

# Mechanism and Linear Free Energy Relationships in the Kinetics of Formation of Bicyclo[3.3.1]nonane Derivatives from 1,3,5-Trinitrobenzene, Benzoylacetones, and Base

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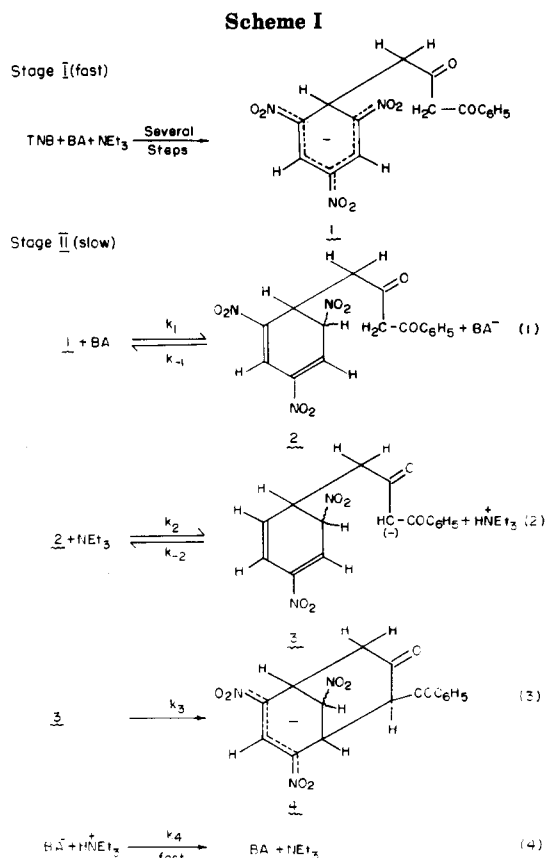
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The kinetics and mechanism of cyclization of the anionic  $\sigma$  complex obtained from the reaction of *sym*-trinitrobenzene (TNB) and benzoylacetone (BA) in the presence of triethylamine ( $\text{NEt}_3$ ) have been studied in  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$  (80% v/v). The order of the reaction has been found to be zero in TNB, unity in BA, fractional in  $\text{NEt}_3$ , and negative and nonintegral in  $\text{H}^+\text{NEt}_3$ . When the solvent is changed from  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$  (80% v/v) to  $\text{CH}_3\text{CN}$  the order with respect to TNB is zero, BA is unity,  $\text{NEt}_3$  is unity, and  $\text{H}^+\text{NEt}_3$  is negative and nonintegral. The fractional order with respect to  $\text{NEt}_3$  in  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$  (80% v/v) was found to be due to the involvement of  $\text{Me}_2\text{SO}$  in proton abstraction and hence in cyclization. DMF also brought about the cyclization in a similar manner. The plot of rate constants for the formation of bicyclic complexes from substituted benzoylacetones and TNB vs.  $\sigma^+/\sigma$  concaved downward indicating a change in the rate determining step.

Strauss et al. have examined the kinetics and mechanism of formation and cyclization of some carbanionic  $\sigma$  complexes and reported that all cyclizations are mechanistically similar.<sup>2,3</sup> Previous studies in our laboratories<sup>4</sup> on the cyclization of 1:1 Meisenheimer adduct derived from 1,3,5-trinitrobenzene (TNB) and acetoacetanilide in the presence of  $\text{NEt}_3$  have also established the same mechanistic picture as that of Strauss et al. However the cyclization process of the 1:1 Meisenheimer adduct derived from TNB and benzoylacetone (BA) in the presence of excess  $\text{NEt}_3$  differs to a certain extent mechanistically, as suggested and confirmed by the different kinetic data. Since the ketone selected for the present investigation has highly acidic hydrogen atoms, the reaction is initiated and cyclization completed by highly basic solvents such as  $\text{Me}_2\text{SO}$  and DMF even in the absence of an external base such as  $\text{NEt}_3$ . We report here the kinetics of the cyclization of 1:1 TNB-BA complex in  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$  (80% v/v, a basic solvent) and  $\text{CH}_3\text{CN}$ , a solvent with lower basicity than  $\text{Me}_2\text{SO}$ . A kinetic study of cyclization of TNB-BA and Meisenheimer adduct brought about by  $\text{Me}_2\text{SO}$  was also made. This is the first report in which a solvent brings about  $\sigma$  complex formation which is followed by cyclization. In all the experiments pseudo-first-order conditions were maintained and good kinetic plots resulted. The results are reproducible within 5% error.

Only one report has so far appeared on the structure-reactivity correlations in the conversion of  $\sigma$  complexes to bicyclo[3.3.1]nonane derivatives.<sup>5</sup> In order to expand the scope of correlation analysis in this field, in the present investigation, rate constants were correlated with substituent constants for the formation of bicyclic complexes from carbanions derived from different benzoylacetones and TNB in the presence of  $\text{NEt}_3$  in  $\text{CH}_3\text{CN}$  and in the absence of  $\text{NEt}_3$  in  $\text{Me}_2\text{SO}$ .

The addition of excess of  $\text{NEt}_3$  to a solution of BA and TNB in  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$  (80% v/v) gives rise immediately upon mixing to a visible spectrum with two maxima at 473 and 584 nm characteristic of 1:1 Meisenheimer complex and this rapidly changes to give a peak at 515 nm owing to the formation of the bicyclic adduct. These spectral changes, are illustrated in Figure 1. As reported earlier,<sup>3</sup>



in the present study, the slow disappearance of 1:1 Meisenheimer complex has been followed at 570 nm.

## Results and Discussion

In  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$  (80% v/v), at 40 °C, the cyclization rate was observed to be zero order in TNB (Figure 2, line A), first order in BA (Figure 2, line B, slope 0.99, and line c, slope 0.99), fractional order in  $\text{NEt}_3$  (Figure 2, line D, slope 0.66, and line E, slope 0.78), and negative nonintegral order in  $\text{H}^+\text{NEt}_3$  (Figure 3, curve A, slope  $\sim -0.47$ , and curve B, slope  $\sim -0.40$ ) and increased by increasing ionic strength (Figure 3, line c). A similar rate picture was noticed even at lower temperatures and at 580 nm. When the same cyclization process was carried out in a less basic solvent,  $\text{CH}_3\text{CN}$ , the rate was found to be zero order in TNB (Figure 4, line B), first order in BA (Figure 4, line A, slope 0.96), first order in  $\text{NEt}_3$  (Figure 4, line C, slope 0.97), and

(1) To whom all inquiries should be addressed.

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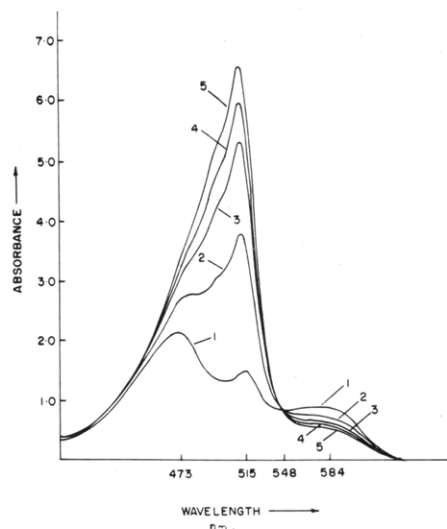


Figure 1. Visible spectral changes on conversion of 1 to 4. Repeated scans at 1 min intervals at 35 °C.

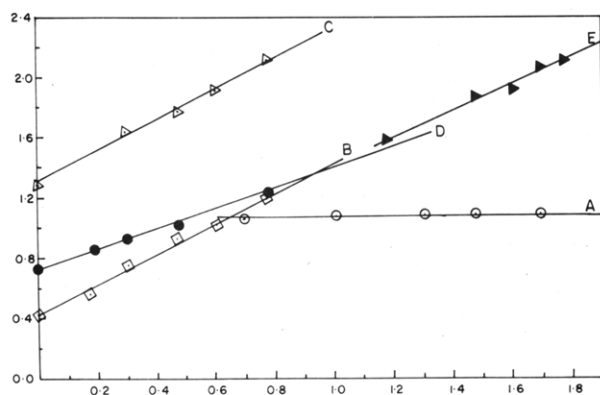


Figure 2. Effect of TNB, BA, and  $\text{NET}_3$  concentrations on the rate of stage II in  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$  [80%, v/v] at 40 °C. (A)  $\circ$ ,  $4 + \log [\text{TNB}]$  vs.  $2 + \log k_{\text{obsd}}$ ; [BA] = 0.04 M; [ $\text{NET}_3$ ] = 0.05 M; [ $\text{H}^+\text{NET}_3\text{Cl}^-$ ] = 0.003 M; [ $^+\text{NET}_4\text{Cl}^-$ ] = 0.015 M. (B)  $\square$ ,  $2 + \log [\text{BA}]$  vs.  $2 + \log k_{\text{obsd}}$ ; [TNB] = 0.0008 M; [ $\text{NET}_3$ ] = 0.03 M. (C)  $\Delta$ ,  $2 + \log [\text{BA}]$  vs.  $3 + \log k_{\text{obsd}}$ ; [TNB] = 0.0008 M; [ $\text{NET}_3$ ] = 0.04 M; [ $\text{H}^+\text{NET}_3\text{Cl}^-$ ] = 0.005 M. (D)  $\bullet$ ,  $2 + \log [\text{NET}_3]$  vs.  $2 + \log k_{\text{obsd}}$ ; [TNB] = 0.0008 M; [BA] = 0.04 M. (E)  $\blacktriangle$ ,  $3 + \log [\text{NET}_3]$  vs.  $3 + \log k_{\text{obsd}}$ ; [TNB] = 0.0008 M; [BA] = 0.04 M; [ $\text{H}^+\text{NET}_3\text{Cl}^-$ ] = 0.005 M.

negative nonintegral order in  $\text{H}^+\text{NET}_3$  (Figure 4, curve E, slope  $\sim -0.57$ ) and increased by increasing ionic strength (Figure 4, line D). Our latter observations are consistent with the detailed mechanism illustrated in Scheme I.

Since methylene protons of BA are highly acidic, step 1 is significant and enters into the kinetic picture and hence, the rate expression for this reaction is different from that of Strauss.<sup>3</sup> The rate of formation of 4 can be given as

$$\frac{d[4]}{dt} = -\frac{d[1]}{dt} = k_3[3] \quad (5)$$

For the sequence of reactions under stage II outlined in Scheme I, two rate limiting expressions can be derived. On the basis of steady-state treatment

$$\frac{d[4]}{dt} = -\frac{d[1]}{dt} = \frac{K_1 k_2 k_3 [1] [\text{NET}_3] [\text{BA}]}{k_{-2} [\text{H}^+\text{NET}_3] [\text{BA}^-] + k_3 [\text{BA}^-]} \quad (6)$$

On the basis of preequilibrium treatment

$$\frac{d[4]}{dt} = -\frac{d[1]}{dt} = \frac{K_1 K_2 k_3 [1] [\text{NET}_3] [\text{BA}]}{[\text{H}^+\text{NET}_3] [\text{BA}^-]} \quad (7)$$

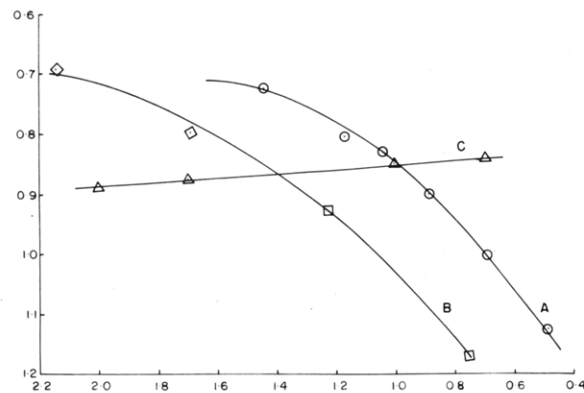


Figure 3. Effect of  $\text{H}^+\text{NET}_3\text{Cl}^-$  and  $^+\text{NET}_4\text{Cl}^-$  concentrations on the rate of stage II in  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$  [80% v/v] at 40 °C. (A)  $\circ$ ,  $3 + \log [\text{H}^+\text{NET}_3\text{Cl}^-]$  vs.  $2 + \log k_{\text{obsd}}$ ; [TNB] = 0.0008 M; [BA] = 0.03 M; [ $\text{NET}_3$ ] = 0.06 M. (B)  $\square$ ,  $4 + \log [\text{H}^+\text{NET}_3\text{Cl}^-]$  vs.  $2 + \log k_{\text{obsd}}$ ; [TNB] = 0.0008 M; [BA] = 0.03 M; [ $\text{NET}_3$ ] = 0.04 M; [ $^+\text{NET}_4\text{Cl}^-$ ] = 0.05 M. (C)  $\Delta$ ,  $3 + \log [^+\text{NET}_4\text{Cl}^-]$  vs.  $2 + \log k_{\text{obsd}}$ ; [TNB] = 0.0008 M; [BA] = 0.03 M; [ $\text{NET}_3$ ] = 0.025 M.

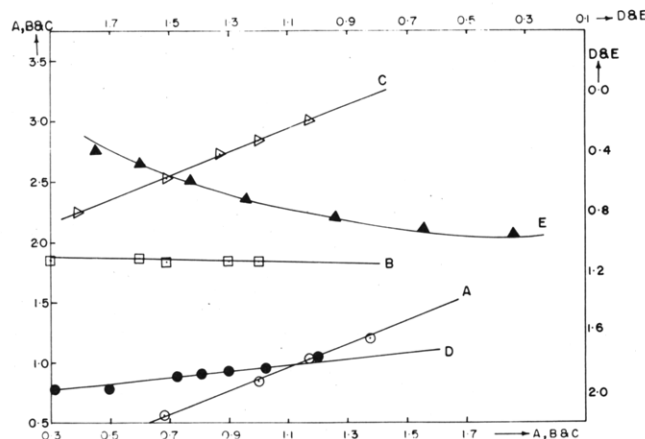
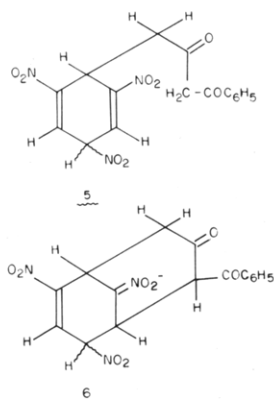


Figure 4. Effect of BA, TNB,  $\text{NET}_3$ ,  $^+\text{NET}_4\text{Cl}^-$ , and  $\text{H}^+\text{NET}_3\text{Cl}^-$  concentrations on the rate of stage II in  $\text{CH}_3\text{CN}$  at 30 °C. (A)  $\circ$ ,  $2 + \log [\text{BA}]$  vs.  $2 + \log k_{\text{obsd}}$ ; [TNB] = 0.0005 M; [ $\text{NET}_3$ ] = 0.1 M; [ $\text{H}^+\text{NET}_3\text{Cl}^-$ ] = 0.00878 M; [ $^+\text{NET}_4\text{Cl}^-$ ] = 0.2296 M. (B)  $\square$ ,  $4 + \log [\text{TNB}]$  vs.  $3 + \log k_{\text{obsd}}$ ; [BA] = 0.1 M; others same as A. (C)  $\Delta$ ,  $2 + \log [\text{NET}_3]$  vs.  $4 + \log k_{\text{obsd}}$ ; others same as B. (D)  $\bullet$ ,  $3 + \log [^+\text{NET}_4\text{Cl}^-]$  vs.  $3 + \log k_{\text{obsd}}$ ; [TNB] = 0.0004 M; [BA] = 0.1 M; [ $\text{NET}_3$ ] = 0.1 M. (E)  $\blacktriangle$ ,  $3 + \log [\text{H}^+\text{NET}_3\text{Cl}^-]$  vs.  $2 + \log k_{\text{obsd}}$ ; others same as B.

According to eq 6 and 7 the reaction rate should be zero order in TNB, first order in BA, and first order in  $\text{NET}_3$ . A plot of first-order rate coefficients vs. [ $\text{H}^+\text{NET}_3$ ] is curvilinear (Figure 4, curve E, slope  $\sim -0.57$ ) and hence rate expression 6 is applicable for the cyclization process. When  $\text{H}^+\text{NET}_3$  is constant (equal to the initially added TNB) and  $^+\text{NET}_4$  is varied, little effect on the rate of cyclization is seen (Figure 4, line D). This is expected for a reaction in which charge is neither created nor destroyed. The very slight increase in rate with increasing salt concentration can be attributed to the stabilization of 3 which is formed from the neutral entity 2.

Protonation of 1 at  $\text{C}_4$  results in 5. One would expect adduct 5 to undergo a similar type of reaction as 2 as represented in Scheme I to give bicyclic adduct 6. Formation of adduct 6 has been ruled out due to the following reasons: (i) An NMR spectrum of the isolated adduct has a peak at  $\delta$  5.7 due to a bridging proton and a peak at  $\delta$  8.4 due to the propenide proton. These protons are absent in adduct 6. (ii) Adduct 4 is more stable than adduct 6 due to its delocalized charge.

We have also considered the possibility of proton transfer from the highly acidic methylene group of the side

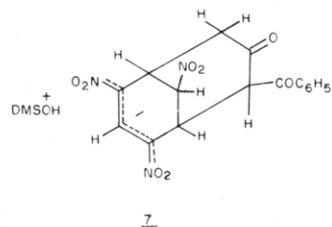


chain to the ring in 1, followed by intramolecular attack on the resultant dinitro diene function of 3. This mechanism can be dismissed on the ground that the kinetic data are consistent with the reaction sequence specified in Scheme I.

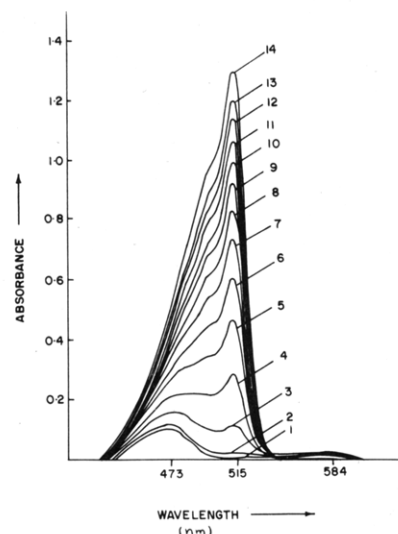
In  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$  (80% v/v) eq 6 holds except that order with respect to  $\text{NEt}_3$  is fractional. This is due to the fact that  $\text{Me}_2\text{SO}$  also initiates proton abstraction and carbanionic  $\sigma$  complex formation and also effects the cyclization process.

**Cyclization Process Catalyzed by  $\text{Me}_2\text{SO}$ .** In the absence of  $\text{NEt}_3$ , when a solution of TNB in  $\text{Me}_2\text{SO}$  was mixed with excess BA in  $\text{Me}_2\text{SO}$ , two absorption maxima were noticed at 473 and 584 nm immediately in the visible spectrum, which changed to give a peak at 515 nm. These spectral changes (Figure 5) are similar to those illustrated in Figure 1 and clearly indicate that the same type of adducts are formed in the absence and in the presence of  $\text{NEt}_3$  in  $\text{Me}_2\text{SO}$ . Since the basicity of  $\text{Me}_2\text{SO}$  is less than that of  $\text{NEt}_3$ , the amount of 1:1 Meisenheimer adduct produced by the former is also less as indicated by smaller optical density values at 473 and 584 nm. Hence in the present study the rate of cyclization catalyzed by  $\text{Me}_2\text{SO}$  has been conveniently measured by observing the increase in absorbance at 510 nm rather than the decrease in absorbance at 570 nm.

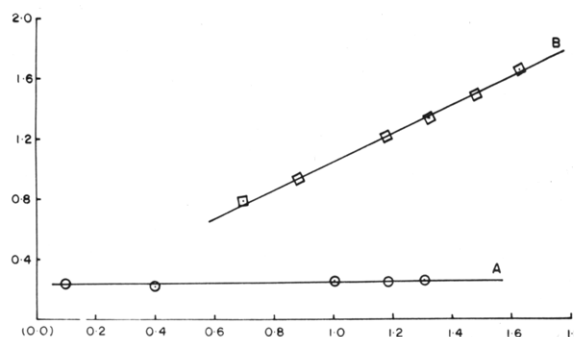
Double logarithmic plots of  $k_{\text{obsd}}$  with concentration of TNB (Figure 6, line A) and BA (Figure 6, line B) are linear with slopes 0 and 0.96, respectively. It has also been noticed that the cyclization rate decreased with decreasing percentage of  $\text{Me}_2\text{SO}$ . Repeated attempts to isolate 7 were unsuccessful. Since the cyclization process of the TNB-BA- $\text{NEt}_3$  system is catalyzed by both  $\text{NEt}_3$  and  $\text{Me}_2\text{SO}$  in  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ , log-log plots of  $\text{NEt}_3$  concentration vs.  $k_{\text{obsd}}$  have slopes less than unity, 0.66 and 0.78 in the absence and presence of added salt, respectively.



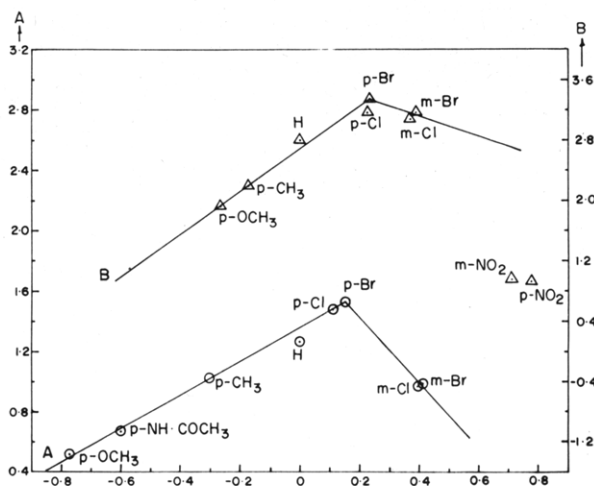
**Substituent Effect.** The rate constants for the formation of bicyclic adducts from the 1:1 Meisenheimer adducts of TNB and various substituted benzoylacetones in the presence of  $\text{NEt}_3$  in  $\text{CH}_3\text{CN}$  and those in the absence of  $\text{NEt}_3$  in  $\text{Me}_2\text{SO}$  at three different temperatures are presented in Table I. Figure 7, curve B, reflects good correlation at 35 °C between the rate constants of the  $\text{NEt}_3$  catalyzed cyclization reaction and  $\sigma$  ( $r = 0.99$ ,  $s = 0.10$ ,  $\rho = 2.82$ ) and Figure 7, curve A, indicates excellent corre-



**Figure 5.** Visible spectral changes on conversion of 1 to 4 for the  $\text{Me}_2\text{SO}$  catalyzed cyclization reaction. Repeated scans at 15-min intervals at 35 °C.



**Figure 6.** Effect of TNB and BA concentrations on the rate of stage II of the  $\text{Me}_2\text{SO}$  catalyzed cyclization reaction at 40 °C. (A)  $\odot$ ,  $5 + \log [\text{TNB}]$  vs.  $3 + \log k_{\text{obsd}}$ ;  $[\text{BA}] = 0.1 \text{ M}$ ;  $[\text{NEt}_4\text{Cl}] = 0.00887 \text{ M}$ . (B)  $\square$ ,  $2 + \log [\text{BA}]$  vs.  $4 + \log k_{\text{obsd}}$ ;  $[\text{TNB}] = 0.00005 \text{ M}$ ;  $[\text{NEt}_4\text{Cl}] = 0.00887 \text{ M}$ .



**Figure 7.** (A)  $\odot$ ,  $\sigma^+$  vs.  $4 + \log k_{\text{obsd}}$ . Substituent effect in  $\text{Me}_2\text{SO}$  catalyzed cyclization reaction at 35 °C. (B)  $\Delta$ ,  $\sigma$  vs.  $4 + \log k_{\text{obsd}}$ . Substituent effect in  $\text{NEt}_3$  catalyzed reaction; solvent,  $\text{CH}_3\text{CN}$ ; temperature, 35 °C.

lation when rate constants of the  $\text{Me}_2\text{SO}$  catalyzed reaction are plotted against  $\sigma^+$  ( $r = 0.99$ ,  $s = 0.05$ ,  $\rho = 1.14$ ) at 35 °C.

The point of interest in the present investigation is that the plot of  $\log k_{\text{obsd}}$  vs. substituent constant in either the  $\text{NEt}_3$  catalyzed cyclization reaction or  $\text{Me}_2\text{SO}$  catalyzed



crystallized from ethanol-water solutions with decolorizing carbon.

**Kinetic Runs in 80% Me<sub>2</sub>SO and CH<sub>3</sub>CN.** Stock solutions of TNB, BA, NEt<sub>3</sub>, and the salts were prepared in either of the solvents and thermostated at the experimental temperature, and the quantities for each run were pipetted into volumetric flasks and diluted to the required volume. The decrease in absorbance as a function of time was then recorded at 570 nm against solvent blank by employing a nonrecording Carl-Zeiss VSU2-P spectrophotometer.

**Kinetic Runs in Me<sub>2</sub>SO.** Kinetics of the cyclization process catalyzed by Me<sub>2</sub>SO were followed by mixing the appropriate solutions (preequilibrated to required temperature) and transferring the reaction mixture to a thermostated cell in a Carl-Zeiss VSU2-P spectrophotometer. The increase in absorbance as a function of time was then recorded at 510 nm against solvent

blank. Figures 1 and 5 were obtained on a Carl-Zeiss UV-vis spectrod.

**Acknowledgment.** We are very grateful to the Department of Science and Technology, Government of India, for a research grant.

**Registry No.** 1:1 TNB-(*p*-OCH<sub>3</sub>)BA complex, 95346-53-5; 1:1 TNB-(*p*-NHCOCH<sub>3</sub>)BA complex, 95346-54-6; 1:1 TNB-(*p*-CH<sub>3</sub>)BA complex, 95346-55-7; 1:1 TNB-BA complex, 95346-56-8; 1:1 TNB-(*p*-Cl)BA complex, 95346-57-9; 1:1 TNB-(*p*-Br)BA complex, 95346-58-0; 1:1 TNB-(*m*-Cl)BA complex, 95346-59-1; 1:1 TNB-(*m*-Br)BA complex, 95346-60-4; 1:1 TNB-(*m*-NO<sub>2</sub>)BA complex, 95346-61-5; 1:1 TNB-(*p*-NO<sub>2</sub>)BA complex, 95346-62-6; NEt<sub>3</sub>, 121-44-8.

## Direct Synthesis of 5-Methyl-3-aryl-1,2,4-oxadiazoles from Aryl Aldehydes, Nitroethane, and Ammonium Acetate

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The condensation of 2,5-dimethoxybenzaldehyde (**1b**) with nitroethane and ammonium acetate in glacial acetic acid has been found to give three different products, depending on reactant ratio and reaction time. At an aldehyde:nitroethane:ammonium acetate ratio of 1:1.5:0.8 a normal Knoevenagel condensation occurred, yielding 1-(2,5-dimethoxyphenyl)-2-nitropropene. At a reactant ratio of 1:3:2 (same reactant sequence), the primary product was 2,5-dimethoxybenzoxazole, and at a reactant ratio of 1:40:8, with extended reflux time, the major product was 3-(2,5-dimethoxyphenyl)-5-methyl-1,2,4-oxadiazole (**8b**). This last reaction served as a prototype for a new oxadiazole synthesis which was then extended to include six additional 5-methyl-3-aryl-1,2,4-oxadiazoles (**8a-c-g**; where aryl = Ph, 2,5-dimethoxyphenyl, 2,4-dichlorophenyl, *m*-chlorophenyl, *p*-tolyl, 3,5-dimethoxyphenyl, and *p*-carboxyphenyl), whose structures were assigned on the basis of <sup>13</sup>C NMR characteristics of known reference compounds. Benzoxazole also reacted with excess nitroethane and ammonium acetate to yield 5-methyl-3-phenyl-1,2,4-oxadiazole (**8a**). The overall mechanism of oxadiazole formation is shown to be dependent on a preliminary reaction wherein the nitroalkane, in the presence of ammonium acetate and acetic acid, is first transformed into the corresponding alkanic acid and hydroxylamine. Hydroxylamine then converts the aromatic aldehyde, via the intermediary nitrile, to the oxadiazoles following reactions of established precedent.

Major synthetic routes to the 1,2,4-oxadiazoles have been recently reviewed by Clapp,<sup>1</sup> who pointed out that 95% of the practical preparations are encompassed by two general methods; viz., (a) the condensation of amidoximes with carboxylic acid derivatives, and (b) the dipolar cycloaddition of nitrile oxides to nitriles. Subsequently, Lin and co-workers<sup>2</sup> reported a new general method in which *N'*-acyl-*N,N*-dimethylamides react with hydroxylamine to form 3,5-disubstituted or 5-monosubstituted 1,2,4-oxadiazoles in high yields.

We have now observed a new and unusual formation of 5-methyl-3-aryl-1,2,4-oxadiazoles (**8a-g**, Table I) from the reaction of aromatic aldehydes with nitroethane in the presence of ammonium acetate and report here several examples of the synthesis along with evidence concerning the mechanism of the transformation (Scheme I).

The Henry (Knoevenagel) condensation of aromatic aldehydes with nitroalkanes is by now a classical route to β-nitrostyrenes.<sup>3</sup> In a particular application of this process

Table I. <sup>1</sup>H and <sup>13</sup>C NMR Resonance Assignments<sup>a</sup> for the 5-Methyl-3-aryl-1,2,4-oxadiazoles **8a-g**

8	Ar	δ (ppm)			
		5-Me	5-Me	C-3	C-5
a	phenyl	2.54	11.8	168.0	176.1
b	2,5-dimethoxyphenyl	2.65	12.2	166.8	175.4
c	2,4-dichlorophenyl	2.68	12.0	166.2	176.0
d	<i>m</i> -chlorophenyl	2.64	12.3	167.4	176.8
e	<i>p</i> -tolyl	2.38	12.2	168.3	176.2
f	3,5-dimethoxyphenyl	2.46	12.4	168.4	176.5
g	<i>p</i> -carboxyphenyl	2.70	12.0	167.0	177.7

<sup>a</sup> δ values are ppm with respect to Me<sub>4</sub>Si.

we had prepared 1-(2,5-dimethoxyphenyl)-2-nitropropene (**2b**) from 2,5-dimethoxybenzaldehyde (**1b**), nitroethane, and ammonium acetate (ratio 1:1.5:0.8) via a 3-h reflux in acetic acid essentially as described in the literature.<sup>4</sup> While the yield was quite adequate (70%), an attempt was made to improve it by altering the proportions of **1b**:

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