Reaction of 2,4-Dinitrofluorobenzene with *o*-Anisidine in Benzene. Further Evidence of the "Dimer" Mechanism[1]

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The reaction of 2,4-dinitrofluorobenzene with *o*-anisidine (B) in benzene exhibits a quadratic dependence of the observed second-order rate coefficient, k_A, with [B], and similar behavior is found in the reaction with *p*-anisidine, as was previously reported in the literature. The kinetic results are interpreted in terms of a "dimer" nucleophile, B:B, which forms a cyclic intermediate with the substrate. This interpretation is confirmed by the data of the reaction run in the presence of varying amounts of pyridine, where an additional mixed adduct, B:P, is present.

The reaction of 2,4-dinitrohalobenzenes with *p*-anisidine in benzene was studied by Bernasconi and Zollinger.[2] While the second-order rate coefficient, k_A, for the reaction of 2,4-dinitrochlorobenzene (DNCl) increases steadily with the *p*-anisidine concentration, [B], the reaction of 2,4-dinitrofluorobenzene (DNF) exhibits a quadratic dependence of k_A with [B]. As was mentioned in the preceding paper for the reactions of dinitroanisoles, the plot of $k_A/[B]$ vs. [B] for the reaction of DNF also gives a straight line, and the kinetic results could be explained by the effect of a hydrogen-bonded *dimer* of *p*-anisidine as the nucleophile. In order to search into the extent of this new mechanism, we studied the reaction of the same sustrate with *o*-anisidine at three temperatures. Since *o*-anisidine is a relatively weak base, the influence of an added tertiary amine, pyridine, which is known to form a 1:1 complex with *o*-anisidine,[3] was also investigated. The reaction of DNF with *o*-anisidine was studied for several pyridine concentrations at various fixed *o*-anisidine concentrations, and the existence of mixed associated nucleophiles was thus confirmed.

Results

The rate of reaction of *o*-anisidine with DNF in benzene was determined at *o*-anisidine concentrations from 0.1 to 0.8 M. Formation of *N*-(2,4-dinitrophenyl)-2-methoxyaniline was quantitative, the initial substrate concentration was ca. 10^{-4} M, and pseudo-first-order kinetics were observed throughout the work. The second-order rate coefficient k_A was found to increase rapidly with *o*-anisidine concentration, [B], as shown in Table I. A plot (not shown) of k_A vs. [B] shows a quadratic dependence. As was reported in the preceding paper for the reactions of dinitroanisoles, if the quotient $k_A/[B]$ is plotted against [B], straight lines are also obtained for this reaction at the three temperatures (Figure 1).

When the reaction is run in the presence of a fixed amount of a tertiary amine, pyridine, there is also a curvilinear dependence of k_A with [B], but the plot of $k_A/[B]$ vs. [B] is no longer a straight line.

A complete study of the combined influence of both amines was then outlined; reactions were run at a fixed *o*-anisidine concentration (in the range 0.1–0.8 M) in the presence of varying amounts of pyridine (P; up to 0.06 M). The specific four concentrations of pyridine used were the same for the six values of *o*-anisidine concentration studied, thus producing also a set of data of varying [B] at constant [P]. Results are set forth in Table II. As can be observed in Figure 2, the plot of k_A vs. [P] gives straight lines for all the B studied in the whole range of [P], and excellent correlation coefficients are obtained. The slopes and the intercepts are also given in Table II.

Table I. Kinetics of the Reaction of 2,4-Dinitrofluorobenzene with *o*-Anisidine (B) in Benzene[a]

[B], M	$10^6 k_A$, s^{-1} M^{-1}		
	35 °C	50 °C	60 °C
0.105	1.15	1.95	2.72
0.201	2.86	4.41	6.22
0.300	5.93	8.40	11.6
0.377	8.47	12.8	16.6
0.525	15.9	23.6	30.0
0.593	21.3	30.1	36.5
0.818			64.3

[a] $\Delta H^{\ddagger}$ ranged from 7.6 to 5.0 kcal mol^{-1}, and $-\Delta S^{\ddagger}$ ranged from 63 to 66 cal K^{-1} mol^{-1}.

Discussion

The quadratic dependence of k_A with [B] in the reaction of DNF with *o*- and *p*-anisidine in benzene can be interpreted as in the preceding paper: a hydrogen bonded dimer of anisidine operating as the main nucleophile. In their discussion of the kinetic results of the reaction between *p*-anisidine and DNF, Bernasconi and Zollinger[2] mention that in addition to its base-catalysis effect *p*-anisidine could influence the reaction rate by "a solvation or association effect". They also considered the possibility of a complex between *p*-anisidine and pyridine as an alternative explanation for the accelerating effect of pyridine (instead of the base catalysis which they prefer), but they disregarded the existence of such a complex on the following grounds: (1) A complex between two piperidine molecules might be of comparable stability as an adduct between *p*-anisidine and pyridine, and, therefore, piperidine should catalyze the reaction with DNCl as is the case with the supposed *p*-anisidine pyridine complex. (2) From the association constants of other systems, an estimation of the concentration of the complex reveals that it should be extremely small.

Although piperidine is known to form dimers in benzene,[4] objection 1 no longer holds since it is known that the zwitterionic intermediate formed in the aromatic nucleophilic substitution (ANS) reactions of DNCl is easily decomposed to products, i.e., $k_5 >> k_{-4}$ (see Scheme I), and competition between monomer and dimer nucleophilic attack should not be noticeable for DNCl. Objection 2 can be disregarded in view of the experimental evidence of a

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[1] Presented in part at the 2nd Argentine Physical Organic Chemistry Symposium, Córdoba, Argentina, Oct 1981.

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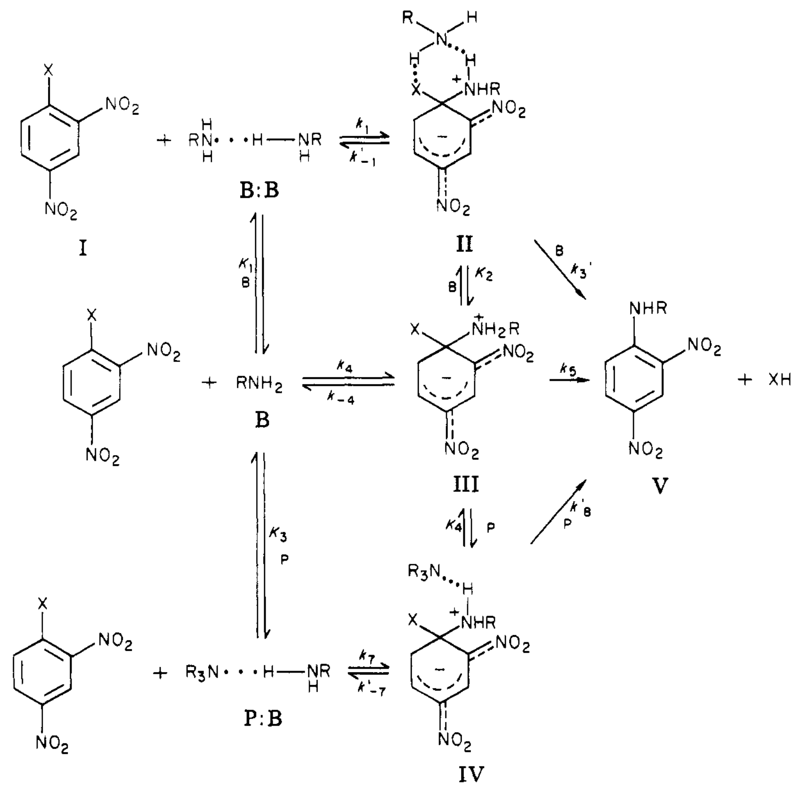
0022-3263/83/1948-1613$01.50/0

Scheme I



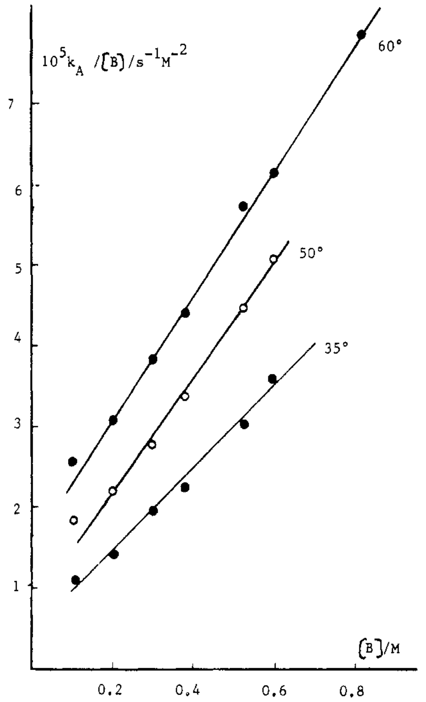


Figure 1. Reaction of 2,4-dinitrofluorobenzene with *o*-anisidine (B) in benzene.

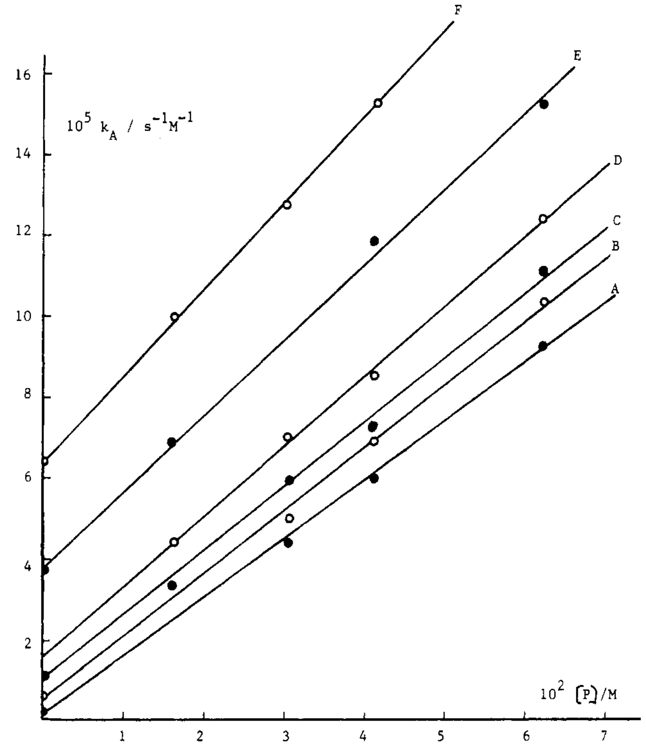


Figure 2. Reaction of 2,4-dinitrofluorobenzene with *o*-anisidine (B) and pyridine (P) in benzene at 60 °C. [B], M: A, 0.105; B, 0.201; C, 0.300; D, 0.399; E, 0.593; F, 0.818.

hydrogen-bonded complex between *p*-anisidine and pyridine.[5] Furthermore, it is not required that the amount of associated complex be very high for the associated complex mechanism to be observable, since k_{-4} is greater than k'_{-8} and k'_{-7}.

That association of the nucleophile, at relatively high [B], should increase its nucleophilicity was earlier suggested in ANS[2,6] and was recently invoked in the *n*-butylaminolysis of tetrachloro-*N*-*n*-butylphtalimide[7] in aprotic media. In this last reaction, the kinetic order with respect to the nucleophile was three, and it was postulated that a dimer of the amine catalyzes the formation of the tet-

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Table II. Kinetics[a] of the Reaction of 2,4-Dinitrofluorobenzene with *o*-Anisidine (B) and Pyridine (P) in Benzene at 60 °C

	[B], M					
10^2[P], M	0.105	0.201	0.300	0.399	0.593	0.818
0	0.272	0.622	1.16		3.65	6.43
1.60			3.30	4.42	6.92	9.96
3.07	4.40	5.00	5.98	7.04		12.8
4.15	6.01	6.91	7.25	8.57	11.9	15.3
6.20	9.32	10.4	11.2	12.5	15.3	
10^3 slope,[b] s^{-1} M^{-2}	1.44	1.56	1.61	1.72	1.89	2.11
10^6 interc, s^{-1} M^{-1}	1.41	4.65	9.60	16.6	38.1	64.4

[a] $10^5 k_A$, s^{-1} M^{-1}. [b] In all cases the correlation coefficient was ≥0.998.

rahedral intermediate between the substrate and butylamine. It is known that primary and secondary amines are partially self-associated in aprotic media[8] which explains the great variety of kinetic order observed for amines in these solvents.[9-11] Particularly, for the case of *o*-anisidine the formation of hydrogen-bonded complexes in aprotic solvents, benzene included, has been proved with different experimental evidence.[3,5,12,13]

Therefore, in view of the compelling experimental evidence for the presence of the two different kinds of complexes (a dimer, B:B, formed by two molecules of *o*-anisidine and an association complex between a molecule of *o*-anisidine and pyridine, B:P) the whole mechanism sketched in Scheme I is proposed for the reaction between DNF and *o*- or *p*-anisidine (B) when the reaction is run in the presence of pyridine (P). A similar mechanism can be postulated for the reaction run in the presence of Dabco. The influence of the mixed complex B:Dabco should be stronger due to the known properties of this last amine.

Three competing nucleophile reactions are shown: attack by the dimer (measured by k_1), by the monomer (determined by k_4), and by the complex B:P (measured by k_7). An equilibrium between the three possible tetrahedral intermediates is established, k_{-4} being greater than k'_{-1} and k'_{-7} as was discussed in the preceding paper. In order to simplify the equations, the following replacements are made (eq 1–4). The whole expression for k_A on the basis of the steady-state treatment is given by eq 5. As

$$k_{-1} = k'_{-1}/K_2 \qquad (1)$$

$$k_3 = k'_3/K_2 \qquad (2)$$

$$k_{-7} = k'_{-7}/K_4 \qquad (3)$$

$$k_8 = k'_8/K_4 \qquad (4)$$

$$k_A = k_4k_5 + (k_3k_4 + k_1k_5K_1)[B] + k_1k_3K_1[B]^2 + (k_1k_8K_1 + k_3k_7K_3)[B][P] + (k_5k_7K_3 + k_4k_8)[P] + k_7k_8K_3[P]^2/k_{-4} + k_5 + (k_{-1} + k_3)[B] + (k_{-7} + k_8)[P] \qquad (5)$$

can be observed, there are terms in first and second order for each one of the amines present (B and P) and a mixed term which depends on both [B] and [P].

When [P] = 0, eq 5 transforms into the given expression for the dimer attack.[14] It is observed that the curves pass through the origin which means that k_4k_5 is negligible. The plot of k_A/[B] vs. [B] is linear in the whole range of [B].

Table III. Rate Coefficients[a] of the Kinetic Law for Reaction of 2,4-Dinitrofluorobenzene with *o*-Anisidine and Pyridine in Benzene at 60 °C

k_α,[b] s^{-1} M^{-2}	k_β,[b] s^{-1} M^{-3}	k_γ,[c] s^{-1} M^{-3}	k_δ,[c] s^{-1} M^{-2}
0.152	0.780	9.22	13.5

[a] $10^4 k$. [b] Range of [B] was 0.201–0.818 M; correlation coefficient of 0.9995. [c] Correlation coefficient 0.998.

This would imply that $k_{-4} \gg k_5 + (k_3 + k_{-1})[B]$, and, therefore, the expression for k_A can be simplified to eq 6

$$k_A = \frac{(k_5k_1K_1 + k_3k_4)[B]}{k_{-4}} + \frac{k_1k_3K_1[B]^2}{k_{-4}} \qquad (6)$$

which expresses the linear dependence of k_A/[B] with [B]. Table III gathers the slopes, the intercepts, and the correlation coefficients obtained from the data of Table I by application of eq 6.

If the proposed mechanism is valid, the assumptions that led to eq 6 should hold in the presence of pyridine too, i.e., k_4k_5 negligible and $k_{-4} >> k_5 + (k_3 + k_{-1})[B]$, which allows some simplifications in the whole expression for k_A (eq 5), which can be written in the condensed form of eq 7, where

$$k_A = \frac{k_0 + k'[P] + k''[P]^2}{k_{-4} + (k_8 + k_{-7})[P]} \qquad (7)$$

k'' stands for $k_7k_8K_3$ and k_0 and k' are given by expressions 8 and 9. As is shown in Figure 2, a sharp linear relationship is observed between k_A and [P], when [B] is held constant. For eq 7 to express that linear dependence it is required that $k_{-4} \ll (k_8 + k_{-7})[P]$ and $k''[P]^2 \ll k_0 + k'[P]$.

$$k_0 = (k_3k_4 + k_1k_5K_1)[B] + k_1k_3K_1[B]^2 \qquad (8)$$

$$k' = (k_1k_8K_1 + k_7k_3K_3)[B] + k_5k_7K_3 + k_4k_8 \qquad (9)$$

An alternative possibility could be that $k_{-4} \ll (k_8 + k_{-7})[P]$ and that $k'[P] + k''[P]^2 \gg k_0$; these inequalities would also reduce eq 7 to the mathematical form of a linear relationship between k_A and [P]. Nevertheless, this alternative should be rejected on the following grounds: for [P] = 0, k_A would simplify to $k_A = k'/(k_8 + k_{-7})$; i.e., it should be linearly dependent on [B] which does not agree with the experimentally observed k_A quadratic dependence on [B]. Furthermore, the slopes of k_A vs. [P] should be $k''/(k_8 + k_{-7})$, which, taking into account the definition of k'', should also be independent of [B]. Therefore, the general expression 5 can be reduced to eq 10 that can be written in the condensed form of eq 11.

$$k_A = ((k_3k_4 + k_1k_5K_1)[B] + k_1k_3K_1[B]^2 + (k_1k_8K_1 + k_7k_3K_3)[B][P] + (k_5k_7K_3 + k_4k_8)[P])/k_{-4} \qquad (10)$$

$$k_A = k_\alpha[B] + k_\beta[B]^2 + k_\gamma[B][P] + k_\delta[P] \qquad (11)$$

To evaluate k_γ and k_δ, we ran several experiments at fixed [B] at 60 °C; the slopes $k'/k_{-4} = (k_\gamma[B] + k_\delta)$ of the

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[8] See ref 15 of: Nudelman, N. S.; Palleros, D. *J. Org. Chem.*, previous paper in this issue.

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[14] Equation 8 of the preceding paper.[8]

Table IV. Kinetics[a] of the Reaction of 2,4-Dinitrofluorobenzene with *o*-Anisidine (B) and Pyridine (P) in Benzene at 60 °C at Low [B]

	[B], M		
10^2[P], M	0.0248	0.0521	0.0736
3.07	3.93	4.09	4.24
6.20		8.92	

[a] $10^5 k_A$, s^{-1} M^{-1}.

plot of k_A vs. [P] are gathered in Table II. Application of the least-squares method to these data allows the determination of k_γ and k_δ as the slope and the intercept of the linear correlation of k'/k_{-4} vs. [B], respectively. From the reactions at [P] = 0, k_α and k_β can be evaluated, and the four constants are given in Table III.

Experiments at Low [B]. Heretofore, it has been shown that eq 11 holds in the range of [B] = 0.1–0.8 M. It is possible that the assumptions that led to eq 10 are no longer valid at lower [B]. Therefore, some experiments were run in the range [B] = 0.025–0.1 M at 60 °C in the presence of [P] = 0.037 and 0.062 M. The data are gathered in Table IV. At these low values of [B] the points for k_A vs. [B] tend toward a straight line of slope 5.9×10^{-5} s^{-1} M^{-2} and intercept 3.8×10^{-5} s^{-1} M^{-1} (for [P] = 0.037 M). If the eq 11 holds, the slope of k_A vs. [B] at the origin is a measure of $k_\alpha + k_\gamma$[P]. From the data of Table III, this term can be evaluated, and the value of 4.4×10^{-5} s^{-1} M^{-1} is obtained, which agrees fairly well with the value of 5.9×10^{-5} s^{-1} M^{-1} found for the runs at low [B]. This evidence allows one to conclude that eq 11 holds in the whole range of [B] studied, i.e., 0.02–0.8 M.

From the magnitude order of the calculated constants it is possible to estimate a higher limit for the value of the uncatalyzed term in eq 11; since k_δ[P] is between 2 and 8 10^{-5} s^{-1} M^{-1}, the uncatalyzed term should be $<6 \times 10^{-7}$ s^{-1} M^{-1}. For measurement of this term it would be necessary to work at very low [B] and also at very low [P], but the reactions would become too low to be measured under those conditions.

Further Remarks. In the preceding treatment the term in $[P]^2$ was considered to be negligible for the present reaction since linear dependence of k_A with [P] is observed experimentally. This behavior could also be explained on the basis of a pyridine-catalyzed decomposition of the zwitterionic intermediate III without the intermediation of an adduct between *o*-anisidine and pyridine which would form intermediate IV. Previously studied reactions of the same substrate with butylamine,[15] benzylamine,[16] piperidine,[17,18] and *N*-methylbenzylamine[16] also exhibit a linear dependence of the observed rates with increasing amounts of pyridine, which was interpreted in the classical terms for base catalysis.

To account for the complete kinetic results presented here, one can see that a reaction scheme including intermediates II and III and an additional pyridine-catalyzed pathway (k_6[P]) from III to V would also be satisfactory. The resulting overall rate law would be eq 12. Although

$$k_A = k_4k_5 + (k_3k_4 + k_1k_5K_1)[B] + k_1k_3K_1[B]^2 + k_4k_6[P] + k_1k_6K_1[B][P]/k_{-4} + k_5 + (k_{-1} + k_3)[B] + k_6[P] \quad (12)$$

both reaction schemes are indistinguishable on the grounds of the present results, the mechanism depicted in Scheme I is somewhat preferred for the following reasons: (a) pyridine is known to form a 1:1 complex with *o*-anisidine, and the intermediate IV should be more stable than intermediate III; (b) in the reaction of DNF with morpholine (M) in benzene[19] the dependence of k_A with [P] departs from the line (upward curvature), and this was considered to be a medium effect due to the relatively high [P] used (up to 0.5 M). Nevertheless, if data are treated as if a 1:1 complex between morpholine and pyridine is formed, an empirical equation can be formulated (eq 13) for the overall-rate second-order rate coefficient which contains a term in $[P]^2$.

$$k_A = k_0 + k_M[M] + k_P[P] + k_{P \cdot M}[P]^2 \quad (13)$$

If the terms independent of [P] are divided by [P] and the quotient plotted against [P], a straight line is obtained, which demonstrates the validity of eq 13 and the existence of a nonnegligible term in $[P]^2$ for this case. In the reactions studied in the present work [P] was not too high (<0.07 M), and that might be the reason why the term in $[P]^2$ was not detected.

Although there are other kinetically indistinguishable mechanisms, we feel the evidence presented here strongly supports the operation of the dimer.

Experimental Section

Reagents and Solvents. *N*-(2,4-Dinitrophenyl)2-methoxyaniline was prepared by standard procedures[20] from 2,4-dinitrochlorobenzene and *o*-anisidine and was crystallized from ethanol; mp 167–168 °C (lit.[20] mp 164 °C). The structure was fully supported by ^{1}H NMR and mass spectra. *o*-Anisidine (Fluka) was distilled twice under nitrogen at reduced pressure, and the fraction at 124.5–125.5 °C (27 mmHg) was stored in sealed bulbs under nitrogen and kept in the dark. Pyridine (ucb) was left over sodium hydroxide for several days and distilled immediately before use. Benzene was kept over sodium wire for several days, distilled over sodium, and stored in a special vessel which allows delivery without air contamination.

Ancillary Spectrophotometric Measurement. UV and visible spectra of the substrate and of the product of its interaction with *o*-anisidine were recorded in a Beckman DK 2A spectrophotometer. The extinction coefficients were determined in a Beckman DU 2 spectrophotometer at the maximum absorbance wavelength of the substitution product, 360 nm. They are 184, 0.0162, and 15076 M^{-1} cm^{-1} for DNF, *o*-anisidine, and *N*-(2,4-dinitrophenyl)-2-methoxyaniline, respectively. The solutions were found to obey Beer's law. Pyridine is transparent under these conditions.

Kinetic Procedures. The reactions were studied spectrophotometrically.[21] 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 the substrate, *o*-anisidine, and pyridine in benzene were prepared and mixed at room temperature, and portions were put in sealed bulbs and immersed in a thermostat. Samples were taken at intervals and cooled, and the optical densities were measured at 360 nm. Pseudo-first-order rate coefficients, k_ψ, were obtained by the least-squares method as the slope of the correlation ln $(A_\infty - A_t)$ against t, where A_∞ is the optical density of the reaction mixture measured at "infinity" time (more than 10 half-lives) and A_t is the optical density measured at different time intervals and properly corrected by taking into account the substrate and the *o*-anisidine absorbances. The second-order rate coefficients k_A were obtained by dividing k_ψ by the *o*-anisidine concentration. Rate coefficients were reproducible to ±2%. No corrections for expansion coefficients were applied to the concentration values.

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Note Added in Proof. While this paper was in press, two works—one related to a dimer-catalyzed decomposition of the σ-intermediate (Bamkole, T. O.; Hirst, J.; Onyido I. *J. Chem. Soc., Perkin Trans. 2* **1982**, 889) and the other to mechanism II in the preceding paper (Banjoko, O.; Ezeani, C. *Ibid.* **1982**, 1356)—appeared. Comments on these two papers as well as on the role of the third amine molecule in the dimer mechanism and a solvent effects study have been submitted for publication in this journal.

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Registry No. 2,4-Dinitrofluorobenzene, 70-34-8; *o*-anisidine, 90-04-0; pyridine, 110-86-1.

Conversion of Sulfones to Sulfoxides via Hydride Reduction of (Aryloxy)sulfoxonium Salt Intermediates

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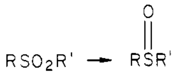
The conversion of sulfones into sulfoxides by a two-stage procedure, involving initial reaction of the sulfone with 4-chlorobenzenediazonium tetrafluoroborate to form an (aryloxy)sulfoxonium salt, $R_2{}^+S(O)OArBF_4{}^-$, and subsequent reduction of this with $NaBH_4 \cdot Al_2O_3$, has been investigated. Variations in the nature and amount of the diazonium salt used and its counterion, the temperature of the reaction, and solvent and concentration effects have been investigated in a largely unsuccessful attempt to improve significantly upon the yields in the first stage. It has been found, by using $NaBD_4$, that the hydride reduction of the (aryloxy)sulfoxonium salt in the second stage proceeds mainly by hydride attack at sulfur, rather than by a Pummerer-type mechanism. The latter mechanism, however, does occur when strong base is added to the (aryloxy)sulfoxonium salt prior to hydride reduction.

The procedure, recently reported in preliminary form,[1] for achieving the novel conversion of sulfone **1** → sulfoxide **2** remains almost a unique method for achieving this



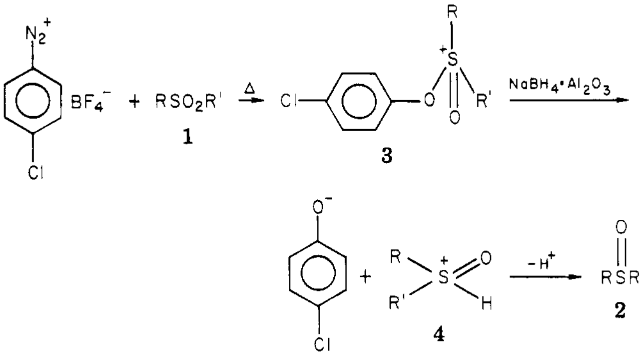
$$RSO_2R' \longrightarrow R\overset{O}{\overset{\|}{S}}R'$$

1 **2**

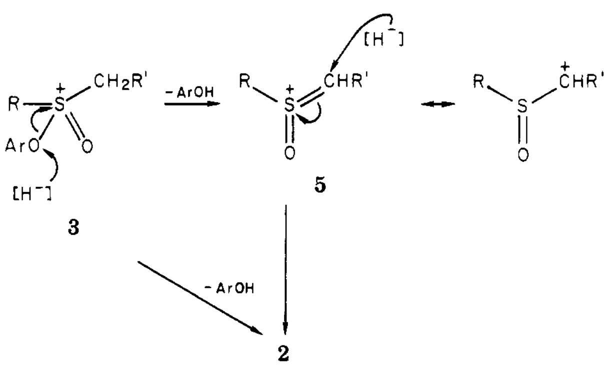
synthetic objective.[2] We were interested in carrying out a number of experiments aimed at improving yields, especially in the first stage of the reaction, the formation of an (aryloxy)sulfoxonium salt from the sulfone, which we found initially[1] gave rather modest, and sometimes variable, yields.

We were also interested in the mechanistic question of how the sodium borohydride reduction of the intermediate (aryloxy)sulfoxonium salt **3** took place. Our earlier proposal was that this involved hydride attack directly on the positively charged sulfur atom in **3**, which is well precedented,[3,4] and is proposed by Whiting et al.[3] to involve initial addition and then elimination, leading via the S-protonated sulfoxide **4** to the sulfoxide (Scheme I). Venier et al.,[5] however, recently suggested that hydride attack was more likely to occur at the α-carbon of a sulfinylcarbenium ion, **5**, via a Pummerer-like elimination–addition sequence (Scheme II). A third, albeit less likely, mechanistic possibility is also shown in Scheme II, namely, hydride attack at the *oxygen* atom in **3**.

Scheme I



Scheme II



The results of both aspects of this investigation will now be presented.

Results and Discussion

The first stage in the reaction involves thermal decomposition of an arenediazonium salt at 130 °C in the pres-

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[1] Still, I. W. J.; Szilagyi, S. *Synth. Commun.* **1979**, *9*, 923.

[2] For a single earlier example, cf.: Anastassiou, A. G.; Wetzel, J. C.; Chao, B. Y. C. *J. Am. Chem. Soc.* **1975**, *97*, 1124. We thank Professor E. Block, SUNY (Albany), for bringing this paper to our notice.

[3] Chalkley, G. R.; Snodin, D. J.; Stevens, G.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1580.

[4] Shimagaki, M.; Tsuchiya, H.; Ban, Y.; Oishi, T. *Tetrahedron Lett.* **1978**, 3435.

[5] Venier, C. G.; Wing, F. A., Jr.; Barager, H. J. *Tetrahedron Lett.* **1980**, *21*, 3159.

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