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Rates and Products of Reactions of *N*-Benzoyloxy-2-nitrobenzenamine with Metal Alkoxides

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A major pathway when *N*-benzoyloxy-2-nitrobenzenamine (1b) reacts with sodium methoxide is attack on carbonyl and production of methyl benzoate. In a competing pathway, proton abstraction is followed by loss of benzoate and formation of 2,1,3-benzoxadiazole *N*-oxide (4). With the more bulky *t*-butoxide base, only the latter pathway is followed, though the heterocyclic product undergoes subsequent destruction. Both the detection in the visible spectrum of a red transient intermediate, and a lack of an electron spin resonance spectrum, indicate it to be the anion (2b). The rates of the reactions of potassium *t*-butoxide with (1b) and *N*-benzoyloxy-4-nitrobenzenamine (7) are very similar, which rules out the possibility that the *ortho*-nitro group in (1b) provides neighbouring group assistance for loss of benzoate ion from the anion (2b).

Rate measurements show that the loss of benzoate from (2b) is 39 times slower than chloride loss from the analogous anion (2a).

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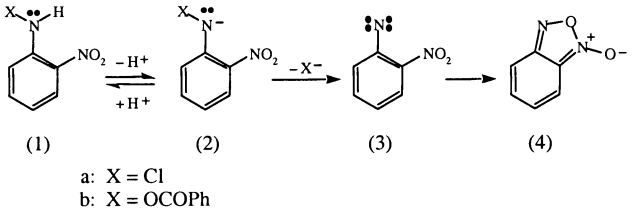
Introduction

We have previously reported[1] the base-promoted stepwise α-elimination of hydrogen chloride from *N*-chloro-2-nitrobenzenamine (1a) to form 2,1,3-benzoxadiazole* *N*-oxide (4) (henceforth called benzofuroxan) (Scheme 1).



Scheme 1

We found that mixing the base (methoxide or *t*-butoxide) with the *N*-chloro compound produced a red colour that faded rapidly ($t_{½}$ 2 s at 0°C). Arguments based on the visible spectrum of the red species, rate measurements on its fading, the absence of an electron spin resonance (ESR) spectrum during the reaction, and the steric effects of a 6-methyl group, were used to formulate the above mechanism. The red species was identified as the anion (2a), and we concluded that the loss of the chloride ion to form the singlet nitrene (3) is rate-determining.

It should be possible to achieve the chemistry outlined in Scheme 1 with other starting materials such as *N*-benzoyloxy-2-nitrobenzenamine (1b). This compound has the advantage over (1a) of being stable. On the other hand, the literature on *N*-acyloxyarenamines indicates that bases might act as nucleophiles on amino nitrogen,[2,3] or acyl carbon,[3,4] in (1b). The present paper reports experiments in which the reaction described by Scheme 1 was achieved despite the competing nucleophilic attack on acyl carbon with no evidence seen for the attack on amino nitrogen. It has proved possible to compare the relative abilities of chloride and benzoate anions to act as leaving groups from the anion (2).

Results and Discussion

Reaction of N-*Benzoyloxy-2-nitrobenzenamine (1b) with Sodium Methoxide*

When equal volumes of (1b) (7.9×10^{-4} M in methanol) and sodium methoxide (0.10 M) were mixed, a red colour was obtained instantaneously. In the first time-resolved ultraviolet–visible (UV–vis) measurement (2 s after mixing), the spectrum of (1b) (λ_{max} 362 nm) was already replaced by one with maxima at 308 and 515 nm, and a shoulder at 541 nm. The red colour faded rapidly and was swamped by the development of an intense blue colour (λ_{max} 552 nm, with shoulders at 512 and 585 nm). Weaker maxima at 353 and 371 nm corresponded to those of benzofuroxan, which formed in yields of 16, 12, and 8% for sodium methoxide concentrations (pre-mix) of 0.10, 0.20, and 1.0 M, respectively. The 308 nm peak also faded as the reaction progressed. The spectra underwent no further change after 60 s.

The λ_{max} values of the blue species are close to those reported by Kuhn and Weygand[5] for the conjugate base of 2-nitrophenylhydroxylamine (500, 546, and 587 nm, in aqueous solution).

* Common name is benzofurazan.

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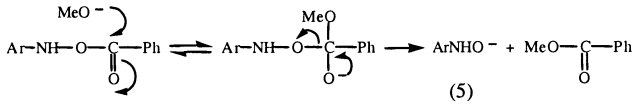
A product run ((1b) 0.05 M, sodium methoxide 0.4M) yielded methyl benzoate (59%), benzofuroxan (53%), and benzoic acid (50%). No attempt was made to isolate 2-nitrophenylhydroxylamine, which is unstable. Instead, it was allowed to stand in alkaline solution and undergo aerial oxidation to the corresponding nitroarene.[3] In the course of five days, the yield of 1,2-dinitrobenzene increased from 4 to 40%. It is interesting that no 2,2′-dinitroazoxybenzene was formed during the oxidation. Possibly its formation, by nucleophilic addition of the arylhydroxylamine to the intermediate nitroso compound, is prevented by severe steric hindrance from the *ortho*-nitro group in each reactant.

Formation of methyl benzoate and the anion (5) indicated that basic methanolysis (Scheme 2) is a serious competitor to the reaction of α-elimination (Scheme 1) that we were attempting to achieve. This methanolysis is very fast, which indicates that the anion (5) is an extremely good leaving group. Scheme 2 is undoubtedly a simplified version: it is probable that (1b) reacts as its conjugate base and proton transfers must occur.



Scheme 2

The formation of benzofuroxan and benzoic acid in essentially equal proportions is consistent with the α-elimination mechanism shown in Scheme 1. The internal trapping of the nitrene centre in (3) must be very efficient. When Novak and co-workers[4] reacted *N*-pivaloyloxy-3(or 4-)-chlorobenzenamine with basic amines in methanolic solution, they obtained the corresponding azo and azoxy compounds, and arenamine. They attributed these products to the reactions of an arylnitrene. Nitrene-derived products (azepines, arenamines, and azo compounds) have also been reported[6] in the reactions of *N*-sulfonyloxyarenamines with amines. There are no such products from the reaction of our substrate (1b) with sodium methoxide.

Reaction of (1b) with Potassium t-*Butoxide in* t-*Butanol*

Mixing equal volumes of the alcoholic solutions of (1b) (9.76×10^{-4} M) and potassium *t*-butoxide (0.196 M) at 25°C immediately produced a red colour. When the first spectrum was recorded ($t = 2$ s), the broad band (λ_{max} 363 nm) of (1b) was no longer visible. New bands had appeared at 355 and 379 nm (benzofuroxan), and 516 and 542(sh) nm. Extrapolation of the decay curve for the 516 nm peak to the time of mixing gave ε ca.5000 $cm^2\ mol^{-1}$. After 30 s, the 516 and 542 nm maxima were replaced by a single maximum at 460 nm, and at 120 s this band had resolved into a broad maximum at 440 nm with a shoulder at 476 nm. At $t = 5$ min, most of the benzofuroxan was gone, and none of it remained after 10 min. At this time, the broad maxima of the product(s) were at 449 and 478 nm, with a shoulder at 425 nm. This last set of maxima corresponded reasonably well with those observed in a separate experiment when benzofuroxan was allowed to react with potassium *t*-butoxide.

Similar results were obtained when the experiment was repeated with 0.02 M alkoxide, except that the benzofuroxan was consumed less rapidly.

The destruction of the benzofuroxan in a secondary reaction complicated the study of reaction products. At the high-substrate concentration of a product run, only 2% benzofuroxan survived, and the only useful results were the isolation of benzoic acid in 95% yield and the absence of *t*-butyl benzoate. These results, and the absence of the blue anion (5) in the time-resolved spectra, indicate that the pathway shown in Scheme 2 is not followed with *t*-butoxide base.

The best yields of benzofuroxan, measured spectrophotometrically after 15 elapsed half-lives at 25°C, were 87 and 77%. (Initial [$KOBu^t$] 0.01 and 0.05 M respectively; initial [(1b)] 5.1×10^{-4} M.) At higher base concentrations, yields were as low as 60%. It is probable that conversion of (1b) to benzofuroxan in the primary reaction is quantitative. The products of the secondary reaction did not interfere with the spectroscopic measurement of the rate of decay of the intermediate red species and, with the competing reaction of Scheme 2 absent, it was practicable to carry out the kinetic measurements described later.

The reason for methoxide following the path of nucleophilic addition to carbonyl to a considerable extent, and *t*-butoxide not doing so at all, cannot simply be attributed to the latter base shifting the equilibrium between (1b) and (2b) further to the right (see Scheme 1). The time-resolved spectra show that all, or nearly all, of the substrate (1b) is converted to the transient red species immediately upon adding the large excess of base, irrespective of whether it is methoxide or *t*-butoxide. These observations are best accommodated by concluding that both bases achieve essentially complete conversion of (1b) to (2b). If we assume that the pK_a of *N*-benzoyloxy-2-nitrobenzenamine is not too different from the value of 13.2 reported by Novak, Martin, and Heinrich[7] for *N*-pivaloyloxy-4-nitrobenzenamine (methanol solution), then the argument is reasonable.

The failure of *t*-butoxide to displace the blue anion (5) from *N*-benzoyloxy-2-nitrobenzenamine is most likely due to severe steric hindrance to attack on the carbonyl group by this bulky nucleophile.

The Nature of the Red Species Formed From (1b) and Potassium t-*Butoxide*

The data indicate that the red species is the conjugate base (2b) of *N*-benzoyloxy-2-nitrobenzenamine. We have argued elsewhere,[1] for the *N*-chloro analogue (1a), that a λ_{max} value above 500 nm is too high for a singlet arylnitrene, and that the bases used in this work are not powerful enough to produce a Meisenheimer adduct. Another possibility, that the red colour is due to a radical anion, is discounted by our ESR experiments. The ESR signal observed when *N*-benzoyloxy-2-nitrobenzenamine was treated with potassium *t*-butoxide was much too feeble to belong to the red intermediate. Moreover, after the red colour had all faded, the observed ESR signal had actually become more

intense. It probably arose from the secondary reaction between the benzofuroxan product and the *t*-butoxide ion.

If the mechanism portrayed in Scheme 1 is correct, then the red species is the same irrespective of whether the base is methoxide or *t*-butoxide. In the UV–vis spectra, the λ_{max} values of the red species (515 and 516 nm in methanol and *t*-butanol respectively) match, as do the shoulders (541 and 542 nm respectively) on these peak maxima.

It follows that the α-elimination of benzoic acid from (1b) is a stepwise process.

The identification of the conjugate base (2b) as the red intermediate has support from studies by Novak and coworkers[4] with *N*-pivaloyloxy-4-nitrobenzenamine. This compound reacted with methanolic dimethylamine to give a red-orange solution, λ_{max} 474 nm. This colour did not develop when *N*-methyl-*N*-pivaloyloxy-4-nitrobenzenamine was treated with the same base.

Another reaction pathway that must be considered is attack on the arenamino nitrogen by the alkoxide nucleophile (Scheme 3). Such reactions of *N*-acyloxyarenamines have been reported[2,3] when the nucleophile is an amine. Related substrates, *O*-diphenylphosphinoyl arylhydroxylamines ($ArNHOPOPh_2$), are reported[8] to undergo competing α-elimination and attack on amino nitrogen when treated with amine nucleophiles.

$$ArNHOCOPh + RO^- \rightarrow ArNHOR + PhCO_2^- \rightarrow PhN^-OR \rightarrow PhN \rightarrow (4) \quad (6)$$

(Ar = 2-nitrophenyl; R = methyl or *t*-butyl)

Scheme 3

The transient red intermediate would then be (6), and our spectroscopic evidence that the same intermediate is formed by both methoxide and *t*-butoxide bases cannot be accommodated. Moreover, it is difficult to believe that the first step in Scheme 3 would occur instantaneously on mixing the reagents.

Reaction Between Benzofuroxan (4) and Potassium t-*Butoxide or Sodium Methoxide*

When equal volumes of benzofuroxan (2.08×10^{-3} M in *t*-butanol) and potassium *t*-butoxide (0.5 M) were mixed at 25°C, the peaks in the UV–vis spectrum due to substrate steadily diminished in intensity. After 5 min, little benzofuroxan remained, and none could be detected after 30 min. New peaks (λ_{max} 432, with a shoulder at 480 nm) were visible after 1 min, and became more intense until $t = 30$ min, with the maximum shifting to 442 nm (480 nm shoulder). In repeat experiments with pre-mix base concentrations of 0.0095 and 0.978 M, the amounts of benzofuroxan surviving after 5 min were 100 and 0% respectively.

This reaction is presumed to be the one that consumes the benzofuroxan produced when the *N*-benzoyloxy compound (1b) is treated with potassium *t*-butoxide. ESR studies on benzofuroxan by Russell, Janzen, and Strom[9] have shown that electron transfer from the *t*-butoxide ion to benzofuroxan is an efficient process, and work[10] on the related electron transfer to aromatic nitro compounds suggests its kinetics would be second-order in *t*-butoxide. Therefore, it is not surprising that, in our experiments with (1b), little benzofuroxan survived at high *t*-butoxide concentrations. We noted some variation in the extent of this benzofuroxan destruction, probably because it was impractical to deoxygenate our reactants.

In our earlier kinetic work[1] with *N*-chloro-2-nitrobenzenamine (1a) and *t*-butoxide base, benzofuroxan (4) was produced in quantitative yield, and its subsequent destruction by the base was not noted. However, in those experiments the yield was measured spectrophotometrically after the elapse of ten half-lives, which was only 25 s. No significant destruction of (4) is to be expected in that brief time, at a lower temperature (0 instead of 25°C), and with quite low concentrations of base (≤ 0.074 M).

Sodium methoxide did not react with benzofuroxan. The UV–vis spectrum of a solution 1×10^{-4} M in benzofuroxan and 0.2 M in sodium methoxide did not change over a period of 5 h.

Kinetic Results for Reactions of (1b) with Potassium t-*Butoxide*

The decompositions of the ion (2b) in *t*-butanol solvent were smoothly first-order, even as far as five half-lives. There was an effect of changing the concentration of potassium *t*-butoxide (see Table 1), but it was not one to suggest a kinetic dependence. At low values of [$KOBu^t$] (0.01–0.02 M) the observed rate constants were appreciably lower than those obtained in the range 0.05–0.25 M. At the lowest end of the [$KOBu^t$] range, the ratio of base to substrate (1b) was only 21 : 1, and may in reality have been much smaller since no precautions were taken against uptake of carbon dioxide. The absorbance of the red species in the kinetic runs with very low base concentration was lower than usual, and the corresponding low rate constants are attributed to an incomplete conversion of (1b) to the anion (2b). The rate constants attained a broad plateau with [$KOBu^t$] in the range 0.05–0.25 M, and then slowly decreased at still higher base concentrations. This overall pattern of rate-constant variation is strikingly similar to that we reported for the *N*-chloro compound (1a). With the reactions between (1a) and lithium methoxide, we demonstrated that lithium salts

Table 1. Effect of varied [$KOBu^t$] on measured rate constants for *N*-benzoyloxy-2-nitrobenzenamine (1b)
Initial [(1b)] 4.5×10^{-4} M. *t*-Butanol solvent

Temperature K	Initial [$KOBu^t$] M	$10^2 k_1$ s	10^2(deviation)[A]
298.2	0.00960	3.94	0.11
	0.0239	6.28	0.09
	0.0477	8.38	0.04
	0.0960	8.74	0.05
	0.162	8.67	0.10
	0.245	8.52	0.17
	0.343	7.73	0.10
	0.489	6.49	0.05
413.2	0.096	27.3	1.0
	0.162	27.8	0.6

[A] These are the deviations from the mean of duplicate runs.

added to the methanolic reaction mixture depressed the rate constants. It is probable that similar salt effects operate at high [KOBu^t] for the reactions of (1b), but other potassium salts are not sufficiently soluble in *t*-butanol to check this point experimentally.

Subsequent rate data for (1b) were obtained with [KOBu^t] values in the range 0.05–0.25 M to avoid either incomplete deprotonation or sizeable salt effects.

In Table 2, it is demonstrated that changing the concentration of the substrate (1b) does not affect the observed first-order rate constants. Thus, the fading of the red-coloured species is a unimolecular process. Since there was no evidence for neighbouring group participation by the *ortho*-nitro group (see next section of this discussion) the mechanism described in Scheme 1 adequately describes the overall reaction, with stage (2b)→(3) assumed to be rate-determining. The insolubility of potassium benzoate in *t*-butanol precluded direct testing of whether this step is reversible. However, the observation of strict first-order kinetics even as far as five half-lives suggests that benzoate ion has no effect on the reaction rate.

Table 2. Effect of varied initial [*N*-benzoyloxy–2-nitrobenzenamine (1b)] on rate constants
t-Butanol solvent.Temperature 298.2 K

Initial 10^4[(1b)] M	Initial [KOBu^t] M	10^2k_1 s
5.1	0.0477	8.41
8.8	0.0477	8.34
4.5	0.245	8.52
10.3	0.245	8.53

Slow unimolecular solvolyses have been reported[11,12] for certain *N*-acyloxyarenamines. However, when *N*-benzoyloxy-2-nitrobenzenamine was dissolved in either methanol or *t*-butanol, the UV–vis spectrum did not change in 48 h. The very fast reactions with *t*-butoxide described in the present paper clearly involve a different sort of reaction requiring a strong base, such as the postulated process (2b)→(3).

The effects of temperature on rate (Table 3) reveal that the entropy of activation is large and negative, which is consistent with a requirement of substantial solvent reorganization to solvate the departing benzoate ion. The

Table 3. Arrhenius data for reaction of *N*-benzoyloxy-2-nitrobenzenamine (1b) with KOBu^t in Bu^{t}OH solution
Initial [(1b)] 4.8×10^{-4} M. Initial [KOBu^t] 0.162 M

Temperature K	10^2k_1 s	Arrhenius parameters[A]
298.2	8.77, 8.56	E_{act} 58.4 ± 2.4 kJ mol^{-1}
303.2	13.8, 14.2	ΔS_{act} –77.4 ± 8.1 J K^{-1} mol^{-1}
308.2	18.8, 17.8	$\log_e A$ 21.163 ± 6.100
313.2	27.2, 28.4	

[A] The errors in E_{act}, ΔS_{act}, and $\log_e A$ are quoted as 90% confidence limits.

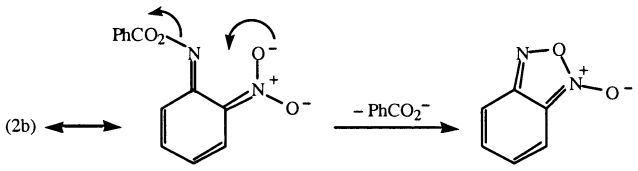
Table 4. Effect of varied [KOBu^t] on measured rate constants for *N*-benzoyloxy-4-nitrobenzenamine (7) at 298.2 K
Initial [(7)] ca. 3×10^{-4} M. *t*-Butanol solvent

Initial [KOBu^t]	k_1 (s)
0.0477	0.215, 0.191
0.096	0.334, 0.329
0.162	0.513, 0.494
0.245	0.746

observed value (–77 J K^{-1} mol^{-1}) is a little larger than that (–51) we observed[1] for *N*-chloro-2-nitrobenzenamine.

Possibility of Neighbouring Group Participation

In principle, the *ortho*-nitro group in the anion (2b) could assist the loss of benzoate ion, and then the free nitrene (3) would not be an intermediate. Scheme 4 represents one possible formulation of this neighbouring group participation.



Scheme 4

Whether such assistance to benzoate ion loss actually occurs can be determined by comparing rates for the *ortho*-isomer (1b) and the *para*-isomer, *N*-benzoyloxy-4-nitrobenzenamine (7).

While the very low solubility of *N*-benzoyloxy-4-nitrobenzenamine in *t*-butanol severely limited the scope of kinetic experiments, sufficient data were obtained for our present purpose. On mixing with potassium *t*-butoxide, the peak maximum at 332 nm was immediately replaced by a new one at 480 nm. This new spectrum can confidently be assigned to the conjugate base of (7), being close in λ_{max} value to the figure of 474 nm reported by Novak and his coworkers[4] for the conjugate base of *N*-pivaloyloxy -4-nitrobenzenamine (methanol solution).

This 480 nm peak underwent rapid first-order decay, and a new peak developed at 390 nm. This 390 nm peak, which corresponds in λ_{max} to the anion of 4-nitro-phenyl-hydroxylamine, also decayed, but much more slowly than the peak at 480 nm had done.

The observed pseudo-first order rate constants for decay of absorbance at 480 nm (see Table 4) showed a precise linear dependence on [KOBu^t], and extrapolation to zero concentration of the base yielded a non-zero rate constant (7.00×10^{-2} s^{-1}). (See Equation 1.)

$$k_1 = 0.0700 + 2.72[\text{KOBu}^t] \quad (1)$$

(correlation coefficient $r = 0.9983$)

This behaviour fits a scenario in which a bimolecular process (presumed from the absorbance spectrum to be displacement of the anion of 4-nitrophenylhydroxylamine) runs parallel to the unimolecular loss of benzoate from the conjugate base of (7).

The rate constant for the unimolecular reaction (k_1 = 7.0 × 10^{-2} s^{-1}) is so close to the value of 8.67 × 10^{-2} s^{-1} recorded for *N*-benzoyloxy-2-nitrobenzenamine that one must conclude there is no significant neighbouring group participation when the conjugate base of the latter compound loses benzoate ion.

In extrapolating the observed rate constants for (7) to zero [KOBu^t] to obtain the rate constant for the unimolecular reaction, it is assumed that (7) has been completely converted to its conjugate base at all the concentrations of potassium *t*-butoxide used in the kinetic experiments. The lack of curvature in the plot of *k* versus [KOBu^t] supports the view that this complete conversion to conjugate base has occurred.

Leaving Group Abilities

Table 5 lists data obtained with substrate (1b) to enable a comparison of its rates with those for the *N*-chloro compound (1a) obtained in the same solvent mixture (3:1 v/v CCl_4/*t*-BuOH). There is no evidence for an effect on rate from changing [KOBu^t] over a small range.

Table 5. Rate data for the reaction between *N*-benzoyloxy-2-nitrobenzenamine (1b) and KOBu^t in 3:1 (v/v) CCl_4/Bu^{t}OH at 298.2K

Initial [(1b)] 4.42 × 10^{-4} M

Initial [KOBu^t] M	10^2k_1 [A] s
0.081	6.91
0.171	7.08
0.171	6.83

[A] Average 10^2k_1 = 6.94 ± 0.09 s^{-1}.

The rate constant for (1b) at 298.2K is 6.94 × 10^{-2} s^{-1}, and extrapolation of the published data[1] for (1a) yields k_1 = 2.73 s^{-1} at this temperature. Thus chloride ion is 39.3 times better than benzoate as a leaving group in this situation.

Conclusions

N-Benzoyloxy-2-nitrobenzenamine (1b) reacts with sodium methoxide in two fast, competing reactions. Nucleophilic addition to acyl carbon yields methyl benzoate and 2-nitrophenylhydroxylamine, while α-elimination leads to benzofuroxan (2,1,3-benzoxadiazole *N*-oxide) and benzoic acid. The bulkier *t*-butoxide base reacts only by the α-elimination route, but destroys some of the benzofuroxan in a secondary reaction. The nitrene centre formed in the α-elimination is efficiently captured internally by the adjacent nitro group and does not yield products in intermolecular reactions.

A short-lived red intermediate, shown to be identical in the reaction of (1b) with either methoxide or *t*-butoxide, is identified as (2b), the conjugate base of (1b). The α-elimination therefore occurs stepwise, and a comparison of reaction rates with those of *N*-benzoyloxy-4-nitrobenzenamine show that there is no neighbouring-group participation in the loss of benzoate ion from the species (2b).

Kinetic studies found that benzoate expulsion from this intermediate (2b) occurs 39 times slower than chloride loss from the corresponding chloro anion (2a).

Experimental

Materials

We have reported the synthesis and characterization of *N*-benzoyloxy-2-nitrobenzenamine previously.[13] A freshly-prepared sample was recrystallized from ethyl acetate/light petroleum prior to use, and purity was checked by thin-layer chromatography (TLC) (silica gel G, $CHCl_3$ elution).

The *t*-butanol (2-methylpropan-2-ol) was dried on Linde type 5A molecular sieves and was then distilled from sodium to remove residual water. Methanol was analytical reagent grade (Univar) containing less than 0.1 mmol of water per litre. Potassium *t*-butoxide was prepared by the reaction of *t*-butanol with potassium,[14] and sodium methoxide by the reaction of sodium with methanol under a nitrogen atmosphere. These metal alkoxide solutions were stored under nitrogen, and their molarities were established by acid titration.

Synthesis of N-*Benzoyloxy-4-nitrobenzenamine (7)*

A suspension of 4-nitrophenylhydroxylamine (175 mg, 1.14 mmol) in benzene (20 mL) was degassed with a nitrogen stream and then stirred at room temperature while redistilled benzoyl chloride (175 mg, 1.25 mmol) in dry pyridine (3 mL) was added during 1 min. The stirring was continued for 30 min, and the reaction mixture was then washed with water (100 mL), sulfuric acid (1 M, 10 mL), and water again (2 × 10 mL). Evaporation of the dried benzene solution yielded a bright yellow solid, which was crystallized from ethyl acetate/light petroleum to obtain pale yellow micro-needles (91 mg, 31%). Melting point (m.p.) 139–142°C. TLC (silica gel G, $CHCl_3$ elution) gave a major and a minor spot. The purity was not improved by recrystallization and the material was not sufficiently soluble for chromatographic purification. The infrared (IR) spectrum detected no 4-nitrophenylhydroxylamine: ν_{max}($CHCl_3$) 3255 (NH); 1740 (C=O); 1522 and 1347 (NO_2) cm^{-1}. On a direct insertion mass spectrometer probe the substance decomposed thermally. Mass spectrum (direct CI, NH_3) *m*/*z* 288 ($M^{+\bullet}$ for a dinitroazoxybenzene, 5%), 276 (MNH_4^+ for (7), 38), 259 (MH^+ for (7), 99), and 105 (100).

Apparatus

Routine UV–vis spectra were recorded with a Varian DMS-90 instrument, and IR spectra with a Perkin Elmer Paragon 1000 Fourier transform spectrometer. ESR spectra were measured with a Bruker ER 200D-SRC instrument by Dr S. Brumby.

Kinetic Measurements and Time-Resolved Spectra

The electronic spectra of transitory species were recorded (250–750 nm) with a Hewlett-Packard 8450A UV–vis spectrometer equipped with a model 7225 plotter and a 89100A temperature controller (±0.1°C). The spectra were tape-filed at 5 s intervals.

To conduct a kinetic run, the solution of *N*-benzoyloxy-2-nitrobenzenamine was pipetted into one half of a split sample cell (total width 1 cm), and a solution of potassium *t*-butoxide was used to fill the other half of the cell to the same level. When temperature equilibrium was reached, the cell was rapidly inverted several times to mix the contents. A red colour (λ_{max} 516, with shoulder at 542 nm, in *t*-butanol) appeared instantaneously on mixing. The fading of this colour was actually measured at 550 nm to avoid interference from a secondary product which appeared late in the reaction. The infinity absorbance, A_∞, taken after 10 half-lives, was always close to zero. One reaction

product, potassium benzoate, has very low solubility in *t*-butanol, but in none of our runs did it precipitate until after A_∞ had been recorded.

At the selected wavelength, absorbance readings during the kinetic runs could be taken at intervals as short as 1 s. Depending on the rate of the reaction, between 6 and 15 absorbance readings were taken, always extending across at least two half-lives and sometimes as many as five. The first-order rate constants were evaluated graphically.

In all the Tables of rate constants reported here, the concentrations refer to those in the split sample cell after the two reactants had been mixed.

In order to compare rates for the *N*-benzoyloxy compound (1b) with those previously obtained for *N*-chloro-2-nitrobenzenamine (1a), some rates were measured with solvent mixtures that ended up three parts (v/v) CCl_4 and one part Bu^{t}OH after mixing the reactants in the cell. Occasionally, in this mixed solvent, a fine white suspension (presumed to be potassium *t*-butoxide and/or potassium benzoate) appeared before the run was over and elevated the baseline absorbance. These runs were discarded.

Stock solutions of (1b) in methanol or *t*-butanol were used within 2 h of preparation. A check of these solutions by UV–vis spectroscopy detected no change after 48 h.

For kinetic runs with *N*-benzoyloxy-4-nitrobenzenamine (7), a saturated solution of this sparingly soluble material was prepared in *t*-butanol. The filtered solution was estimated to be approximately 6×10^{-4} M. Thereafter, the procedure was as described above for its isomer.

Kinetic Measurements on the Reaction Between Sodium Methoxide and N-*Benzoyloxy-2-nitrobenzenamine (1b)*

The overlaps of the broad bands at 515 and 552 nm made it impossible to measure accurate rate constants for either the fade of the red colour (λ_{max} 515 nm) or the appearance of the blue species (λ_{max} 552 nm). Based on the first 40% of reaction, the 515 nm band decayed with $k_1 = 4.3 \times 10^{-2}$ s^{-1} at 25°C. (Initial concentrations, after mixing the two reagents, were: [(1b)] 3.95×10^{-5} M, [NaOMe] 0.050 M). Under these same reaction conditions, the development of the product with λ_{max} 552 nm (monitored on its absorption flank at 650 nm) had $k_1 = 8.7 \times 10^{-2}$ s^{-1}.

Products of Reaction of N-*Benzoyloxy-2-nitrobenzenamine* (*1b*) *with Sodium Methoxide*

Methanolic sodium methoxide (0.4 M, 10 mL, 4 mmol) was added to (1b) (129 mg, 0.5 mmol) at 20°C. There was an instantaneous flash of red colour, which changed immediately to a dark inky blue. After 30 min, the mixture was diluted with water (50 mL) and then extracted with ether (2 × 25 mL). The extract was washed with water (10 mL) and then dried ($MgSO_4$). Careful removal of the solvent (by rotary evaporation followed by a gentle stream of nitrogen) left a pale yellow oil (79 mg). The IR spectrum showed this oil to be a mixture of methyl benzoate, benzofuroxan, and a trace of 1,2-dinitrobenzene.

Five days later, the alkaline-aqueous residue from the ether extraction had faded in colour from blue to pale orange, and colourless needles were present. These crystals were collected by filtration and then dried. Yield, 29 mg. The IR spectrum ($CHCl_3$ solution) was an exact match to that of 1,2-dinitrobenzene. These needles had m.p. of 119.5–120.5°C and mixed m.p. of 118.5–120°C with an authentic sample (m.p. 119.5–121°C).

The filtrate from collection of the needles was acidified with dilute sulfuric acid and then extracted with chloroform to recover a pale yellow crystalline residue. The IR spectrum ($CHCl_3$ solution) was identical with that of benzoic acid. Calculations of yield based on key bands at 1694, 1451, and 1026 cm^{-1} gave 30.2 ± 1.2 mg (50%).

IR analysis of the neutral oil fraction showed it to consist of 40 ± 0.4 mg (59%) of methyl benzoate (analysed at 1719, 1452, and 1437 cm^{-1}) and 36 mg (53%) of benzofuroxan (analysed at 1542 cm^{-1}). 1,2-Dinitrobenzene (3 mg) was left behind when the mixture was taken up in light petroleum.

The various IR spectra gave no indication of 2-nitrobenzenamine, 2,2′-dinitroazobenzene, or the corresponding azoxy compound.

Products of Reaction of N-*Benzoyloxy-2-nitrobenzenamine* (*1b*) *with Potassium* t-*Butoxide*

The *N*-benzoyloxy compound (1b) (216 mg) was dissolved in *t*-butanol (20 mL) and treated at room temperature with KOBu^t (20 mL, 0.1 M). The immediate red-brown coloration faded to pale brown within 30 min. The mixture was then acidified with HCl (0.2 M), diluted with water, and extracted with ether. Some material (15 mg) was insoluble. Extraction of the ether solution with aqueous $NaHCO_3$ recovered benzoic acid (97 mg, 95%) whose IR spectrum matched that of an authentic sample. The ether solution yielded a fraction (48 mg) shown by TLC (silica gel G, $CHCl_3$) to have at least seven components. Benzofuroxan (2% yield) was identified in the ether distillate by UV–vis spectroscopy.

ESR Experiments

The compound (1b) (1.0 mg) was dissolved in 1 : 1 v/v *t*-butanol/benzene (5 mL) and then mixed at room temperature with KOBu^t (0.1 M in 5 mL of the same solvent mixture). Within 2 s of mixing, some of this solution was transferred into an ESR tube, which was then capped and transferred into liquid nitrogen. The usual red colour, obtained on mixing these reagents, persisted in the frozen sample.

At 160 K, and maximum gain, there was a minor absorption over and above the quartz tube signal. This signal faded out on warming to 240 K. At 280 K the frozen mixture melted, and after 10 min the red species was non-existent and a pale yellow solution remained. There was no ESR spectrum at this temperature, but on cooling to 160 K the frozen sample had a signal about three times as intense as before. This signal cannot belong to the red species and must arise in a slower secondary reaction.

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