b]	-1.580[a]	+5.433[b]

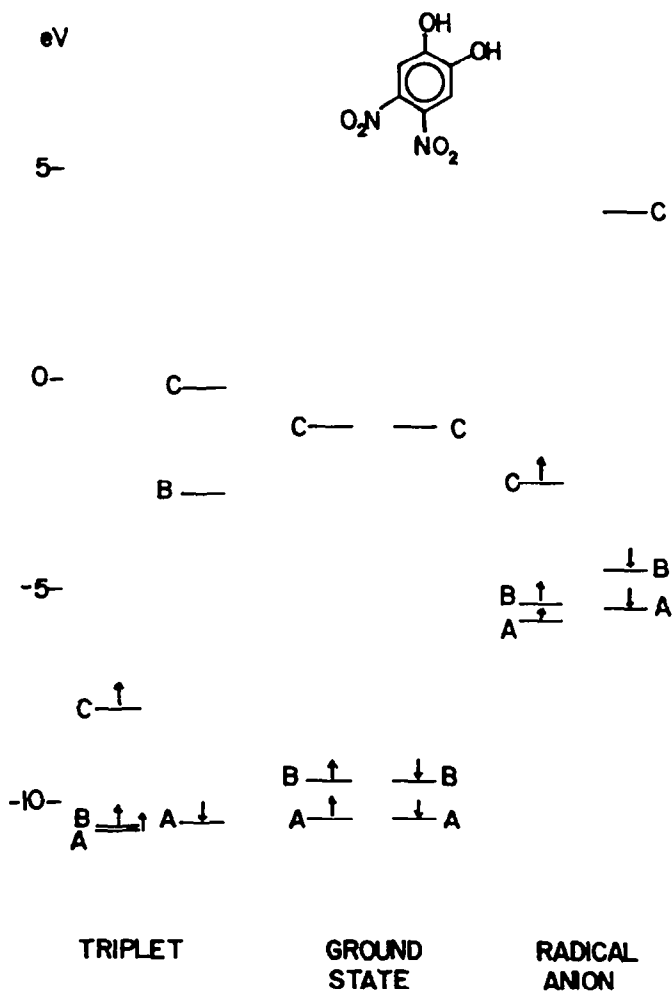[a] α-HOMO energy;   [b] β-LUMO energy.

Figure 1.- Energies of the spin orbitals involved in the changes from ground state to the triplet excited state and to the radical anion for 4,5-dinitroguaiacol. the descriptorst A, B and C represent the orbital correlations between the considered species.

repulsion resulting from the presence of an extra electron, but for the β-LUMO, we are concerned with two different orbitals. The β-LUMO of the triplet correlates with the ground state HOMO, while the β-LUMO of the radical anion does so with the ground state LUMO, therefore being much more energetic. Another interesting feature is the variation of the energy gap between the frontier orbitals in the ground states ($\underline{21}$<$\underline{6}$<$\underline{5}$), suggesting that the amount of photochemical energy needed to reach the triplet state in each case will follow the same order. Finally, the relative triplet β-LUMO energies allow to predict the relative electroaffinities. In this sense, the ability of a triplet to evolve into a radical anion should increase in the direction $\underline{6}$ to $\underline{21}$ to $\underline{5}$. These results are confirmed by total energy calculations. Figure 2 shows the photochemical energy needed for the ground states to pass to the triplet states and the recovered energy when the latter incorporate an extra electron giving the radical anion. The needed energy for the transition $S_o \longrightarrow T_1$ increases in the direction $\underline{21}$ to $\underline{6}$ to $\underline{5}$, and the achieved stabilization when passing to the radical anion increases in the direction $\underline{6}$ to $\underline{21}$ to $\underline{5}$.
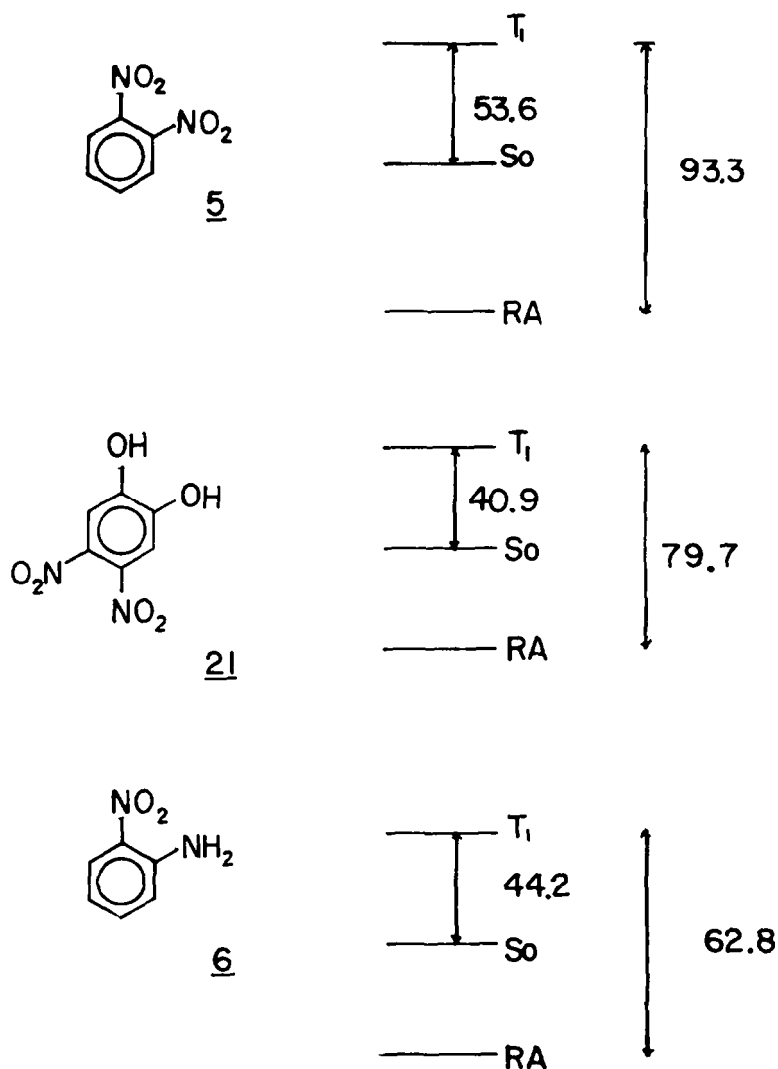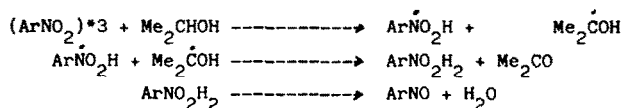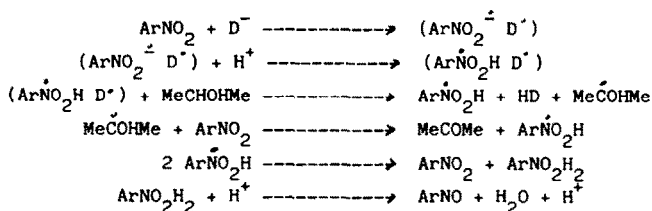

Figure 2.- Energy differences (Kcal/mol) between the ground states, triplets and radical anions for o-dinitrobenzene, $\underline{)}$; 4,5-dinitroguaiacol, $\underline{21}$; and o-nitroaniline, 6.

DISCUSSION

In Schemes III and IV the two mechanisms proposed in the literature for photoreductions of aromatic nitrocompounds, are shown. Levy and Cohen[12] propose the mechanism indicated in Scheme III for the photoreductions of nitroaromatics in isopropanol and in the absence of electron donors. On the other hand Testa and coworkers[17] have indicated that in the presence of electron donors (chloride ion) the process is iniciated by electron transfer from the donor to the nitroaromatic (Scheme IV).

$$(ArNO_2)^{*3} + Me_2CHOH \longrightarrow Ar\dot{N}O_2H + \qquad Me_2\dot{C}OH$$
$$Ar\dot{N}O_2H + Me_2\dot{C}OH \longrightarrow ArNO_2H_2 + Me_2CO$$
$$ArNO_2H_2 \longrightarrow ArNO + H_2O$$

SCHEME III

$$ArNO_2 + D^- \longrightarrow (ArNO_2^{\dot{-}} \; D^{\cdot})$$
$$(ArNO_2^{\dot{-}} \; D^{\cdot}) + H^+ \longrightarrow (Ar\dot{N}O_2H \; D^{\cdot})$$
$$(Ar\dot{N}O_2H \; D^{\cdot}) + MeCHOHMe \longrightarrow Ar\dot{N}O_2H + HD + Me\dot{C}OHMe$$
$$Me\dot{C}OHMe + ArNO_2 \longrightarrow MeCOMe + Ar\dot{N}O_2H$$
$$2 \; Ar\dot{N}O_2H \longrightarrow ArNO_2 + ArNO_2H_2$$
$$ArNO_2H_2 + H^+ \longrightarrow ArNO + H_2O + H^+$$

D: electron donor (i.e. chloride ion or amines)

SCHEME IV

In Table III the calculated frontier orbital energies for some amines are reported. The HOMO energy increases continuously from hard (ammonia) to soft (triethylamine). Considering Koopmans theorem,[29] confirmed by known experimental values,[30] the ionization potential follows a reverse order, that of the triethylamine being the smallest.

The results obtained in experiments with 4,5-dinitroveratrole, 1, and various amines (Table I) can be explained considering that a process of electron transfer from the amine to the excited state of the substrate takes place with dimethyl and triethylamine, giving rise to a radical anion which evolves mainly to reduction products, in a process with the scheme proposed by Testa (Scheme IV), being the amine the electron donor and the same amine or the methanol present the hydrogen atom donor. In Figure 3 a general mechanistic scheme for our reactions (photosubstitutions[31] and photoreductions) is shown. The threshold for electron transfer to 1 to occur seems to be in the reaction with n-butylamine.

Table III. Calculated Frontier Orbital Energies (eV) of some Amines

	NH_3[a]	H_2NCH_2COOMe[b]	$MeNH_2$[a]	$n\text{-}BuNH_2$[a]	Me_2NH[a]	Et_3N[b]
LUMO	+3.593	+1.305	+2.320	+2.082	+1.583	+0.995
HOMO	−10.071	−9.503	−9.206	−9.190	−8.578	−8.347

[a] Reference 4; [b] This work

The fact that a unique substrate gives rise to photosubstitution, or photoreduction or both, in reactions wherein the only change is the amine used, suggests the involvement of the same excited state in both reaction types. One can safely assume that this excited state is the triplet, according to our own results and to literature data. The photoreaction results depend only on the ionization potential of the amine used (electron donor). Our calculations indicate that the lowest triplet state of our substrate (4,5-dinitroguaiacol, 21) is mainly of the $n-\pi^*$ type. Reports in the literature[32] propose n-π^* triplet excited states as responsible for photoreductions of aromatic nitrocompounds and $n-\pi^*$ triplet excited states as responsible for nucleophilic aromatic photosubstitutions of nitrophenyl ethers.
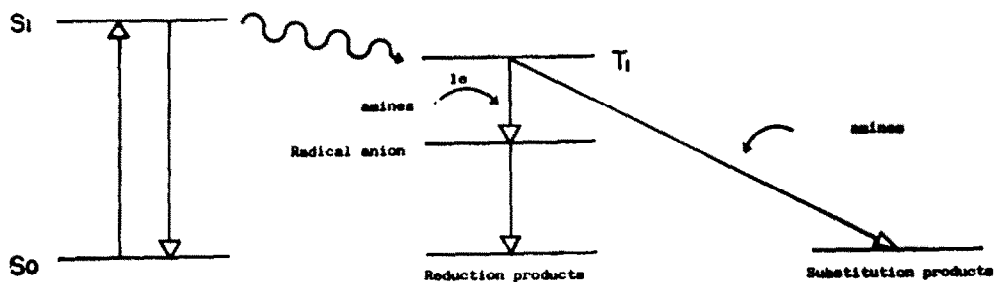

Figure 3.- Pathways for photosubstitution and photoreduction reactions. Levels are arbitrary.

Figure 2 indicates that, according to our calculations, the radical anion of 21 is 79.7 Kcal/mol more stable than the corresponding triplet excited state. However, the process including the donor amine is endothermic, since the amine is largely destabilized by giving the radical cation. The calculated ionization potential for triethylamine using Koopman's theorem[29], is 192 Kcal/mol. Therefore, the overall process of electron transfer from triethylamine to our substrate is endothermic by about 112 Kcal/mol. All the calculations refer to the gas phase. Therefore, this value should be considered as the minimum energy provided by solvation of the ion-radical pair for photoreduction to occur. A similar calculation places the corresponding threshold value in the case of n-butylamine at 132 Kcal/mol. Therefore, the real ion-radical pair solvation energy for the solvent mixture used in our photoreactions should be around or slightly higher than this value.

Considering the photoreductions of several dinitrocompounds (Scheme I), it is remarkable that when the aromatic nucleus is electronically poor enough (electroaffinity of the triplet excited state high enough (See Table II), and bears no good leaving group (from the aromatic photosubstitution viewpoint), the reactions are very clean giving monoreduction products. A mechanism initiated by hydrogen atom transfer has been proposed[12,23] (Scheme III) for photoreductions of nitroaromatics in isopropanol. However, in our cases the reactions are greatly accelerated in the presence of triethylamine (in its absence the photoreduction of 4,5-dinitroveratrole in isopropanol does not occur at a measurable rate). These facts suggest that the process is initiated by electron transfer from the amine to the excited state of the substrate (Scheme IV), as it has been proposed above for the photoreductions of 4,5-dinitroveratrole in methanol-water. A consideration of the frontier orbital (Table II) and excited state energies (Figure 2) of the starting material (i.e. o-dinitrobenzene, 5) and final product (i.e. o-nitroaniline, 6) shows clearly that the latter has a very reduced tendency to give the radical anion intermediate. Since the stabilization achieved by the conversion of the triplet into the radical anion is 30 Kcal/mol less than in the case of the starting material, it is understandable that the reaction stops at the nitroaniline stage.

EXPERIMENTAL

All melting points are uncorrected. ^{1}H NMR and ^{13}C NMR were recorded at 80 and 20 MHz on a Brucker WP80SY spectrometer using TMS as internal standard. IR Spectra were recorded on a Perkin-Elmer 1310 spectrophotometer. Mass spectra were recorded on a Hewlett-Packard 5985B mass spectro-

meter. The GC/MS analyses were performed using a 12 m capillary column OU-101. Veratrole, o-, m- and p-dinitrobenzenes, 5, 7 and 9, 1-chloro-2,4-dinitrobenzene, 11, and 2,4-dinitroanisole, 14, were commercially available. Irradiations were carried out in an immersion well photochemical reactor using 400W medium pressure Hg lamps.

4,5-Dinitroveratrole (1). A solution of 9.66 g (0.07 mol) of veratrole in 9.5 ml of acetic acid was added dropwise under stirring into 26.6 ml of fuming nitric acid (0.63 mol). During the addition (10 min) the temperature of the mixture was controlled (cold water) to mantain smooth reaction. The mixture was left under stirring at room temperature for 0.5 h. Finally, it was poured into 500 ml of ice-water. The formed precipitate was filtered to afford 15 g (90%) of 1, mp (from ethanol) 128-130°C (lit.^{33} mp 128-130°C); IR(KBr) 1515, 1350 cm^{-1}; ^{1}H NMR(CDCl$_3$) 4.0(s,6), 7.3(s,2); ^{13}C NMR(acetone-d$_6$) 57.3, 108.1, 137.1, 153.1; mass spectrum m/e 229(M+1,11),228(M,7),- 140(21), 136(42),93(45),69(32),50(24).

Photoreaction between 1 and methylamine (Experiment 1, Table I). A mixture of 291 mg (1.27 mmole) of 1, 63 g of methylamine hydrochloride (0.93 mole), 250 ml of methanol and 300 ml of a pH 8 buffer solution (155 ml of 0.1M NaH$_2$PO$_4$ and 145 ml of 0.1M NaOH) was irradiated for 4 h in a Pyrex immersion well with a 400W medium pressure Hg lamp. The solvent was partially evaporated and the aqueous solution was basified and extracted with methylene chloride. The organic layer was dried and evaporated to afford a residue (269 mg) which was chromatographed through 40 g of acidic alumina using hexane-methylene chloride as eluent. Starting material (137 mg, 47%) was recovered. N-Methyl-4,5-dinitro-2-methoxyaniline, 2a, (56 mg, 19% yield, 36% with respect to reacted 1) was eluted next. Product 2a: mp 192-193°C; IR(KBr) 3400, 1530, 1305 cm^{-1}; ^{1}H NMR(CDCl$_3$-acetone- -d$_6$) 3.0(s,3),4.0(s,3),6.7(s,1), 7.4(s,1); ^{13}C NMR(CDCl$_3$-acetone-d$_6$) 28.9, 55.9, 101.4, 104.7, 128.4, 140.8, 144.0, 145.9; mass spectrum m/e 228(M+1,8),227(M,100), 139(24), 135(49), 120(43), 92(95), 77(24), 51(23), 50(23), 46(33), 42(28). Anal. Calcd for C$_8$H$_9$N$_3$O$_5$: C, 42.30; H, 3.94; N, 18.64. Found: C, 42.56; H, 3.92; N, 18.76.

Photoreaction between 1 and Ethyl Glycinate (Experiment 2, Table I). Same procedure as for experiment 1 using 1 (412 mg, 1.8 mmol), ethyl glycinate hydrochloride (1.68 g, 12 mmol), 150 ml of acetonitrile and 450 ml of a pH 8 buffered aqueous solution. The eluted products were: 1, 168 mg (41%), and N-ethoxycarbonylmethyl-4,5-dinitro-2-methoxyaniline, 2b, mp 134-137°C; IR(KBr) 3420, 3350, 1735, 1720, 1540, 1380, 1350 cm^{-1}; ^{1}H NMR(acetone-d$_6$) 1.2(t,3, J = 7 Hz), 4.1(s,3), 4.2(q,2, J = 7 Hz), 4.3(d,2, J = 6 Hz), 6.4(broad s,1), 7.0(s,1), 7.6(s,1); ^{13}C NMR(acetone-d$_6$) 14.2, 44.9, 57.1, 61.7, 104.1, 106.5, 130.7, 143.7, 147.6, 169.9; mass spectrum m/e 299(M,17), 226(100), 134(58).Anal. Calcd for C$_{11}$H$_{13}$N$_3$O$_7$: C, 44.15; H, 4.38; N, 14.04. Found: C, 43.91; H, 4.22; N, 14.23.

Photoreaction between 1 and n-Butylamine (Experiment 3, Table I). Same procedure as for experiment 1 using 1 (291 mg, 1.27 mmole), n-butylamine (0.70 g, 9 mmol), 350 ml of methanol and 200 ml of a pH 8 buffered solution. The eluted products were: 1, 37 mg,(13%); 5,6-dimethoxybenzo- furazane, 3, (26 mg, 13% with respect to reacted 1), mp 178-181°C; ^{1}H NMR(CDCl$_3$) 4.0(s,6), 6.9(s,2); ^{13}C NMR(CDCl$_3$) 56.4, 90.7, 146.7, 155.5; n-butyl-4,5-dinitro-2-methoxyaniline, 2c, (126 mg, 42% with respect to the reacted 1), mp 75-77°C; IR(KBr)3315, 1520, 1380, 1335 cm^{-1}; ^{1}H NMR 0.9(t,3, J = 6 Hz),1.1-1.8(m,4), 3.2(q,2, J = 6 Hz), 3.9(s,3), 4.9-5.2(broad s,1), 6.6(s,1), 7.3(s,1); ^{13}C NMR(CDCl$_3$) 13.6, 20.1, 31.0, 43.0, 56.5, 102.4, 105.4, 129.2, 141.2, 143.3, 146.1; mass spectrum m/e 270(M+1,3), 269(M,22), 226(100), 134(31). Anal. Calcd for C$_{11}$H$_{15}$N$_3$O$_5$: C, 49.07; H, 5.62; N, 15.61. Found: C, 48.92; H, 5.44; N, 15.68.

Photoreaction between 1 and dimethylamine (Experiment 4, Table I). Same procedure as for experiment 1 using 1 (500 mg, 2.19 mmole), dimethylamine (0.69 g, 15.35 mmole), 350 ml of methanol and 200 ml of a pH 8 buffered solution. The eluted products were: 1 (387 mg, 57%); 3 (15 mg, 8% with respect to reacted 1): 4,5-dimethoxy-2-nitroaniline, 4, (21 mg, 8% with respect to reacted 1) mp 169-171°C (lit.^{34} mp 171°C).

Photoreaction between 1 and Triethylamine (Experiment 5, Table I). Same procedure as for experiment 1 using 1 (291 mg, 1.27 mmole), triethylamine 0.53 g, 9 mmol), 350 ml of methanol and 200 ml of a pH 8 buffered solution. The eluted products were: 1 (39 mg, 13%); 3 (12 mg, 6% with respect to reacted 1); 4 (14 mg, 6% with respect to reacted 1).

Photoreduction of o-dinitrobenzene (Experiment 6, Scheme I). A solution of o-dinitrobenzene, 5, (213 mg, 1.27 mmole), benzophenone (23 mg, 10.13 mole) and triethylamine (0.53 g, 9 mole) in 550 ml of isopropanol was purged with argon in a quartz inmersion well and then irradiated for 4 h with a 400W medium pressure lamp. The solvent was evaporated and the residue (286 mg) was chromatographed under pressure through silica-gel using hexane-methylene chloride as eluent. 2-Nitroaniline, 6, (119 mg, 66%) was obtained, mp 67-69°C. The product was characterized by comparison with an authentic sample.

Photoreductions of m-dinitrobenzene, 7; p-dinitrobenzene, 9; 1-chloro-2,4-dinitrobenzene, 11; 2,4-dinitroanisole, 14; and 4,5-dinitroveratrole,1. (Experiments 7-11, Scheme I). In all cases the procedure was the same as described for experiment 6.
Experiment 7: 21% of 3-nitroaniline, 8, mp 114°C.
Experiment 8: 20% of 4-nitroaniline, 10, mp 147-148°C.
Experiment 9: 18% of 4-chloro-3-nitroaniline, 12, mp 103°C. In this case the irradiation time was 2 h.
Experiment 10: 27% of starting material 14, and 8% (with respect to reacted 14) of 2-methoxy-5- -nitroaniline, 15, mp 115-116°C. In this case the irradiation time was 3 h.
Experiment 11: 19% of 4,5-dimethoxy-2-nitroaniline, 4, mp 169-171°C. In this case the irradiation time was 1 h.
The products were characterized by their spectra and comparison of their melting points with the reported in standard tables.

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