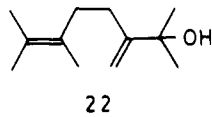


- (25) During the preparative VPC, the two first peaks elute together but an important part of the second product disappears. This again is an indication of the AA structure, the most unstable of the three diolefins.
- (26) On standing at room temperature for weeks in a closed Pyrex bottle, the diolefin BB gradually disappears although the liquid remains perfectly colorless. The capillary chromatograph reveals a new product eluting after *n*-dodecane. It is in fact the tertiary alcohol **22** as evidenced by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, and mass spectrometry. Such a reaction is known to proceed rapidly in the presence of sensitizers like benzophenone.<sup>46,47</sup>



- (27) Spectroscopic data follow. Compound BB (neat): <sup>1</sup>H NMR 1.63 (s); 2.05 (s); <sup>13</sup>C NMR 20.58, 20.02, and 18.65 (q), 33.61 (t), 123.73 and 128.02 (s). Compound AB (neat but slightly contaminated by AA): <sup>1</sup>H NMR 1.05, 1.65, 1.78, and 2.19 (s), 4.78 (m); <sup>13</sup>C NMR 20.00, 20.80, 21.57, and 27.53 (q), 45.30 and 109.56 (t), 40.81, 126.45, 126.84, and 153.11 (s). Compound AA (diluted in AB): <sup>1</sup>H NMR 1.08 and 1.81 (s), 4.89 (br s); <sup>13</sup>C NMR 151.92 (s), 44.25 (s?), 114.10 (t?), 24.71 (q), 23.45 (q?).
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## Kinetics of the Interaction of Nitrosobenzenes with Substituted Benzaldehyde Phenylhydrazones

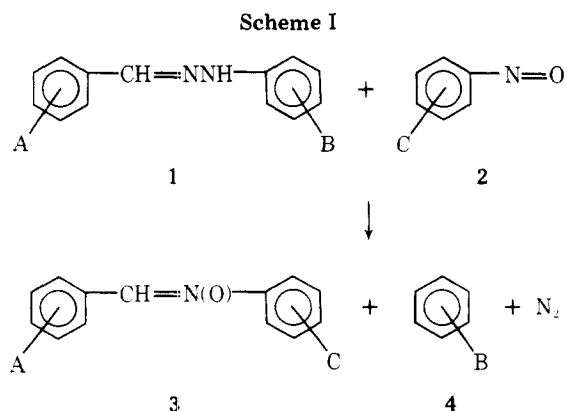
Brent A. DellaColetta, John G. Frye, Tim L. Youngless, James P. Zeigler, and Robert G. Landolt\*

*Department of Chemistry, Muskingum College, New Concord, Ohio 43762*

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The reaction of benzaldehyde phenylhydrazone with nitrosobenzene follows second-order kinetics in either air or nitrogen at ambient temperature. Rates of reactions under nitrogen utilizing reactants substituted at meta and para positions of each of the three available aromatic rings have been correlated using the Hammett treatment. Reactions are facilitated by electron-donating substituents on benzaldehyde phenylhydrazones and by electron-withdrawing substituents on nitrosobenzenes. Oxygen exerts a more dramatic inhibition on reaction rates of substituted substrates than of parent compounds.

Benzaldehyde phenylhydrazone reacts with nitrosobenzene at ambient temperature to give nitrones, nitrogen, and benzene.<sup>1</sup> Phenylhydrazone derivatives of aromatic ketones and substituted benzaldehydes yield the corresponding nitrones, and product yields are sensitive to oxygen. The probable course of the reaction using reactants substituted at various aromatic rings may be summarized as shown in Scheme I.



Kinetics of this reaction have been studied to determine the order of the initial reaction of nitrosobenzenes with hydrazone substrates and to explore causes for oxygen sensitivity. The consequence of substitution (A, B, and C) at the aromatic rings has been investigated in order to elucidate the impact of electronic effects on the reaction.

### Results and Discussion

General applicability of Scheme I is illustrated both by earlier synthetic work,<sup>1</sup> in which A- and B-ring substitution was investigated, and by formation of  $\alpha$ -phenyl-*N*-*m*-chlorophenyl nitrone (**3**, A = H, C = *m*-chloro) from reaction of *m*-chloronitrosobenzene with benzaldehyde phenylhydrazone (BPH). All three rings of reactants therefore could provide sites for substitution in this reaction system.

Initial kinetic investigations centered on the interaction of (unsubstituted) BPH with nitrosobenzene, and results indicated first-order rate dependency on both reactants. Plots of 1/(nitrosobenzene absorbance) vs. time for reactions in benzene, using equal initial concentrations of both reactants, were shown to be linear for at least three half-lives under both air and nitrogen atmospheres (average correlation coefficients of 0.9996 and 0.9995, respectively). It therefore was considered

Table I. Kinetics of Reactions of Phenylhydrazones with Nitrosobenzenes in Benzene at  $24.2 \pm 0.2$  °C

Registry no.	Reaction <sup>a</sup>	1		2	$k, M^{-1} s^{-1}$		
		A	B	C	First half-life	Overall	
588-64-7	586-96-9	1-0	H	H	H	0.136	0.120
		1-1 <sup>b</sup>	H	H	H	0.134	0.119
2829-27-8		2-0	<i>p</i> -NO <sub>2</sub>	H	H	0.0738	0.0751
		2-1 <sup>c</sup>	<i>p</i> -NO <sub>2</sub>	H	H	0.0482	0.0448
7539-23-3		3-0	<i>m</i> -NO <sub>2</sub>	H	H	0.108	0.111
		3-1 <sup>b</sup>	<i>m</i> -NO <sub>2</sub>	H	H	0.0871	0.0788
		3-2 <sup>d</sup>	<i>m</i> -NO <sub>2</sub>	H	H	0.0858	0.0819
351-24-6		4-0	<i>m</i> -F	H	H	0.0944	0.0948
34158-77-5		5-0	<i>m</i> -Cl	H	H	0.104	0.100
16917-42-3		6-0	<i>p</i> -Br	H	H	0.144	0.120
2829-26-7		7-0	<i>p</i> -Cl	H	H	0.149	0.145
2829-25-6		8-0	<i>p</i> -CH <sub>3</sub>	H	H	0.171	0.155
352-06-7		9-0	<i>p</i> -F	H	H	0.180	0.176
622-73-1		10-0	<i>p</i> -OCH <sub>3</sub>	H	H	0.229	0.218
2829-28-9		11-0	<i>p</i> -dma <sup>e</sup>	H	H	0.282	0.283
2989-41-5		12-0	H	<i>m</i> -Cl	H	0.0258	0.0242
2833-68-3		13-0	H	<i>p</i> -Cl	H	0.0750	0.0625
62698-28-6		14-0	H	<i>m</i> -CH <sub>3</sub>	H	0.196	0.179
		14-1 <sup>b</sup>	H	<i>m</i> -CH <sub>3</sub>	H	0.180	0.154
352-07-8		15-0	H	<i>p</i> -F	H	0.224	0.248
		15-1 <sup>b</sup>	H	<i>p</i> -F	H	0.204	0.191
1858-99-7		16-0	H	<i>p</i> -CH <sub>3</sub>	H	0.330	0.452
		16-1 <sup>b</sup>	H	<i>p</i> -CH <sub>3</sub>	H	0.383	0.368
10407-20-2		17-0	H	<i>p</i> -OCH <sub>3</sub>	H	1.18	1.38
		17-1 <sup>b</sup>	H	<i>p</i> -OCH <sub>3</sub>	H	0.438	0.246
	623-11-0	18-0	H	H	<i>p</i> -CH <sub>3</sub>	0.0318	0.0253
	352-15-8	19-0	H	H	<i>p</i> -F	0.0612	0.0430
	620-26-8	20-0	H	H	<i>m</i> -CH <sub>3</sub>	0.0985	0.0841
	26595-63-1	21-0	H	H	<i>m</i> -OCH <sub>3</sub>	0.137	0.111
	932-98-9	22-0	H	H	<i>p</i> -Cl	0.409	0.329
	932-78-5	23-0	H	H	<i>m</i> -Cl	1.09	1.18
		23-1 <sup>b</sup>	H	H	<i>m</i> -Cl	0.927	0.765
	7476-79-1	24-0	H	H	<i>p</i> -cbe <sup>f</sup>	3.61	4.92

<sup>a</sup> Unless otherwise indicated, under N<sub>2</sub>. <sup>b</sup> Run in air. <sup>c</sup> From pseudo-first-order reaction. <sup>d</sup> Solvent pretreated with O<sub>2</sub>. <sup>e</sup> Dimethylamino. <sup>f</sup> Carbethoxy.

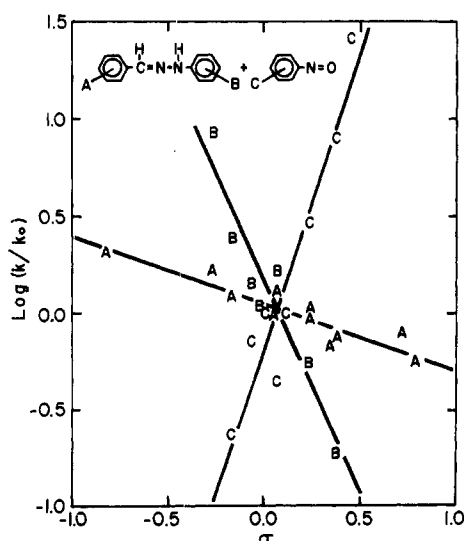


Figure 1. Log  $k/k_0$  vs. Hammett  $\sigma$  for reactions in Table I of nitrosobenzenes with phenylhydrazones of benzaldehydes. For A points, B and C = H, etc.

that reaction rates derived from these plots might be used reliably as standards for a Hammett treatment.

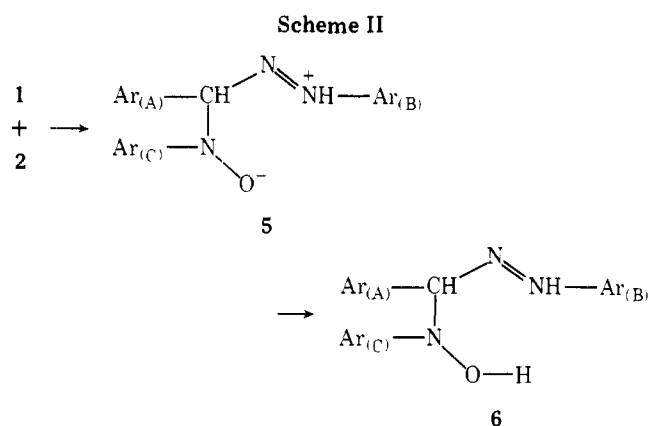
Three series of reactions were carried out employing reactants substituted at meta and para A-, B-, and C-ring positions indicated in Scheme I. Second-order rate constants for these reactions are shown in Table I. Excepting only reactions 16-0 and 17-0, linear second-order plots with correlation coeffi-

icients of at least 0.9999 were recorded for all reactions with a nitrogen atmosphere. Reactions in air proved to be less consistent.

First half-life rate constants for reactions run under nitrogen were used to generate log  $k/k_0$  vs. Hammett  $\sigma$  plots for the three reaction series, and these are shown in Figure 1. Results indicated that reactions are facilitated by meta and para electron-donating substituents at either ring of BPHs (A ring,  $\rho = -0.3$ ; B ring,  $\rho = -2.2$ ) and by electron-withdrawing substituents on nitrosobenzene (C ring,  $\rho = +3.0$ ). Moreover, the relative magnitude of  $\rho$  values showed that the system was significantly more sensitive to substitution at either B- or C-ring sites than at A.

These results are consistent with a mechanism involving initial electrophilic attack by the nitrosobenzene upon the BPH benzylidene carbon, giving rise to intermediate 5 (Scheme II). Stability of this zwitterionic intermediate (and the transition state leading to it) could be greatly affected by either B- or C-ring substitution. A-ring substituents, which are insulated from centers of charge, would have relatively small influence, but electron-donating groups still would favor development of a positive charge on the adjacent, erstwhile hydrazone nitrogens. Hegarty and Scott noted parallel relative sensitivities for A- and B-ring substitution in the electrophilic attack of bromine on hydrazones ( $\rho_A = -0.62$  and  $\rho_B = -2.2$ ) and attributed their results to formation of an intermediate analogous to 5.<sup>2</sup>

As reactions proceeded, it is possible that 5 was more or less rapidly converted to 6, a species analogous to the ene product isolated by Knight from the reaction of nitrosobenzene with 2,3-dimethylbut-2-ene.<sup>3</sup> A similar ene-type product has been



isolated from the reaction of BPHs with alkoxycarbonylazo compounds.<sup>4</sup>

In experiments using ring-substituted hydrazone substrates, reaction rates proved to be more air sensitive than when unsubstituted BPH was used. This is most dramatically illustrated on comparison of reactions 17-0 and 17-1 with 1-0 and 1-1, but generally reactions in air of substituted BPHs not only were slower than in nitrogen initially, but rates also continued to diminish with time. These results were probably due in part to a competing reaction of BPH substrates with oxygen.<sup>5</sup> However, this factor does not explain why *m*-nitrobenzaldehyde phenylhydrazone, upon interaction with nitrosobenzene, was more sensitive to air than was BPH. (Contrast reactions 3-0, 3-1, and 3-2 with 1-0 and 1-1!). The *m*-nitro compound is reported to react more slowly with oxygen than BPH.<sup>5a</sup> Similarly, substrate oxidation does not explain why BPH should show greater sensitivity to air on reaction with *m*-chloronitrosobenzene (reactions 23-0 and 23-1) than with nitrosobenzene (reactions 1-0 and 1-1). Furthermore, experiments on a synthetic scale have shown that yields of the final product nitronium may be enhanced by an air atmosphere.<sup>1</sup>

These results may relate to pathways by which intermediates 5 and/or 6 ultimately were converted to nitronium and the other products in Scheme I. Mechanisms involving either ionic or radical intermediates may be operable;<sup>6a</sup> one possible pathway involves decomposition of intermediate 6 to give a nitronium and an aryl diazene, ArN<sub>2</sub>H. The latter is known to yield, under certain circumstances, nitrogen and the corresponding aromatic compound.<sup>6b</sup>

### Experimental Section

Melting points were determined on a Thomas-Hoover "Unimelt" apparatus and are uncorrected. Spectrophotometric grade benzene (Baker or Mallinckrodt) was used for kinetic studies. Benzaldehyde phenylhydrazones were prepared by standard methods from the corresponding aldehydes and phenylhydrazines or their hydrochlorides (Eastman, Aldrich, or Pierce), and melting points corresponded to literature values. Nitrosobenzene (Aldrich or Kings Labs) was recrystallized from ethanol, mp 66.5–67 °C (lit.<sup>7</sup> mp 64–67 °C). Substituted nitrosobenzenes were generally obtained using the procedure of Coleman and McCluskey:<sup>7</sup> *p*-nitrosotoluene, mp 46 °C (lit.<sup>8</sup> mp 48 °C); *p*-fluoronitrosobenzene, mp 39–40 °C (lit.<sup>9</sup> mp 39 °C); *m*-nitrosotoluene, mp 50–51.5 °C (lit.<sup>10</sup> mp 53 °C); *m*-methoxynitrosobenzene, mp 48 °C (lit.<sup>11</sup> mp 48 °C); *p*-chloronitrosobenzene, mp 89–91 °C (lit.<sup>12</sup> mp 90 °C); and *m*-chloronitrosobenzene, mp 71.5–72.5 °C (lit.<sup>13</sup> mp 72 °C). Ethyl *p*-nitrosobenzoate was synthesized in very moderate yield by a modified Caro's acid method,<sup>13</sup> mp 82 °C (lit.<sup>12</sup> mp 83 °C). Microanalysis was performed by Galbraith Laboratories.

**Kinetic Procedure.** All kinetic work was carried out using a Cary 15 ultraviolet-visible spectrophotometer with cell compartment thermostated by a Precision Scientific "lo-Temptrol" 154 bath set for 24.2 ± 0.2 °C. Concentration vs. absorbance plots for each of the nitrosobenzenes and *p*-nitrobenzaldehyde phenylhydrazone showed

all but ethyl *p*-nitrosobenzoate to obey Beer's law in the concentration ranges under investigation.<sup>14</sup>

In experiments where oxygen was to be excluded, benzene was flushed with nitrogen for 0.5 h and stored for 0.5 h in the 24.2 °C bath before being used to make separate solutions of equal concentrations of a nitroso compound and a phenylhydrazone. The two solutions were added simultaneously to a flask flushed with nitrogen, and, after brief agitation, the reaction mixture was charged into a glass absorption cell. Reactant mixing, cell charging, and placement in the spectrophotometer usually required less than 1 min. Generally, reactions utilized a 5-cm cell and equal reactant concentrations of 0.00775 M. The more rapid reactions (no. 17, 23, and 24, Table I) in the B- and C-ring series used a 10-cm cell with equal reactant concentrations in the range of 0.004 M, and some of the slower reactions (no. 12, 13, 18, 19, 20, and 21, Table I) were carried out in a 1-cm cell at 0.0312–0.0390 M concentrations. Depletion of the nitroso compound absorption at 755 nm routinely was used to follow the progress of reactions through at least three half-lives; however, in reaction 24, the *p*-carboxynitrosobenzene absorption at 774 nm was monitored. Solution preparation and reagent mixing for reactions in the B-ring series were carried out in the dark due to the marked tendency toward light decomposition of certain of the phenylhydrazones.

In the pseudo-first-order reaction (reaction 2-1) of nitrosobenzene (0.0174 M) with *p*-nitrobenzaldehyde phenylhydrazone (1.74 × 10<sup>-5</sup> M), the phenylhydrazone absorption of 410 nm was monitored. After a rapid initial decrease followed by a leveling out period, a slow increase in the absorbance was noted. A plot reflecting only *p*-nitrobenzaldehyde phenylhydrazone disappearance was obtained by (a) extrapolating a first-order appearance plot for the unknown product back to zero time, and (b) subtracting resulting absorbance values from the original plot to give a "difference" plot.<sup>15</sup>

**α-Phenyl-N-m-chlorophenylnitronium.**<sup>16</sup> A 0.196-g sample (1.0 mmol) of benzaldehyde phenylhydrazone was treated with 0.301 g (2.0 mmol) of *m*-chloronitrosobenzene in benzene under a nitrogen atmosphere using the nitronium synthesis procedure outlined in reference 1. Chromatography on silica gel using benzene and benzene-ethyl acetate yielded 0.121 g (0.52 mmol, a 52% yield) of crude product, mp 91 °C. Recrystallization from 50:50 ethanol/water and cyclohexane yielded an off-white solid, mp 96–96.5 °C. Prominent bands in the infrared spectrum were found at 1600, 1560, 1480, 1460, 1410, 1200, 1110, 1090, 840, 800, 770, 740, and 700 cm<sup>-1</sup>.

Anal. Calcd for C<sub>13</sub>H<sub>10</sub>ClNO: C, 67.40; H, 4.35; N, 6.05. Found: C, 67.25; H, 4.34; N, 5.86.

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**Registry No.**—3 (A = H; C = Cl), 32019-34-4.

### References and Notes

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- (15) We are indebted to Dr. G. C. Nieman for this data treatment.
- (16) Work performed by Lloyd E. B. Jones and Mary E. Gerst.