

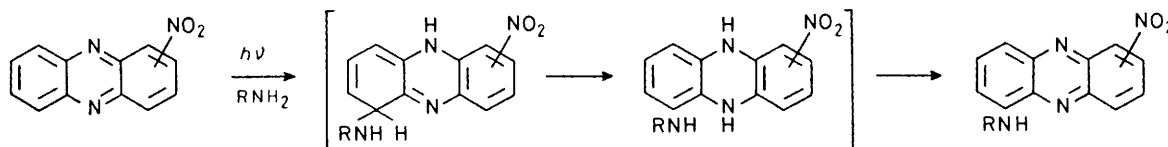
## Photochemical Reactions of Amines on Nitrophenazines. Part 2.<sup>1</sup> Photo-reduction *versus* Photosubstitution

By Angelo Albini, Gian Franco Bettinetti,\* and Giovanna Minoli, Istituto di Chimica Organica dell'Università di Pavia, V. le Taramelli 10, 27100 Pavia, Italy

The ( $n-\pi^*$ ) singlet excited state of 2-nitrophenazine reacts efficiently with amines. With tertiary amines extraction of a hydrogen atom from the  $\alpha$ -carbon of the amine takes place to yield the 2-nitrophenazinyl radical (limiting quantum yield 0.64). The reaction occurs through the intermediate formation of a non-emitting exciplex, while a ground state complex formed only at high amine concentration is unreactive. The triplet excited state is similarly reduced by triethylamine. On the other hand, primary amines do not reduce but add to the triplet excited state of 2-nitrophenazine yielding addition products which are then dehydrogenated by oxygen and/or other ground state molecules of 2-nitrophenazine to give alkylaminonitrophenazines.

PHENAZINE is known to undergo photoreduction to 5,10-dihydrophenazine with various reducers, notably tertiary amines.<sup>2</sup> Similar photoreductions have been described for several other azines. We reported recently that 1- and 2-nitrophenazine undergo different kinds of reaction in the presence of primary amines: a hydrogen atom is

efficiently than the 1-isomer, with both primary and tertiary amines. The tertiary amines were chosen because it was thought that would give a more complete picture of the interaction between nitrophenazines and amines, as they can participate in photoreduction but not photosubstitution.



SCHEME 1

substituted by the introduction of an alkylamino-group position 6 or 9 and, in the case of 2-nitrophenazine, to a lesser extent in position 4.<sup>1</sup> The smooth photosubstitution of a hydrogen atom in such mild conditions (0.1M amine in acetonitrile) was tentatively explained as addition of the amine to the heterocyclic ring to yield a 5,10-dihydro-derivative, which can then easily re-aromatize. For example, Scheme 1 shows the formation of the product substituted in position 6 by this mechanism.

This paper reports a quantitative study of the photo-reactivity of 2-nitrophenazine (NP), which reacts more

On irradiation with primary amines in acetonitrile NP reacted in the manner previously described. However, it was recovered completely unchanged after irradiation in a solution containing triethylamine in the presence of air. On exclusion of air, a blue colour ( $\lambda_{\text{max}}$ , 570 nm, Figure 1) was observed on irradiation in the presence of both primary and tertiary amines. The blue colour disappeared on admitting air. NP was recovered quantitatively in the experiments with tertiary amines, but in the experiments with primary amines a mixture of NP and substitution products was obtained.

In both cases the species responsible for the blue colour is obviously a reduction product of NP. This is also formed by irradiation in the presence of different hydrogen donors, *e.g.* alcohols, and also is the first intermediate in the catalytic hydrogenation of NP (Figure 1). Therefore, the conditions in which this species forms and is reoxidized show that it is the nitrophenazinyl radical, hereafter indicated as NPH'. Its absorbance spectrum and orange fluorescence are similar to those of the phenazinyl radical itself.<sup>3</sup> However, no e.s.r. signal was detected even at relatively high concentration, and therefore this species is mainly present as the dimer (NPH)<sub>2</sub> (Scheme 2).

The formation of the 2-nitrophenazinyl radical is also in agreement with electrochemical data, which show a distinct one-electron reduction wave for NP.<sup>4</sup> Several polynitrophenazines have also been reported to give a blue colour during their reduction.<sup>5</sup>

In order to understand the relationship between

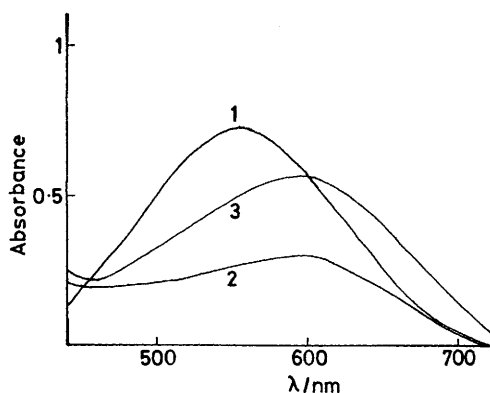


FIGURE 1 Visible spectrum of (NPH)<sub>2</sub> observed after reduction of NP by different means: 1, by irradiation of a degassed acetonitrile solution,  $2 \times 10^{-4}$ M in NP,  $10^{-1}$ M in Et<sub>3</sub>N; 2, by irradiation of a degassed ethanolic solution,  $2 \times 10^{-4}$ M in NP; 3, by catalytic hydrogenation of an ethanolic solution,  $2 \times 10^{-4}$ M in NP in the presence of Pd-C

TABLE 1

Amount of substitution products and reduction product (NPH') formed by irradiation at 366 nm of degassed solutions of 2-nitrophenazine ( $2 \times 10^{-4}\text{M}$ ) in the presence of primary amines ( $10^{-1}\text{M}$ ) in MeCN at 20 °C

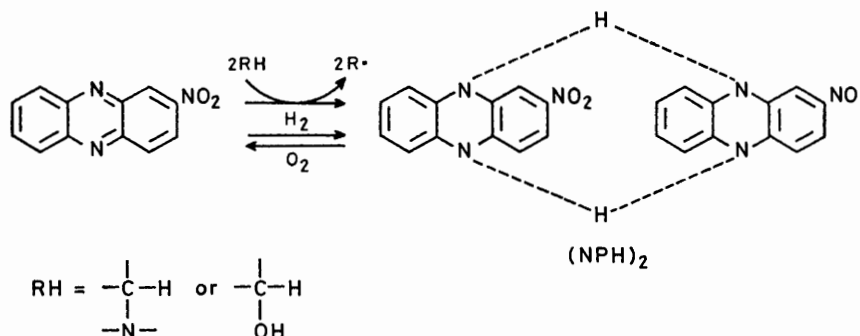
Amine	Irradiation time (min)	[NPH'] (mol %)	[Substitution products] (mol %)	$\frac{[\text{NPH}']}{[\text{Substitution products}]}$	[NP re-covered] (mol %)
Pr <sup>n</sup> NH <sub>2</sub>	0.5	28	12	2.3	86
Pr <sup>i</sup> NH <sub>2</sub>	2	54	25	2.15	75
Bu <sup>n</sup> NH <sub>2</sub>	2	14	5.5	205	92

<sup>a</sup> Sum of the yields of the three isomeric alkylaminonitrophenazines. <sup>b</sup> After reoxidation by shaking with air.

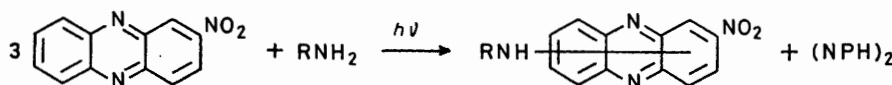
reduction and substitution in the presence of primary amines, experiments were performed in deoxygenated solutions and the yield of substitution products and

*Photoreduction.*—Data on the quantum yield of photoreduction ( $\phi_r$ ), by irradiation at *ca.* 366 nm, of degassed solutions of NP ( $2 \times 10^{-4}\text{M}$ ) in some solvents in the presence or absence of tertiary amines are collected in Table 2. With tertiary amines an efficient photoreduction, depending to some extent on the number of  $\alpha$ -hydrogen atoms in the amine is observed. The type of solvent does not seem to be very important. With triethylamine, the greatest efficiency is observed in acetonitrile, while the efficiency is somewhat lower in ethanol, owing to the competition of the alcohol, which can itself act as a photoreducer, but has a lower efficiency than the amines, as shown from the experiments in neat ethanol.

Table 3 shows the variation in  $\phi_r$  with the concentration of triethylamine in acetonitrile. It can be seen



SCHEME 2



SCHEME 3

(NPH)<sub>2</sub> and the amount of NP recovered after stirring with air were measured. The results, collected in Table 1, show that the substitution products, the formation of which implies an oxidation (see Scheme 1), were already formed before admitting air. Moreover, the yield of these products did not exceed one-third of the initial amount of NP,\* while the amount of NP which was reduced to NPH' was always double the amount which reacted to yield the substitution products. This was the case if the reaction was carried to completion or if it was quenched at partial conversion.

Therefore, with primary amines the formation of (NPH)<sub>2</sub> is due to the participation of two ground state molecules of NP as oxidants in the substitution reaction, while in the case of tertiary amines and alcohols excited NP is reduced directly by the hydrogen donor. The photochemical reactions of NP in the presence of primary and tertiary amines are therefore different and will be discussed separately in the following, in an attempt to identify the part of the mechanism which is common to both and the part which is different.

\* On the contrary, yields as high as 78% were obtained by irradiation in the presence of air.<sup>1</sup>

that  $\phi_r$  is at a maximum at  $[\text{NEt}_3] = 10^{-1}\text{M}$  and is slightly reduced at low concentration (at  $[\text{NEt}_3] = 10^{-3}\text{M}$   $\phi_r$  is *ca.* 78% of the maximum value). A more sizeable decrease is observed at high concentration. This is due to the formation of a ground state complex between NP and the amine, as shown by the change in the absorbance spectrum (Figure 2). Although this complex absorbs in the region used in the irradiation, it is not photochemically reactive, and acts as an internal filter when present in sizeable concentration (at  $[\text{NEt}_3] 0.3\text{M}$  the concentration of the complex is *ca.* 10%).

TABLE 2

Quantum yield of reduction ( $\phi_r$ ) of 2-nitrophenazine in different conditions <sup>a</sup>

Solvent	Amine	$\phi_r$
MeCN	None	$< 10^{-4}$
MeCN	Et <sub>3</sub> N	0.64
MeCN	Pr <sup>i</sup> <sub>2</sub> EtN	0.39
C <sub>6</sub> H <sub>6</sub>	None	$< 10^{-4}$
C <sub>6</sub> H <sub>6</sub>	Et <sub>3</sub> N	0.60
EtOH	None	0.03
EtOH	Et <sub>3</sub> N	0.44

<sup>a</sup> By irradiation at 366 nm of degassed solutions  $2 \times 10^{-4}\text{M}$  in NP and  $10^{-1}\text{M}$  in the amine.

Table 3 also shows the effect of 3,4-dihydro-3,3,4,4-tetramethyl-1,2-diazete 1,2-dioxide (TMDD), an efficient triplet quencher, upon the photoreduction. TMDD has only a slight effect on the photoreduction. A concentration of TMDD in the range  $10^{-1}$ – $10^{-2}$ M in a  $10^{-2}$ -NEt<sub>3</sub> solution reduces  $\phi_r$  by only 17%. However, the effect is more sizeable at a lower amine concentration, with the same NEt<sub>3</sub>:TMDD ratio. For a reactive and quenchable excited state, the relation (1) is valid.<sup>6</sup> The data

$$\phi^{-1} = a + b[\text{Am}]^{-1} + c[\text{Q}][\text{Am}]^{-1} \quad (1)$$

in Table 3 show that the increase in quenching at low amine concentration is higher than predicted by equation (1). Therefore, it must be assumed that both a non-quenchable singlet state and a quenchable triplet state react with amines. The contribution of the latter is obviously more important at low amine concentration, when the singlet state has more time to undergo intersystem crossing to the triplet state before reacting with the amine. Therefore, the minimum reactions which must be considered for the photoreduction are (2)–(11).

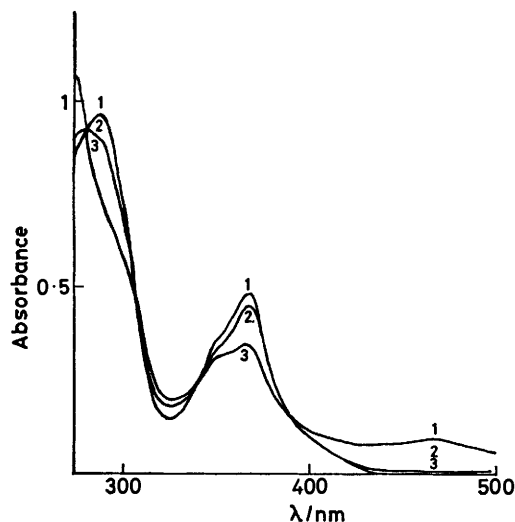
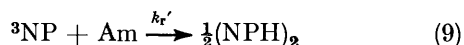
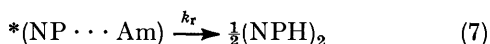
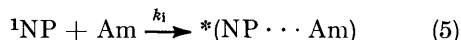


FIGURE 2 Electronic spectrum of NP in MeCN in the presence of amines: 1, no amine added; 2, [Et<sub>3</sub>N] 0.3M; 3, [Et<sub>3</sub>N] 1M. n-Propylamine produces a practically identical effect

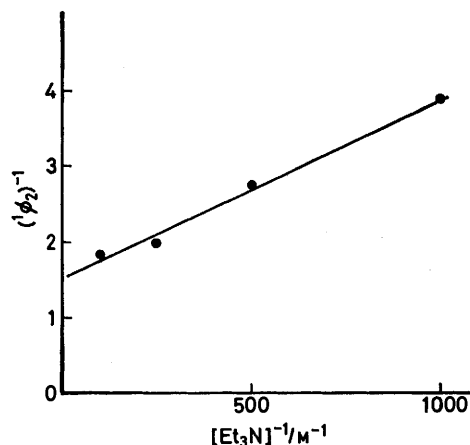


FIGURE 3 Reciprocal plot of the quantum yield of the reduction via the singlet state versus the amine concentration. See notes to Table 3. Slope 0.0023M, intercept 1.52 ( $r$  0.987)

An exciplex is formed by interaction between the amine, as electron donor, and <sup>1</sup>NP. Although it has not been detected spectroscopically, its intervention is necessary to explain why amines react much more efficiently than other hydrogen donors such as alcohols, and, additionally, why the limiting quantum yield is less than one [equations (6) and (8)].\* The exciplex can undergo either reduction or decay to the NP ground state or intersystem crossing to <sup>3</sup>NP. The intervention of the last process is indicated by the possibility of quenching part of the photoreduction even at high amine concentration (0.1M) when <sup>1</sup>NP reacts almost completely with

TABLE 3

Dependence of the quantum yield of reduction of 2-nitrophenazine on triethylamine concentration and on the presence of TMDD<sup>a</sup>

[Et <sub>3</sub> N]/M	$\phi_r$	${}^1\phi_r^b$	${}^3\phi_r^c$
$10^{-3}$	0.50	0.26	0.24
$2 \times 10^{-3}$	0.51	0.36	0.15
$4 \times 10^{-3}$	0.64	0.51	0.13
$10^{-2}$	0.64	0.53	0.11
$10^{-1}$	0.64	0.54	0.10
$3 \times 10^{-1}$	0.51		
1	0.14		

<sup>a</sup> By irradiation at 366 nm of degassed solutions (MeCN)  $2 \times 10^{-4}$ M in NP. <sup>b</sup> Quantum yield of reduction via singlet state measured in the presence of TMDD ( $10^{-2}$  and  $10^{-1}$ M). <sup>c</sup> Quantum yield of reduction via triplet state, by difference.

the amine. The photoreduction is due to three different contributions, and thus the dependence of  $\phi_r$  on [Am] is complex. In effect, while the contributions given by the exciplex [equations (5) and (7) and (5), (8), and (9)] are reduced when the amine concentration is reduced, the contribution given by <sup>3</sup>NP formed directly from <sup>1</sup>NP [equations (4) and (9)] is increased, at least within certain limits.

In the presence of a sufficient amount of TMDD the triplet reaction is completely quenched and the relation (12) is valid. Figure 3 shows that in these conditions

\* Compare with the analogous behaviour of ketones with amines.<sup>7</sup>

$(^1\phi_r)^{-1}$  is linearly dependent on  $[Am]^{-1}$  for  $Am \leq 0.1M$ . At higher amine concentrations the presence of the

$$(^1\phi_r)^{-1} = \frac{k_d' + k_r + k_c'}{k_r} \left( 1 + \frac{k_d + k_c}{k_i} [Am]^{-1} \right) \quad (12)$$

previously mentioned ground state complex must be taken into account and a reduction in  $\phi_r$  results. By extrapolating the linear part of the plot in Figure 3, the value 0.64 is obtained for  $^1\phi_r$  in pure amine, if no ground state complex were formed. The ratio between slope and intercept gives  $(k_d + k_c)/k_i = 1.5 \times 10^{-3}M$ .

As NP does not fluoresce, the simplest way of measuring  $k_i$  is unavailable. However, as in the case of the closely related molecule 2-nitrophenazine 10-oxide the fluorescence quenching was measured as taking place at a rate close to diffusion controlled, it can be assumed that for NP  $k_i$  is also very near to  $k_{diff.}$  ( $= 1.8 \times 10^{10} l mol^{-1} s^{-1}$  in acetonitrile<sup>8</sup>). The high efficiency of this reaction at low amine concentration supports the assumption, and therefore the lifetime of the singlet excited state,  $^1\tau = 1/(k_d + k_c)$ , can be assumed to be *ca.*  $3.7 \times 10^{-8} s$ .

The photoreduction of NP can be compared with other photoreductions of azines, aromatic hydrocarbons, ketones, *etc.* with amines,<sup>2b,7,9</sup> which occur by the formation of exciplexes.

Unlike most ketones, but analogously to phenazine<sup>2a</sup> and to 2-nitrophenazine 10-oxide,<sup>10</sup> NP is efficiently reduced through the singlet excited state. The lowest singlet excited state of NP corresponds to an ( $n-\pi^*$ ) transition appearing as a long tail in the electronic spectrum of NP (in the region 400–430 nm, see Figure 2). Other simple nitrogen heterocycles in which the singlet ( $n-\pi^*$ ) state was shown to be reactive include 9,10-

through the singlet (*e.g.* 2-nitrophenazine 10-oxide<sup>10</sup>) and the triplet excited state (*e.g.* fluorenone<sup>13</sup>). In the first case, it was proved that this is independent of the amine ionization potential, primary amines quenching 2-nitrophenazine 10-oxide fluorescence almost as efficiently as tertiary amines, and it is very likely that for NP  $k_i$  also depends little on the type of amine. Thus, the inefficiency of primary amines as reducers has to be

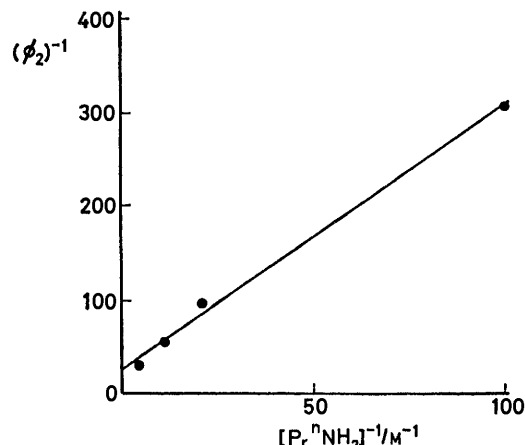
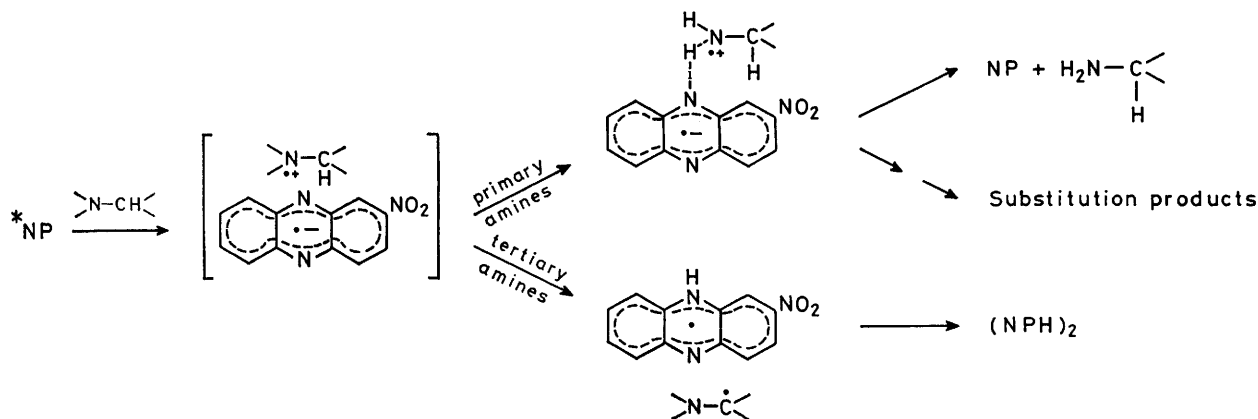


FIGURE 4 Reciprocal plot of the quantum yield of substitution versus  $Pr^aNH_2$  concentration. See notes to Table 4. Slope 2.75M, intercept 27.1 ( $r$  0.998)

ascribed to an intrinsic difficulty in the transfer of a hydrogen atom from the  $\alpha$ -carbon of the amine to NP within the exciplex or between the radical ions formed from it.

The simplest explanation is the easy and reversible formation of a hydrogen bond between the N-H of primary amines and the heterocycle which stabilizes the



SCHEME 4

diazaphenanthrene and acridine<sup>11</sup> in addition to the above mentioned phenazine.\*

It can be noted that the inefficiency of primary amines in the photoreduction observed here for NP was also observed for other photoreductions, occurring both

\* Compare with photoreduction in the presence of other hydrogen donors.<sup>12</sup>

exciplex and eventually leads to unproductive decay to the ground state, as tentatively depicted in Scheme 4.

*Photosubstitution.*—The formation of alkylaminonitrophenazines by irradiation in the presence of primary amines exhibited behaviour quite different from the photoreduction. This reaction was much less efficient

TABLE 4

Quantum yield of substitution of 2-nitrophenazine in the presence of primary amines <sup>a</sup>

Amine	Molarity	$\phi_a^b$
Pr <sup>n</sup> NH <sub>2</sub>	10 <sup>-1</sup>	0.018
Pr <sup>n</sup> NH <sub>2</sub>	10 <sup>-2</sup>	0.003
Bu <sup>t</sup> NH <sub>2</sub>	10 <sup>-1</sup>	0.01

<sup>a</sup> By irradiation at 366 nm of degassed solutions (MeCN) 2 × 10<sup>-4</sup>M in NP. <sup>b</sup> Sum of the three isomeric alkylamino-nitrophenazines.

and, unlike the photoreduction, strongly dependent on the amine concentration (Figure 4 and Table 4) and strongly quenched by TMDD (Figure 5). The quantum yield of photosubstitution was halved in the presence of a concentration of TMDD twenty times lower than the amine concentration. This value is close to that

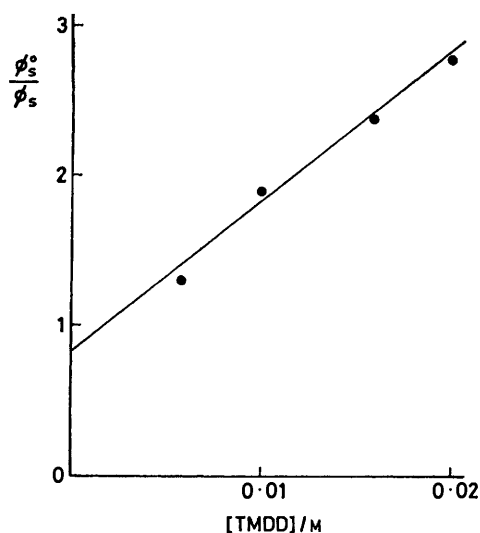
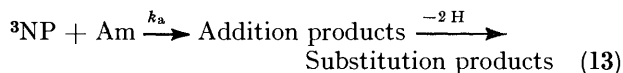


FIGURE 5 Dependence of the quantum yield of substitution on TMDD concentration. Irradiation at 366 nm of degassed acetonitrile solutions, 2 × 10<sup>-4</sup>M in NP, 2 × 10<sup>-1</sup>M in Pr<sup>n</sup>NH<sub>2</sub>. Slope 101M<sup>-1</sup>, intercept 0.79 ( $r$  0.989)

measured for the quenching of the reaction of the triplet excited state of ketones with amines.<sup>14</sup> <sup>3</sup>NP is thus the state implied in the reaction with primary amines, which, as previously shown, consists of a photoaddition followed by a ground state oxidation. Equations (13) and (14)



take into account the productive and non-productive reaction of the triplet excited state with amines. Neglecting the formation of the ground state complex, which is important only at concentrations higher than those used in these experiments, expression (15) for the quantum yield of the photosubstitution is obtained. This is identical with the yield of the initial addition products, as the end products are formed quantitatively from the adducts; <sup>3</sup> $\phi$  is the total quantum yield for the formation of the triplet excited state.

This reaction only takes place at a significant rate at a relatively high amine concentration ( $\geq 0.01\text{M}$ ). Therefore, the effect of amine concentration could be explored

$$\begin{aligned} \phi_s &= \phi_a \\ &= \frac{k_a[\text{Am}]}{(k_c + k_d + k_i[\text{Am}])\{k_d'' + (k_a + k_d''')[\text{Am}]\}} \\ &\quad \left( k_c + \frac{k_c'k_i[\text{Am}]}{k_c' + k_d' + k_r} \right) \\ &= {}^3\phi \frac{k_a[\text{Am}]}{k_d'' + (k_a + k_d''')[\text{Am}]} \quad (15) \end{aligned}$$

within a rather limited range. Figure 4 shows that under these conditions  $\phi_s^{-1}$  is linearly dependent on  $[\text{Am}]^{-1}$ . Equation (15) shows that <sup>3</sup> $\phi$  is therefore substantially constant within this range. This could be predicted since <sup>3</sup> $\phi$  has been previously shown to be constant within this range of amine concentrations in the case of the reaction with triethylamine, which in the primary step behaves identically, except for the reducing power.

In the presence of TMDD the quenching of the triplet state must be taken into account. The substitution quantum yield is then given by equation (16) where

$$\frac{\phi_s^0}{\phi_s} = 1 + \frac{k_q[\text{Q}]}{k_d'' + (k_a + k_d''')[\text{Am}]} \quad (16)$$

$\phi_s^0$  is the quantum yield in the absence of TMDD. Figure 5 shows the experimental verification of equation (16). From Figure 4,  $k_i''/(k_d'' + k_c) = 0.1\text{M}$  is evaluated, showing that the interaction with the amine is slow compared to the lifetime of the triplet state.

**Conclusions.**—The ( $n-\pi^*$ ) singlet excited state reacts efficiently with amines. With tertiary amines, extraction of a hydrogen atom from the  $\alpha$ -carbon of the amine follows to yield the reduction product (NPH)<sub>2</sub>. The comparison between the photoreduction of NP and the parent molecule phenazine, which both occur through the ( $n-\pi^*$ ) singlet state, shows that the limiting quantum yield are close to each other. In the case of NP, however, the ratio  $k_i/(k_d + k_c)$  is higher. As neither molecule fluoresces, it has not been established whether this can be ascribed to a longer lifetime or higher reactivity of NP. The triplet excited state of NP is analogously reduced by triethylamine. The alkylaminonitrophenazines which are formed through addition of primary amines to the triplet state of NP and following dehydrogenation by oxygen and/or ground state NP, can be obtained in high chemical yield, despite the low quantum yield of the first step of the reaction, because primary amines, in contrast to tertiary amines, do not reduce either the triplet or the singlet state of NP.

#### EXPERIMENTAL

**Materials.**—Triethylamine and methyl-di-isopropylamine were fractionated in the presence of naphthyl isocyanate. Commercial (Merck and C. Erba) spectroscopic grade solvents were used after distillation. All other materials were purified as previously described.<sup>1</sup>

*Apparatus.*—U.v. and visible spectra were recorded on a Perkin-Elmer 200 spectrophotometer, fluorescence spectra on an Aminco-Bowman SPF spectrofluorimeter, and e.s.r. spectra on a Varian 4500 X band spectrometer (courtesy of Professor A. Fautitano, Pavia).

*Quantum Yield Determinations.*—Samples were prepared immediately before use by mixing the appropriate amounts of solutions of NP and of the desired amine. 3,4-Dihydro-3,3,4,4-tetramethyl-1,2-diazete 1,2-dioxide<sup>15</sup> was added in reaction quenching experiments. Aliquots (3 ml) were transferred into Pyrex tubes (10 mm i.d.) and degassed using four freeze-pump-thaw cycles and sealed off. The samples were irradiated on an optical bench by a super high pressure mercury lamp (Osram HBO 200W/2). The 366 nm region of the arc was isolated by using a combination Spinder and Hoyer glass filter ( $\lambda_{\text{max}}$  368 nm,  $\Delta\lambda$  38 nm). The reaction was quenched at ca. 10% conversion except for the total conversion experiments referred in Table 1. The amount of (NPH)<sub>2</sub> formed was determined measuring the absorbance at 570 nm.\* To determine the amount of substitution products formed, the irradiated samples were evaporated at reduced pressure at room temperature. Some toluene was added in order to avoid an increase in the amine concentration during evaporation of the solvent. The photoproducts were separated by means of column chromatography on 0.5 cm i.d. columns filled with silica gel (2 g; Merck 70—325 mesh) with cyclohexane-ethyl acetate (95:5) as eluant. Their amount was determined by absorbance measurements. The light intensity was monitored by ferrioxalate actinometry.<sup>16</sup> It was ascertained that no thermal reactions took place in these experimental conditions. Reaction quenching experiments were always run in parallel with experiments without quencher.

\* The spectrum after irradiation in the presence of triethylamine shows complete conversion into (NPH)<sub>2</sub>. Therefore the absorptivity of (NPH)<sub>2</sub> can be evaluated ( $\epsilon_{570}$   $1.44 \times 10^4$  l mol<sup>-1</sup> cm<sup>-1</sup>).

Financial support by Consiglio Nazionale delle Ricerche (Rome) and Alexander-von-Humboldt Stiftung (Bonn) is gratefully acknowledged.

[8/1717 Received, 29th September, 1978]

#### REFERENCES

- <sup>1</sup> Part I, A. Albini, G. F. Bettinetti, E. Fasani, and G. Minoli, *J.C.S. Perkin I*, 1978, 299.
- <sup>2</sup> (a) G. A. Davis, J. D. Gresser, and P. A. Carapellucci, *J. Amer. Chem. Soc.*, 1971, **93**, 2179; (b) D. G. Whitten, 'Photo-reduction and Photoaddition Reactions of Heterocyclic Compounds,' in 'Photochemistry of Heterocyclic Compounds,' ed. O. Buchardt, Wiley-Interscience, New York, 1976, p. 534.
- <sup>3</sup> W. Rubaszewka and Z. B. Grabowski, *J.C.S. Perkin II*, 1975, 417.
- <sup>4</sup> (a) Y. S. Rozum, S. B. Serebryanyi, E. F. Karabou, V. P. Chernetskii, and M. J. Dronkina, *Zhur. obshchei. Khim.*, 1964, **34**, 2599; (b) L. L. Gordienko, *Elektrokhimiya*, 1965, **1**, 1497.
- <sup>5</sup> (a) F. Kehrman and J. Riera y Punti, *Ber.*, 1911, **44**, 2622; (b) G. A. Swan and D. G. I. Felton, 'Phenazines,' ed. A. Weissberger, Interscience, New York, 1957, p. 42.
- <sup>6</sup> E. Havinga and J. Cornelisse, *Pure Appl. Chem.*, 1976, **47**, 1.
- <sup>7</sup> S. G. Cohen, A. Parola, and G. H. Parsons, *Chem. Rev.*, 1973, **73**, 141.
- <sup>8</sup> H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, 1960, **14**, 48.
- <sup>9</sup> (a) J. A. Barltrop, *Pure Appl. Chem.*, 1973, **33**, 179; (b) P. J. Wagner, *Topics Curr. Chem.*, 1977, **66**, 1.
- <sup>10</sup> S. Pietra, G. F. Bettinetti, A. Albini, E. Fasani, and R. Oberti, *J.C.S. Perkin II*, 1978, 185.
- <sup>11</sup> (a) D. G. Whitten and Y. J. Lee, *J. Amer. Chem. Soc.*, 1971, **93**, 961; (b) G. A. Davis and S. G. Cohen, *Chem. Comm.*, 1971, 675.
- <sup>12</sup> A. Castellano, J. P. Cateau, and A. Lablanche-Combier, *Tetrahedron*, 1975, **31**, 2255 and references cited therein.
- <sup>13</sup> G. A. Davis, P. A. Carapellucci, K. Szoc, and J. D. Gresser, *J. Amer. Chem. Soc.*, 1971, **91**, 2264.
- <sup>14</sup> A. M. Parola, A. W. Rose, and S. G. Cohen, *J. Amer. Chem. Soc.*, 1975, **97**, 6202.
- <sup>15</sup> E. Ullman and P. Singh, *J. Amer. Chem. Soc.*, 1971, **94**, 5077.
- <sup>16</sup> L. C. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A253**, 318.