Reactions of Nitroanisoles. Part 2.[1] Reactions of 2,4- and 2,6-Dinitroanisole with Piperidines in Benzene

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The reactions of 2,4- (I) and 2,6-dinitroanisole (VIII) with piperidine (II) and *N*-methylpiperidine (NMP) in benzene have been studied. It was found that (I) and (VIII) react with (II) to give not only the expected aromatic nucleophilic substitution (a.n.s.) products, but also the corresponding dinitrophenols, generated by an S_N2 reaction. The rate for each reaction and the overall rates were measured and it was observed that compound (I) has similar rate coefficients for the a.n.s. as well as for the S_N2 reaction. Mild acceleration by base was found for the a.n.s. reaction. When (VIII) reacts with (II) the rate of reaction to form 2,6-dinitrophenol is greater than the rate for the a.n.s. In the reaction with NMP only an S_N2 reaction was observed. Furthermore, the rates of reaction of (VIII) with (II) and with NMP are *ca.* 1 000 and 300 times, respectively, the rate of reaction of (I) with these amines. A field effect is proposed for the increase in rate.

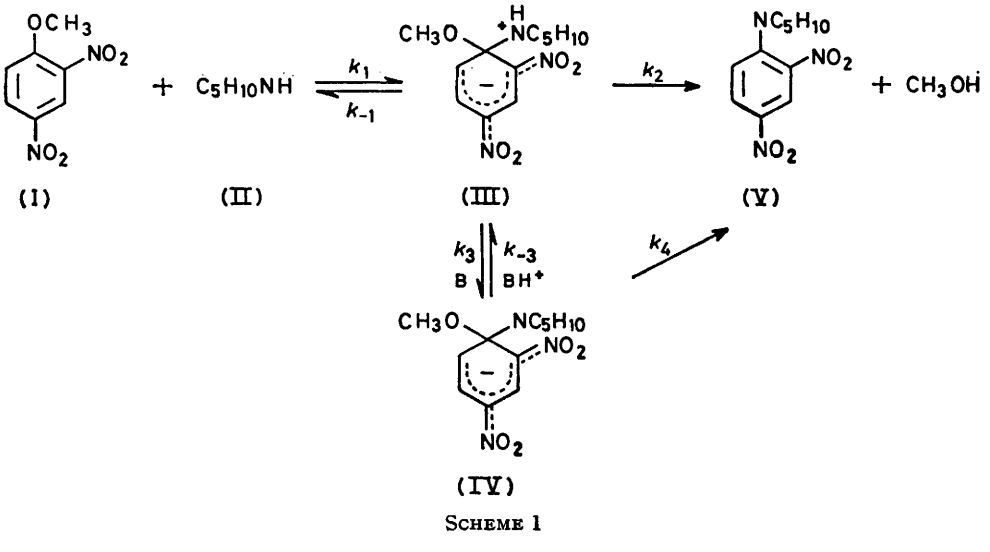
NUCLEOPHILIC displacements of the alkoxy-groups in alkyl 2,4-dinitrophenyl ethers or alkyl picrates by amines is difficult partly because of side-reactions [2] which lead to nitrophenols whose dissociation constants in the reaction media are needed to obtain reliable kinetic results. Moreover, alkoxy-groups are poor nucleofuges and usually the breakdown of the intermediate is rate-determining and the reaction does not occur in a single step.[3,4]

Examination of the literature data [5] shows that an *o*-nitro-group influences the slow step in aromatic nucleophilic substitutions (a.n.s.) and investigation of this effect was carried out by comparing the rate of reaction of 2,4- (I) and 2,6-dinitroanisole (VIII) with piperidine (II) in benzene at different piperidine concentrations. Competition between the a.n.s. and aliphatic nucleophilic substitution (S_N2) was also studied by measuring the rate of each reaction as well as the overall rate of reaction using (II) and *N*-methylpiperidine (NMP) as nucleophiles. It was found that in these media the rupture of the alkyl–oxygen bond competes with the rupture of the aryl–oxygen bond, and in some cases the rate of the S_N2 reaction is higher than the rate of the a.n.s.

RESULTS AND DISCUSSION

Reaction of 2,4-*Dinitroanisole with Piperidine.*—Early work [6] on the reaction of nitroanisoles in neat piperidine reported that the reactions proceed to give the expected substitution products in quantitative amounts and can be described by the generally accepted two-step mechanism depicted in Scheme 1, in which base-catalysed decomposition of the σ-zwitterionic intermediate is also reckoned to take place, since, as alkoxy-groups are poor nucleofuges, the second step is expected to be rate determining.

Our preliminary work showed, however, that the reaction in benzene was not so simple. 2,4-Dinitrophenol (VI) was also formed and then underwent partial dissociation in the basic reaction medium to give 2,4-dinitrophenoxide (VII) (see Experimental section). A similar equilibrium between (II) and methanol was found to affect the rate of a.n.s.[7] Both reactions can be

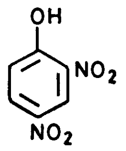


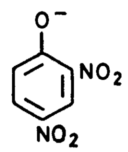
SCHEME 1

described by equation (1) where k_5 represents the overall a.n.s. reaction rate.

$$\text{(I)} + \text{(II)} \begin{cases} \xrightarrow{k_5} \text{(V)} + CH_3OH & \text{(1a)} \\ \xrightarrow[k_6]{} \text{(VI)} + C_5H_{10}NCH_3 & \text{(1b)} \end{cases}$$

Reaction (1) was studied previously in methanol[8] and step (1a) was found to be reversible. To find out if it is also reversible in benzene, the reaction of (V) with


(VI)


(VII)

methanol was studied, and found to be irreversible under the reaction conditions. Analogous results were found for reaction (1b), although it was observed that (VI) reacts with (II) or with NMP to produce (V) when they are mixed in equimolar amounts.

Bunnett and Garst[8] also found that when reaction (1) was performed in methanol, step (1a) was catalysed by methoxide ion, but in that medium they could not determine if the reaction was also catalysed by piperidine, since when the amine concentration was increased more methoxide ion was generated. It seemed, therefore, of interest to determine if amine catalysis could be observed in our conditions. Table 1 shows that k_6 remains almost invariant with increasing piperidine concentration, while k_5 increases more rapidly. Linear regression analysis of the data in Table 1 shows a linear dependence of k_5 on the piperidine concentration. As can be calculated from the data in Table 1, k_b/k_0 ranges from 20 (60°) to 10 (80°). Because of its magnitude (<50) and the mathematical form of the dependence, it is likely that this effect cannot be interpreted as base catalysis but as a case of mild acceleration.

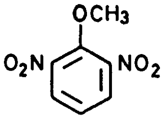
TABLE 1

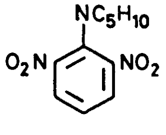
Kinetics of the reaction of 2,4-dinitroanisole with piperidine in benzene[a,b]

	60°		70°		80°	
[(II)]/M	k_5	k_6	k_5	k_6	k_5	k_6
0.0706	1.65	0.68	2.46	1.74	4.72	3.69
0.110	2.19	0.65	3.24	1.66	5.33	4.26
0.211	3.87	0.58	5.34	1.46	8.25	3.67
0.296	4.91	0.71	7.56	1.72	11.1	3.65

[a] $10^6\,k$/l mol^{-1} s^{-1}; [(I)] *ca.* 1×10^{-4}M. Standard deviation of k_T <4%, k_5 <10%, k_6 <20%. The activation parameters calculated at 25° are $\Delta H_5^{\ddagger}$ *ca.* 10 ± 2 kcal mol^{-1}; $-\Delta S_5^{\ddagger}$ *ca.* 55 ± 5 cal K^{-1} mol^{-1}; $\Delta H_6^{\ddagger}$ *ca,* 21 ± 3 kcal mol^{-1}; $-\Delta S_6^{\ddagger}$ *ca.* 26 ± 8 cal K^{-1} mol^{-1}; the errors were calculated from the experimental errors in the k values. [b] The dependence of k_5 with [(II)] follows the equation $k_5 = k_0 + k_b$ [(II)].

Reaction of 2,6-Dinitroanisole with Piperidine.—The rate of reaction of 2,6-dinitroanisole (VIII) with piperidine in benzene was also measured at two different concentrations of nucleophile, the products being *N*-(2,6-dinitrophenyl)piperidine (IX), 2,6-dinitrophenol (X), and 2,6-dinitrophenoxide (XI). The second-order rate coefficients for the formation of (IX), k_9, and of (X), k_{10}, are given in Table 2. The smaller rate for the a.n.s. compared with the rate of the demethylation reaction is unexpected on the basis of the results obtained for the reaction of (I). Although the error in the value of k_9 is higher than in k_{10}, it can be concluded for the runs at [(II)] 0.20 and 0.30M that the reaction is not susceptible to base catalysis. This indicates that the tetrahedral intermediate progresses to products faster than it reverts to reactants.[9]


(VIII)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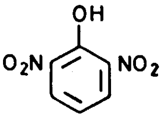
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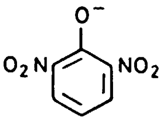

(XI)

When the data for (VIII) are compared with those for (I) a striking feature is evident which is the greater reactivity of (VIII). For the same reaction conditions {[(II)] 0.2M; 60°}, the a.n.s. is more than ten times faster for (VIII), while the S_N2 rate of reaction of (VIII) is 1 000 times the rate of (I). The greater reactivity of (VIII) for the a.n.s. is surprising since electronic effects are similar for the 6- and 4-nitro-groups, while steric requirements are expected to be greater for (VIII). INDO Molecular orbital[10] calculations of several structures for both compounds give a total energy of −162.924 80 for (I) and −162.924 25 a.u. for (VIII)[11] for the minimum energy structures. Although the greater energy favours the higher reactivity of (VIII), the magnitude of the energy difference is not enough to account for the observed increase in rate.

TABLE 2

Kinetics of the reaction of 2,6-dinitroanisole with piperidine in benzene[a]

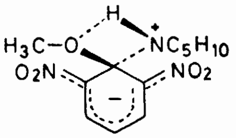
	10^5k_9/l mol^{-1} s^{-1}		10^5k_{10}/l mol^{-1} s^{-1}	
T/°C	[(II)] 0.20M	[(II)] 0.30M	[(II)] 0.20M	[(II)] 0.30M
25	1.9	2.7	7.89	11.0
35	1.5	2.8	13.2	16.9
45	2.5	3.0	25.2	30.6
60	4.0	3.5	67.9	64.1

[a] [(VIII)] *ca.* 1.7×10^{-4}M; Standard deviation of k_9 and k_{10} see Experimental section; $\Delta H_{10}^{\ddagger}$ *ca.* 12 ± 1 kcal mol^{-1}; $-\Delta S_{10}^{\ddagger}$ *ca.* 39 ± 3 cal K^{-1} mol^{-1}, calculated at 25 °C.

As has been discussed previously by one of us[12] classical *ortho*-effects can only increase the rate of step (1) (depending on the nature of the substituent) by increasing the inductive effects and decreasing the resonance effect of the substituent when it is attached to the *ortho*- instead of the *para*-position. Nevertheless, for the case of the nitro-group, the increased inductive effect in the 6-position cannot be the cause of the increased reactivity since, when chlorine is the nucleofuge the rate of reaction for 2,6- is smaller than for 2,4-dinitro-1-chlorobenzene with piperidine.[12]

Therefore, the cause of the increased reactivity should be located in the decomposition of the intermediate complex. Three kinds of steric effects can operate on this step. The first is steric compression in the intermediate between amine and the aromatic ring plus *ortho*-substituent (release of the steric strain enhances k_{-1} and thereby reduces k_2/k_{-1} and k_3/k_{-1}).[13] Steric hindrance by an *ortho*-substituent of the developing resonance in the product should also lead to a lowering of k_2/k_{-1} and k_3/k_{-1}.[14] A third possible steric effect could arise from release of repulsion between the amine moiety and the leaving group as the nucleofuge departs. This effect should increase k_2 and k_3 but the magnitude of the interaction is smaller than for those above. Furthermore, release of the strain should be greater for chlorine than for methoxide.[12] Consequently, although steric effects certainly play a role in discriminating between the reactivity of (I) and (VIII) they are not the only factor.

The increase in rate may be due to an increase in k_2/k_{-1}, or in k_3/k_{-1}, or in both. The mechanism for the uncatalysed step involves a transfer from an ammonium proton to the leaving group in concert with the departure of the nucleophile. When there are two *o*-nitro-groups the quaternary ammonium proton can be hydrogen-bonded to one or the other, and the proton can be assumed to be in a position equidistant from both nitro-groups. A molecular model for the zwitterionic intermediate shows that rotation from one nitro-group to the other is free in conformation (XII) which allows easy transfer of the proton to the leaving group and, thereby, considerably increases k_2. From the data in Table 2, it is evident that there is no increase in k_3/k_{-1} for (VIII). This is also consistent with the idea of a 'looser' ammonium proton in (VIII) compared with (I), and with previous findings that base catalysis is not observed when large steric effects come into play.[15,16]



(XII)

Related Reactions.—If the above proposed hypothesis is valid, it should be expected that reactions for which the second step is slow should show greater reactivity for the 2,6-dinitro-substituted benzenes that for the 2,4-isomers, when the reaction is performed in benzene, whereas the reactivities should be similar or even reversed in methanol, where a concerted decomposition of the intermediate complex is less likely. There are few data for a.n.s. on 2,6-dinitro-substituted benzenes, but a survey of reactions, most of them performed previously in our laboratory, is presented in Table 3.

TABLE 3

Reactions of 2,4- and 2,6-dinitro-X-benzenes with amines at 35 °C

	$k_{2.6}/k_{2.4}$ [a]		
Nucleophile	Benzene	Methanol	Ref.
X = F			
Cyclohexylamine	151	0.79	17
Benzylamine	104	3.34	17
Diethylamine	8.46	0.16	18
Piperidine	0.13	3×10^{-3}	18
X = OCH_3			
Cyclohexylamine	5.90		19
Piperidine	11.6		This work
X = Cl			
Cyclohexylamine	59.9	3.55	20
Benzylamine	42.3	1.28	20
Diethylamine	1.03	0.05	20
Piperidine	0.11	0.17	20
	k_{ortho}/k_{para} [b]		
X = Cl			
Piperidine	45	1.94 [c]	21
X = F			
Piperidine	200 [e]	5.24 [c,d]	22

[a] Second-order rate coefficient ratio for the reaction of 2,6-dinitro-X-benzenes *versus* 2,4-dinitro-X-benzenes. [b] Second-order rate coefficient ratio for the reaction of *o*-halogenonitrobenzenes *versus* *para*-halogenonitrobenzenes. [d] Data of ref. 23. [c] Reactions in ethanol. [e] At 25 °C.

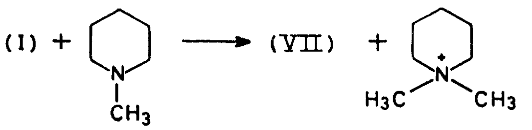
When the nucleofuge is fluorine it is frequently observed that the second step is rate-determining in benzene, and Table 3 shows that 2,6- is more reactive than 2,4-dinitro-1-fluorobenzene (except for piperidine for which 2,4-dinitro-1-fluorobenzene exhibits a large k_3). An inversion of reactivity is observed in methanol.

For the case of X = OCH_3 (Table 3), the greater a.n.s. reactivity of (VIII) compared with (I) in the reaction with piperidine has been discussed above and similar behaviour is observed for the reaction with cyclohexylamine for which only a.n.s. is observed.

When chlorine is the nucleofuge the reactivity ratios in benzene follow a trend similar to that found for **X** = F. Although a search for base catalysis has not been done for the reactions of 2,6-dinitro-1-chlorobenzenes in benzene, it can be predicted on the basis of the overall rate ratios of Table 3 and the above discussion, that an increase in k_2 is expected for the reaction in benzene of the 2,6- compared with the 2,4-dinitro-derivative, at least with primary amines, and not base catalysis is expected. As before, the reactivity ratios diminish when the reaction is performed in methanol.

By way of comparison, the rates of reaction of two mononitrohalogenobenzenes are also included: in both cases the *ortho* : *para* ratio is greater than unity in benzene. For the case of X = Cl, the dependence of the overall rate on the amine concentration was studied and a very mild acceleration by the amine was found only for *p*-chloronitrobenzene in benzene (k_3/k_2 2.4); in the other three cases $k_3/k_2 \leqslant 0.30$.[21]

The S_N2 *Reactions.*—Although the greater reactivity of (VIII) *versus* (I) for the a.n.s. is interesting, the increase in the S_N2 reaction rate is more spectacular. Therefore, it was worth studying the reaction with a nucleophile not able to produce a.n.s. but with basicity, steric requirements, and nucleophilicity similar to piperidine: *N*-methylpiperidine (NMP) was found to be suitable. The reaction occurs according to Scheme 2 and was found to be irreversible under the reaction conditions.



Scheme 2

The influence of the amine concentration on the rate of the reaction of (VIII) in benzene was studied at 60°. The concentration of (VIII) was *ca.* 1.2×10^{-3}M and of [NMP] 0.062 6, 0.095 8, and 0.156M; the values of the second-order rate coefficients, 10^4k l mol^{-1} s^{-1}, were 1.49, 1.49, and 1.47, respectively, with an error of $\pm 0.02 \times 10^{-4}$. These results show that the rate is not changed by an increase of almost thrice in the concentration of NMP. The reaction was then carried out at 70 and 80° and the results are gathered in Table 4, together with the rate of reaction of (I) with NMP at the three temperatures.

Table 4

Reaction of 2,4- and 2,6-dinitroanisole with *N*-methylpiperidine in benzene [a]

T/°C	(I)	(VIII) [b]
60	4.67 [c]	1 490
70	9.78 [c]	2 820
80	28.9 [d]	4 660
$\Delta H^‡$/kcal mol^{-1} [e]	22	14
$-\Delta S^‡$/cal k^{-1} mol^{-1} [e]	24	36

[a] 10^7 k/l mol^{-1} s^{-1}; error <2%. [b] [(VIII)] *ca.* 1.2×10^{-3}M, [NMP] 6.26×10^{-2}M. [c] [(I)] 1.52×10^{-3}M. [d] [(I)] 1.27×10^{-4}M, [NMP] 5.65×10^{-2}M. [e] Parameters calculated at 25 °C $\Delta H^‡$ accurate to ± 1.5 kcal mol^{-1}, $\Delta S^‡$ to ± 4 cal K^{-1} mol^{-1}.

By comparison of the data of Tables 1, 2, and 4 at 60° it can be concluded that piperidine is more effective than NMP in producing demethylation. This result may be due to the steric compression in the developing *NN*-dimethylpiperidinium cation, compared with the *N*-methylpiperidinium ion which is formed in the reaction with (II). This explanation is similar to the well accepted theory for the greater basicity of the secondary compared with tertiary amines.[24]

The surprisingly increased reactivity of (VIII) found for reaction with (II) is again found with NMP. It can be observed from Table 4 that the rate of (VIII) is 300 times the rates of reaction of (I). Obviously, the higher energy of the ground state of the substrate cannot be the only reason for such an increase in rate. In spite of the high activation of the substrate the S_N2 reaction is highly *endothermic*; this indicates that the transition state resembles the products.[25] The developing net charge on the oxygen should, then, play an important role, and the greater reactivity of (VIII) *versus* (I) could be due to the stabilizing field effect [26] of the second *o*-nitro-group, an effect that should be important in the incipient anionic product.[27] The field effect has recently been reckoned to be responsible for the great rate acceleration in other types of reaction.[28]

EXPERIMENTAL

Reagents and Solvents.—2,4-Dinitroanisole (I), 2,4-dinitrophenol (VI), and 2,6-dinitrophenol (X) were crystallised from methanol to constant m.p., 94.5—96, 111—112, and 62—63.5°, respectively. 2,6-Dinitroanisole (VIII) was prepared as previously described,[29] m.p. 117—118° (from methanol), and also *N*-(2,6-dinitrophenyl)piperidine,[20] m.p. 106—106.5° (from ethanol); *N*-(2,4-dinitrophenyl)-piperidine was prepared in a similar way from 2,4-dinitroanisole, m.p. 91—92° (lit.,[20] 92—92.5°). Piperidine (II) and *N*-methylpiperidine were kept over sodium wire, refluxed, and then fractionated over sodium; fractions of b.p. 106—106.5° and 106.5—107°, respectively, were used. Benzene was kept over sodium wire for several days, then distilled over sodium, and stored in a special vessel which allows delivery without air contamination.

Ancillary Spectrophotometric Measurements.—U.v. and visible spectra of the substrates and of the products of their interaction with piperidine were recorded in a Beckman DK 2A spectrophotometer. The extinction coefficients were determined in a Beckman DU 2 spectrophotometer, the solutions were found to obey Beer's law, and the spectral properties are gathered in Table 5.

Kinetic Procedures.—Most of the reactions were studied spectrophotometrically.[30] A Beckman DU 2 spectrophotometer was used with 1.00 cm silica cells. In all cases pseudo-first-order kinetics were observed. Standard solutions of (I) and (II) in benzene were prepared by mixing at room temperature and portions were put in sealed bulbs, immersed in a thermostat. Samples were taken at intervals, cooled, and the optical densities measured at 370 (A_1) and 400 nm (A_2). The dissociation constants, $\bar{K}_c$, for (VI) and (X) in the reaction media, were determined by a spectrophotometric method.[31] They were found to be p$\bar{K}_c$ 1.50, standard deviation 0.10, and p$\bar{K}_c$ 1.28, standard deviation 0.07, for (VI) and (X), respectively.[1] For all the cases $\{[(I)]_0/[B]_0\} > 700$, therefore (VI) was completely converted into (VII). Equations (2)—(4) allow determination of the actual concentrations of (I), (V), and (VII) (a computer program was written in Fortran IV to make the calculations).* The overall second-order rate coefficient,

$$A_1 = \varepsilon_{1(I)}[(I)] + \varepsilon_{1(V)}[(V)] + \varepsilon_{1(VII)}[(VII)] \quad (2)$$

$$A_2 = \varepsilon_{2(I)}[(I)] + \varepsilon_{2(V)}[(V)] + \varepsilon_{2(VII)}[(VII)] \quad (3)$$

$$[(I)]_0 = [(I)] + [(V)] + [(VII)] \quad (4)$$

k_T, for the disappearance of (I) was obtained from the slope of the linear regression analysis of ln [(I)] *versus* time, k_ψ, divided by [(II)]. The second-order rate coefficients, k_5

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* The program is available by writing to N.S.N.

TABLE 5

Spectral properties of reagents and products in benzene [a]

λ/nm	304	340	345	350	370	390	400	434	450
(I)	9 600 [b]				271		26		
(V)				10 815	14 197 [b]		9 290		
(VI)		2 850 [c]		2 652	1 265		95		
(VII)				15 200 [b]	10 387		8 032 [c]		
(VIII)	2 230 [c]		597			70		0	0
(IX)						1 724 [b]		1 045	660
(X)			4 324 [b]			925		53	
(XI)						3 083		8 112 [b]	7 092

[a] Molar extinction coefficients, l mol^{-1} cm^{-1}, spectra recorded from 280 to 500 nm; error $<2\%$. [b] Data measured at $\lambda_{max.}$. [c] Shoulder.

and k_6, were calculated from the k_T and the ratios [(V)]/[(VII)], measured at different times. Application of the more simple method for the calculation of k_T [from the slope of the linear plot of ln ($A_\infty - A$) *versus* t] [30] was not practical since the determination of the 'infinity' absorbances, A_∞, was lengthy (ten half-lives $>$ 1 year for some cases) and imprecise {solutions of [(II)] $\geqslant$ 0.1M in benzene become dark after long heating, notwithstanding the absence of side-reactions which was checked by g.l.c. analysis of the mixture at time intervals}.

Inasmuch as the various rate coefficients are calculated through equations involving several extinction coefficient values, and inasmuch as these are affected by their own error, the error in the calculated rate coefficient is greater than the regular error in the kinetic spectrophotometric method at only one wavelength.

The reaction of (VIII) with (II) was followed at λ 450 nm and k_9 and k_{10} were obtained from k_T, A_∞, $[(VIII)]_0$, and the respective extinction coefficients $\varepsilon_{(IX)}$ and $\varepsilon_{(XI)}$. The standard deviations of k_9 ranges from 5 to 60% depending on the ratio k_{10}/k_9 and the standard deviation of $k_{10} \leqslant 4\%$.

For the reaction of (I) with NMP a procedure similar to that followed for the reaction with (II) was used; formation of (VII) was recorded at 400 nm. An analogous procedure was used for the reaction of (VIII) with NMP, but the formation of (X) was measured at 345 nm by quenching samples with a solution of hydrochloric acid in ethanol (1 : 10, v/v). Since the optical density of the substrate is not zero at that wavelength a correction was introduced into the calculations.

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