and 1.25 (2 overlapping t, superimposed on d, 9, 2 OCH_2CH_3 plus CH_3CHCH_2), 1.82 (d, 3, J = 7 Hz, $=CHCH_3$), 2.58 and 2.62 (2 overlapping d, 2, J = 7–8 Hz, $CH_2C{=}O$), 3.3 (m, 1, methinyl H), 4.05 and 4.15 (2 overlapping q, 4, J = 6–7 Hz, 2 OCH_2CH_3), 6.81 (q, 1, vinyl H); mass spectrum m/e (rel intensity) 228 (7, M^+), 183 (90, M − C_2H_5O), 182 (93), 155 (21), 154 (100), 140 (18), 126 (57), 125 (20), 113 (27), 112 (27), 95 (27), 81 (33), 69 (22), 67 (39), 53 (16).

Saponification of **7** gave **2-ethylidene-3-methylglutaric acid** as needles from benzene–hexane, mp 129–130° (lit.[16] mp 129°).

Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.79; H, 7.09.

From chromatographic effluent d was isolated **4d** (31%).

When this electroreduction experiment was repeated in exactly the same way except that the ethyl crotonate was only stirred with the catholyte (open circuit) for 23 min after reduction of **1d** (alone) was complete, there resulted **4d** (25%) but no **7**.

Acknowledgment.—The authors wish to thank Dr. Henning Lund of Aarhus University, Denmark, and Dr. Lennart Eberson of the University of Lund, Sweden, for discussions of mechanistic aspects of this research.

Registry No.—**1a**, 4192-77-2; **1b**, 29584-63-2; **1c**, 40918-86-3; **1d**, 24393-65-5; **1e**, 40918-88-5; **1f**, 24393-66-6; **1g**, 40918-96-5; **1h**, 40918-97-6; **1i**, 40918-98-7; **1j**, 29584-64-3; **2**, 623-70-1; **3**, 40918-90-9; **4a**, 40918-91-0; **4c**, 40918-92-1; **4d**, 41021-30-1; **4g**, 40918-93-2; **4h**, 40918-94-3; **4i**, 40918-95-4; **4j**, 40919-00-4; **5**, 40919-01-5; **6**, 13351-28-5; **7**, 18418-07-0; **10**, 5462-13-5; benzylamine, 100-46-9; *N*-benzyl-3-(3,4-dimethoxyphenyl)-propionamide, 40958-49-4; 2-ethylidene-3-methylglutaric acid, 40919-04-8.

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Condensation–Cyclization Reactions of Electron-Deficient Aromatics. VII. The Kinetics and Mechanism of Carbanionic σ-Complex Formation and Cyclization

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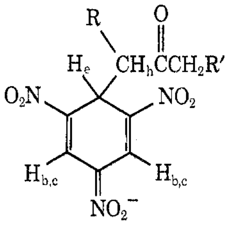
Received April 26, 1973

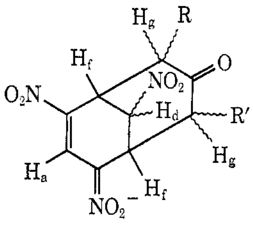
The kinetics and mechanism of formation and cyclization of the anionic σ complex obtained from the reaction of *sym*-trinitrobenzene and dibenzyl ketone are described. The reaction sequence is likely typical of a variety of similar condensation–cyclization reactions of electron-deficient aromatics with carbanions. Very rapid formation of anionic σ complex is followed by slow cyclization to bicyclic nitropropene nitronate.

Anionic σ complexes have been the subject of numerous thermodynamic and kinetic studies, both as metastable intermediates in aromatic nucleophilic substitution reactions and as products of aromatic addition. Much of this work has been summarized in several reviews.[1–5] The factors which govern the stability of such species and the way in which they are formed are now well known for a variety of different systems. In addition, the recently reported kinetic characterization of an observable metastable anionic σ complex intermediate in aromatic nucleophilic substitution in the naphthalene series[6] substantiates many early steady-state kinetic studies which had provided evidence for similar intermediates.[7–9] The resurgent interest in thermodynamic and kinetic characterizations of σ complexes of a variety of organic and inorganic bases with electron-deficient aromatics has provided considerable evidence substantiating the structure of these species and the way in which they form and decompose.

During the past 4 years, it has become clear that many carbanionic σ complexes, **1**, are unstable, not with regard to formation of a substitution product (which would require hydride expulsion), but because they readily undergo an internal cyclization reaction to yield the stable bicyclic nitropropene nitronate salts, **2**.[10–21]



1a, R = R′ = C_6H_5
b, R = R′ = -(CH_2CH_2)-
c, R = R′ = CH_3
d, R = R′ = H



2a, R = R′ = C_6H_5 (trans)
b, R = R′ = C_6H_5 (cis-endo)
c, R = R′ = C_6H_5 (cis-exo)

Isolation of intermediates, as well as qualitative visible and pmr spectral studies of the reaction, has provided evidence for two distinct cyclization mecha-

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nisms when amines are used to catalyze the formation of structures like 2 from potential bis carbanions and *sym*-trinitrobenzene (TNB).[12,13,15-17] These are shown in Schemes I and II.

SCHEME I[a]

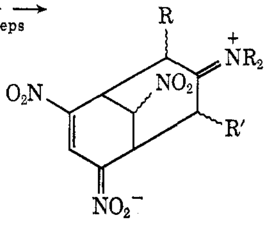
$$\mathrm{TNB} + \mathrm{RCH_2COCH_2R'} + \mathrm{NR_3} \xrightarrow[\text{steps}]{\substack{\text{(fast)}\\ \text{several}}} \mathbf{1},\ \mathrm{H\overset{+}{N}R_3}$$

$$\mathbf{1} \xrightarrow{\text{slow}} \mathbf{2}$$

[a] R and/or R′ of ketone are electron withdrawing or delocalizing. Reaction does not proceed when these groups are electron donating (*i.e.*, alkyl or H).

SCHEME II[a]

$$\mathrm{TNB} + \mathrm{RCH_2COCH_2R'} + \mathrm{HNR_2} \xrightarrow[\text{steps}]{\text{several}}$$



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$$\mathrm{H_2O} + \mathbf{3} \longrightarrow \mathbf{2},\ \mathrm{H_2\overset{+}{N}R_2}$$

[a] R and/or R′ of ketone are electron withdrawing *or* donating.

The qualitative evidence for these two mechanistic routes has been discussed in earlier papers,[11-13,15] and a preliminary kinetic study of the *tertiary* amine catalyzed cyclization of **1a** has been published.[16] We report here a detailed kinetic study of the fast condensation step and slow cyclization step of the tertiary amine catalyzed reaction represented in Scheme I, and propose detailed mechanisms for these steps which are likely typical for condensation–cyclization reactions of electron-deficient aromatics with acidic ketones or keto esters.

The reaction of dibenzyl ketone (DBK) and TNB in DMSO in the presence of triethylamine is particularly well suited for study. The reaction occurs in two stages, as shown in Scheme I, and the spectral characteristics of the intermediate σ complex and the product, as well as the relative rates of the two steps, are favorable for kinetic analysis by stopped flow and conventional spectrophotometric methods. In addition, the detailed product analysis published earlier for this system,[11] which showed that only a single bicyclic product forms in DMSO, has been confirmed in the present study. This observation simplifies kinetic analysis of the cyclization step considerably. A complete study of the DBK–TNB–NEt$_3$ system provides evidence that the proposed mechanism in this instance is similar to condensation–cyclization reactions of electron-deficient aromatics with a variety of acidic ketones and keto esters. Our observations will be shown to be consistent with the detailed mechanism illustrated in Scheme III.

Results

General Features of the Reaction.—Adding excess triethylamine to an equimolar solution of TNB and DBK in DMSO yields a brightly colored solution which produces, ultimately, a quantitative yield of the triethylammonium salt of the bicyclic nitropropene nitronate 2. The visible spectral changes which occur show that the reaction takes place in two stages. The first is a rapid formation of a visible spectrum characteristic of the trinitrocyclohexadienate function in **1a**,[1-5] which occurs immediately upon addition of amine to the DMSO solution of TNB and DBK. The rate of this condensation is too fast to follow by conventional means but can be measured by stopped flow spectrophotometric methods. The second stage of the reaction is much slower, and is characterized by the disappearance of absorption due to the σ complex, with concomitant appearance of a spectrum characteristic of the nitropropene nitronate function of 2.[3,14] These spectral changes are illustrated in Figure 1. The structures of the species responsible for the electronic absorption are supported by pmr spectra of the solu-

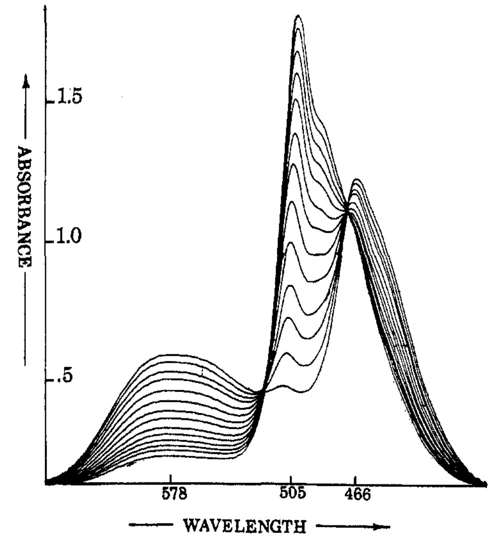
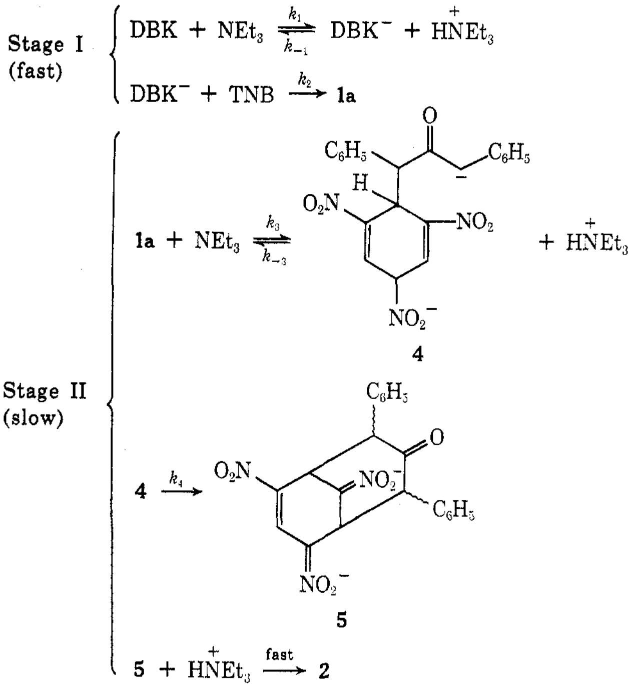


Figure 1.—Visible spectral changes on conversion of **1a** to **2**. Repeated scans at ~5-min intervals at room temperature.

SCHEME III



$$\mathrm{DBK} + \mathrm{NEt_3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{DBK^-} + \mathrm{H\overset{+}{N}Et_3}$$

$$\mathrm{DBK^-} + \mathrm{TNB} \xrightarrow{k_2} \mathbf{1a}$$

$$\mathbf{1a} + \mathrm{NEt_3} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathbf{4} + \mathrm{H\overset{+}{N}Et_3}$$

$$\mathbf{4} \xrightarrow{k_4} \mathbf{5}$$

$$\mathbf{5} + \mathrm{H\overset{+}{N}Et_3} \xrightarrow{\text{fast}} \mathbf{2}$$

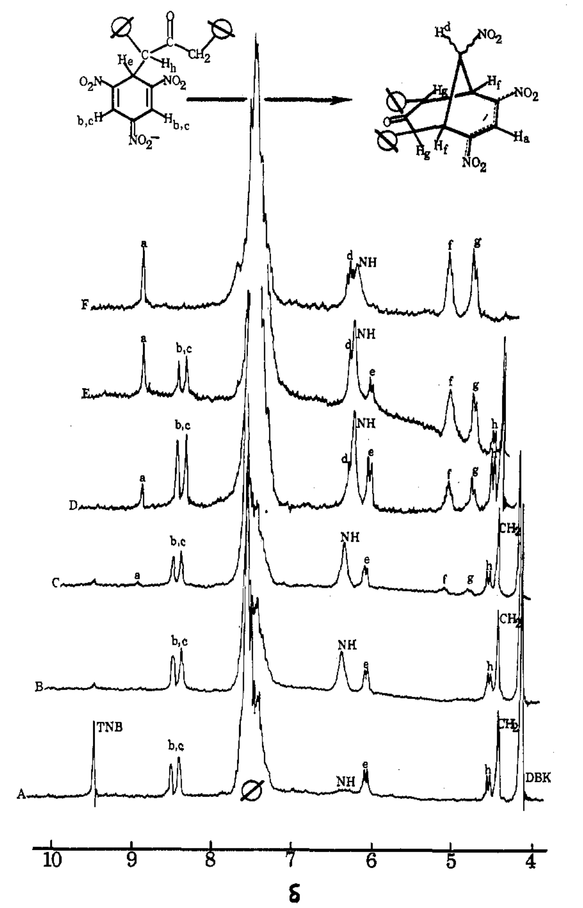
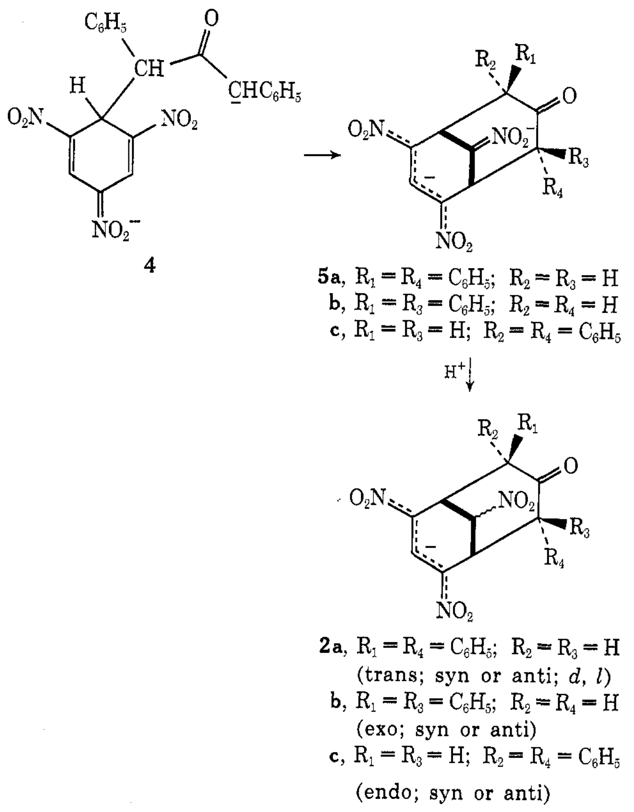


Figure 2.—Nmr spectral changes on conversion of **1a** to **2**: A, 0.11 *M* NEt_3, 0.56 *M* DBK, 0.33 *M* TNB in DMSO-d_6 after 90 sec; B–F, 0.14 *M* NEt_3, 0.17 *M* DBK, 0.11 *M* TNB at ~30-min intervals (B = t_0, spectrum amplitude doubled for D–F).

tions taken over a period of time (Figure 2). The visible spectral changes have been observed with very dilute solutions of reactants and with more concentrated solutions approximating pmr sample concentrations. The latter were obtained with a variable path length quartz cell using path lengths of less than 1 mm. The only species which can be observed in solution by pmr are TNB, DBK, NEt_3, **1a**, and **2b** or **2c**, except at very high concentrations of DBK (*vide infra*). The first three of these have no absorption in the visible region in DMSO solution (separately), whereas **1a** has two maxima at 466 and 578 nm, and **2** has a single maximum at 505 nm. Although **1a** has significant absorption at 575 nm, isolated and purified **2** has none at this wavelength. The rapid appearance and slow disappearance of **1a** could thus easily be followed at 575 nm. Isobestic points are found at 472 and 527 nm.

Although only one 1:1 anionic σ complex, **1a**, can form from TNB and DBK, this complex can cyclize to yield three different bicyclic dianions, **5a**, **5b**, and **5c**. The modes of cyclization of **4**, the dianionic σ complex precursor to **5**, are shown below. Kinetic data substantiating the intermediacy of these dianions is presented in the second section of this paper. In a final rapid step, each of the bicyclic dianions **5** can then be protonated to yield six different singly charged bicyclic products, **2**, since protonation of the unconjugated nitronate moiety in **5** can occur syn or anti to the carbonyl bridge. If the *d* and *l* forms of **2a** are considered, eight isomers are possible. Two of these possible products have been isolated, and there is strong evidence that a third is formed in solution. Before details of the kinetic study are discussed, a presentation of pmr results which clarify these stereochemical problems is pertinent.



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5a, $R_1 = R_4 = C_6H_5$; $R_2 = R_3 = H$
b, $R_1 = R_3 = C_6H_5$; $R_2 = R_4 = H$
c, $R_1 = R_3 = H$; $R_2 = R_4 = C_6H_5$

2a, $R_1 = R_4 = C_6H_5$; $R_2 = R_3 = H$
(trans; syn or anti; *d*, *l*)
b, $R_1 = R_3 = C_6H_5$; $R_2 = R_4 = H$
(exo; syn or anti)
c, $R_1 = R_3 = H$; $R_2 = R_4 = C_6H_5$
(endo; syn or anti)

After 90 sec, a solution of 0.11 *M* NEt_3, 0.56 *M* DBK, and 0.33 *M* TNB in DMSO shows a pmr spectrum characteristic of the triethylammonium salt of the σ complex **1a**, a singlet for excess TNB at low field, and absorptions for excess DBK. This spectrum remains unchanged after 2 hr at room temperature. The relative areas of the residual TNB singlet and DBK singlet (methylenes) of ~1:3 confirm that all of the amine has been used in formation of the complex. *Cyclization to bicyclics like* **5** *does not occur in the absence of excess amine.* The pmr spectrum of **1a** (Figure 2, spectrum A) is interesting in several respects because of asymmetry present at the carbon α to the trinitrocyclohexadienate ring. As expected, H_e and H_h are coupled ($J_{e,h} \sim 3$ cps). The ring protons H_b and H_c of **1a** are magnetically nonequivalent owing to the asymmetry noted, and exhibit different chemical shifts at δ 8.3 and 8.4. They are coupled to each other and to H_e with J values less than 1 cps. The shift difference $\Delta_{b,c}$ of ~8 cps between H_b and H_c[22] provides interesting information about the properties of **1a** and its propensity to undergo cyclization in preferred conformations. It has been shown in an earlier report concerned with asymmetry effects on pmr spectra of such complexes[21] that large $\Delta_{b,c}$ values result from large unequal rotamer populations in complexes like **1a**. In addition, the coupling constant $J_{e,h}$ varies widely in a variety of complexes like **1a**[22] (*i.e.*, **1b**, 1 cps; **1c**, 3 cps; **1d**, 5.5 cps). This also

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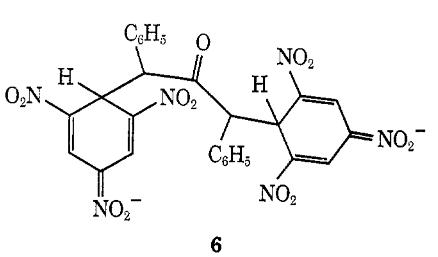
[22] An earlier reported value is 6.5 cps. See M. I. Foreman, R. Foster, and M. J. Strauss, *J. Chem. Soc. B*, 147 (1970).

suggests that such complexes have certain preferred orientations, since vicinal coupling constants depend in large part on the dihedral angle.[23] It is thus not surprising that only certain favored modes of cyclization occur. In a dilute solution of the reactants DBK, TNB, and NEt_3, only one bicyclic product (**2b** or **2c**) is formed. This is shown clearly by changes which occur in the pmr spectrum of the reaction solution with time. In DMSO at concentrations of ~0.14 *M* NEt_3, 0.17 *M* DBK, and 0.11 *M* TNB, rapid formation of **1a** can be observed, followed by its slow disappearance and concurrent formation of **2b** or **2c**. These changes are shown in Figure 2, spectra B–F. Both cis (exo or endo), **2b** or **2c**, and trans, **2a**, bicyclic anions have been prepared as their crystalline triethylammonium salts by methods reported earlier,[11] and their pmr spectra have been discussed. *The spectrum of the cis product* (**2b** *or* **2c**) *is in all respects identical with that which forms in DMSO solution* (*Figure 2*). No attempt has yet been made to assign stereochemistry at the $CHNO_2$ bridge in **2**. This stereochemistry is determined by a final rapid protonation of **5** in any case (*vide infra*), and its mechanistic features do not affect the magnitude of constants in the rate-limiting expression for formation of **2**. An unambiguous distinction between **2b** and **2c** cannot be made.

Interestingly, in DMSO solutions containing increasing amounts of DBK, cyclization occurs to give more than one of the six possible products. As noted previously, both cis and trans products can be *isolated* as crystalline salts when the reaction is carried out in a neat DBK melt.[11] After 4 hr, pmr spectra of highly concentrated solutions of DBK and TNB in DMSO show evidence of three bicyclic products. Three nitropropene nitronate singlets (H_a, Figure 2) appear between δ 8.1 and 8.7 along with the corresponding sets of peaks upfield. An additional complication at such high concentrations is the appearance (at high spectrum amplitude) of a new set of peaks which probably result from the bis complex **6** at about 1–2% of the intensity of the absorptions of **1a**. The complex **6** is likely analogous to the σ complex precursor of the tetracyclic bisnitronate **7**, described earlier, which is formed in strongly basic solutions of TNB and acetone.[18] To avoid complicating factors which would make kinetic studies of the formation of **2** very difficult, all reaction rates were measured in very dilute solutions of both TNB and DBK, with the former at 20–100-fold smaller concentration than any other component of the reaction.



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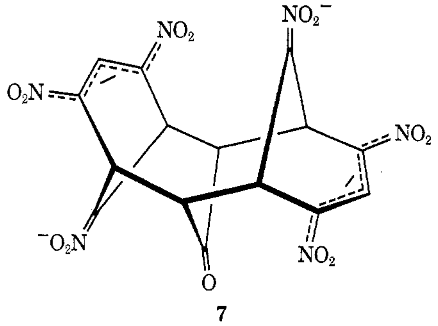

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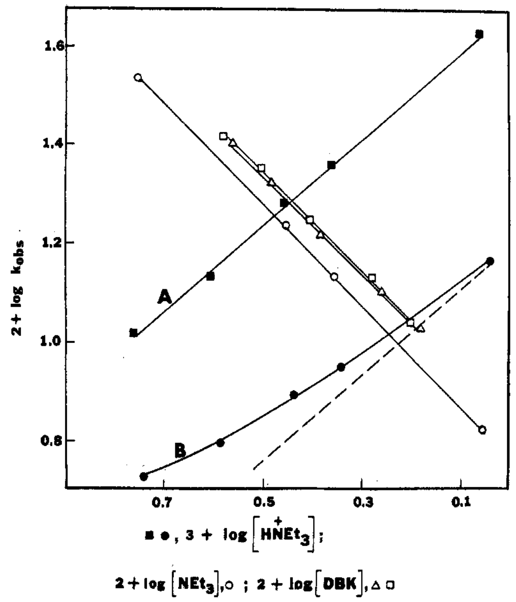

Figure 3.—Effects of NEt_3, $HNEt_3^+$, and DBK on the rate of Stage I.

State I. Formation of the σ Complex 1a.—Formation of carbanionic σ complexes from ketones and electron-deficient aromatics in the presence of tertiary amines has previously been proposed to occur by the Stage I mechanism shown in Scheme III. No kinetic study has ever been made to support this proposal, probably because no other mode of formation of **1a** seems as plausible. Depending on the relative magnitude of the rate constants involved for the reaction carried out in dilute solution, two types of rate expressions can be expected. If k_{-1} is much larger than k_2 (as well as k_1, so that the carbanion concentration is small relative to that of free ketone), then a preequilibrium expression (eq 1) should be applicable throughout the course of the reaction.

$$+\frac{d[\mathbf{1a}]}{dt} = -\frac{d[\mathrm{TNB}]}{dt} = k_2K_{\mathrm{eq}}\frac{[\mathrm{TNB}][\mathrm{NEt_3}][\mathrm{DBK}]}{[\mathrm{H\overset{+}{N}Et_3}]} \quad (1)$$

$$+\frac{d[\mathbf{1a}]}{dt} = -\frac{d[\mathrm{TNB}]}{dt} = \frac{k_1k_2[\mathrm{DBK}][\mathrm{NEt_3}][\mathrm{TNB}]}{k_{-1}[\mathrm{H\overset{+}{N}Et_3}] + k_2[\mathrm{TNB}]} \quad (2)$$

If k_2 is of the same order of magnitude as k_{-1}, the steady-state approximation can be applied yielding expression 2. The results of 42 separate runs varying the concentrations of reactants TNB, DBK, NEt_3, and product $HNEt_3^+$ are shown in Table I. Ionic strength was kept constant with $^+NEt_4$, Br^-. Details of the experimental procedure are outlined in the Experimental Section. Generally, a trace of absorbance *vs.* time was generated on the oscilloscope of a Durrum D-110 stopped flow unit by injecting a solution of TNB-DBK and a solution of NEt_3-$HNEt_3^+$-NEt_4^+, both in DMSO, into the reaction chamber. Another identical overlapping trace was generated and the curve was then recorded with an HP oscilloscope

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[23] M. Karplus, *J. Phys. Chem.*, **30**, 11 (1959).

TABLE I

RATE DATA FOR THE STAGE I CONDENSATION IN DMSO AT 25°

	Concn, mol/l.						
Run	TNB $\times 10^5$	DBK $\times 10^2$	NEt_3 $\times 10^2$	$HNEt_3^+$, Br^- $\times 10^3$	NEt_4^+, Br^- $\times 10^2$	μ $\times 10$	k_{obsd}, sec^{-1}
1	3.228	2.647	2.843	1.151	9.88	1.00	0.422
2	3.228	2.647	2.843	2.301	9.78	1.00	0.228
3 $\Delta HNEt_3^+$, Br^-	3.228	2.647	2.843	2.878	9.74	1.00	0.190
4	3.228	2.647	2.843	4.029	9.59	1.00	0.135
5	3.228	2.647	2.843	5.755	9.42	1.00	0.104
6	3.360	2.773	2.896	1.098		0.0110	0.146
7 $\Delta HNEt_3^+$, Br^- and $\Delta\mu$	3.360	2.773	2.896	2.196		0.220	0.0887
8	3.360	2.773	2.896	2.745		0.0274	0.0779
9	3.360	2.773	2.896	3.843		0.0384	0.0627
10	3.360	2.773	2.896	5.490		0.0549	0.0536
11	3.228	2.647	1.137	2.878	9.71	1.00	0.0740
12 ΔNEt_3	3.228	2.647	2.274	2.878	9.72	1.00	0.151
13	3.228	2.647	2.843	2.878	9.71	1.00	0.191
14	3.228	2.647	5.685	2.878	9.72	1.00	0.384
15	3.360	1.156	3.048	2.766	9.72	1.00	0.119
16	3.360	1.819	3.048	2.766	9.72	1.00	0.141
17 ΔDBK[a]	3.360	2.426	3.048	2.766	9.72	1.00	0.183
18	3.360	3.032	3.048	2.766	9.72	1.00	0.234
19	3.360	3.639	3.048	2.766	9.72	1.00	0.280
20	3.546	1.593	3.172	2.889	9.74	1.00	0.122
21	3.546	1.912	3.172	2.889	9.71	1.00	0.150
22 ΔDBK[b]	3.546	2.549	3.172	2.889	9.70	1.00	0.197
23	3.546	3.186	3.172	2.889	9.70	1.00	0.250
24	3.546	3.823	3.172	2.889	9.71	1.00	0.292
25	3.360	2.773	2.896	2.745	0.997	0.127	0.0962
26	3.360	2.773	2.896	2.745	3.06	0.334	0.127
27 $\Delta\mu$	3.360	2.773	2.896	2.745	4.75	0.503	0.146
28	3.360	2.773	2.896	2.745	6.63	0.691	0.172
29	3.360	2.773	2.896	2.745	8.61	0.889	0.191
30	3.360	2.773	2.896	2.745	10.63	1.09	0.213
31	2.860	2.604	2.401	1.257	0.911	0.1036	0.109
32	2.575	2.604	2.401	1.257	0.911	0.1036	0.110
33 ΔTNB[b]	2.290	2.604	2.401	1.257	0.911	0.1036	0.109
34	2.000	2.604	2.401	1.257	0.911	0.1036	0.112
35	1.715	2.604	2.401	1.257	0.911	0.1036	0.116
36	1.430	2.604	2.401	1.257	0.911	0.1036	0.113
37	2.860	2.510	4.683	1.296	0.911	0.1040	0.239
38	2.290	2.510	4.683	1.296	0.911	0.1040	0.236
39 ΔTNB[a]	1.715	2.510	4.683	1.296	0.911	0.1040	0.241
40	1.145	2.510	4.683	1.296	0.911	0.1040	0.235
41	0.570	2.510	4.683	1.296	0.911	0.1040	0.244
42	0.286	2.510	4.683	1.296	0.911	0.1040	0.242

[a] TNB and DBK in same syringe; NEt_3 and salts in other syringe. [b] DBK, NEt_3, and salts in same syringe; TNB in other syringe.

camera. Solutions of different combinations of reagents were injected, *i.e.*, DBK–NEt_3, to ensure that no preinjection reactions were occurring (*vide infra*). Pseudo-first-order rate constants were obtained assuming that the preequilibrium expression 1 was applicable. Log–log plots of these constants were made against the concentrations of the various reaction components (Figure 3). In all cases, linear relationships were observed with correlation coefficients of 0.999 or greater, which confirms the validity of a mechanism conforming to the preequilibrium expression 1. The slopes of these plots provide the order in each reactant. The individual runs and rate constants are summarized in Table I.

Plots A and B in Figure 3 represent the effects of salt concentration on k_{obsd}. Plot A is constructed from runs 1–5, Table I, and shows the effect of $HNEt_3^+$ concentration at constant ionic strength. The concentration of $HNEt_3^+$ produced as the product geganion of **1a** is at most over 30 times less concentrated than added $HNEt_3^+$, Br^-. The ionic strength was maintained constant with increasing $HNEt_3^+$, Br^- concentration by decreasing the amount of added NEt_4^+, Br^-. The slope of plot A is -0.9. This substantiates the order of -1 predicted by expression 1. In addition, if expression 2 were applicable, a nonlinear log–log plot would be expected. Such a situation is actually observed in the Stage II reaction. Plot B is constructed from runs 6–10 and shows the effect of $HNEt_3^+$, Br^- concentration without added NEt_4^+. At lower $HNEt_3^+$, Br^- concentrations, the slope of this curve approaches -1, but at higher concentrations the increasing ionic strength results in larger rate constants, decreasing the slope, as expected. The overall effect of ionic strength is also as expected for a reaction producing charged species. A plot of log k_{obsd}/k_0 *vs.* $\mu^{1/2}$

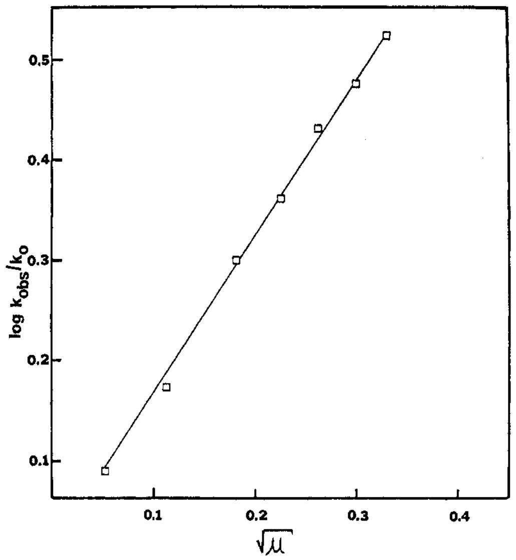


Figure 4.—Effect of ionic strength on Stage I.

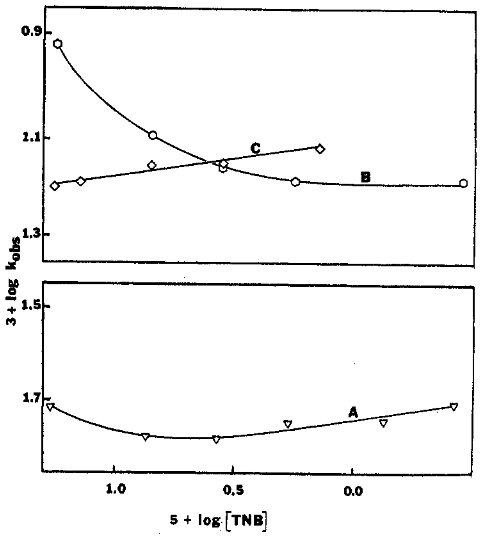


Figure 5.—Effect of TNB concentration on the rate of Stage II: A, runs 49–54; B, runs 43–48; C, runs 55–59.

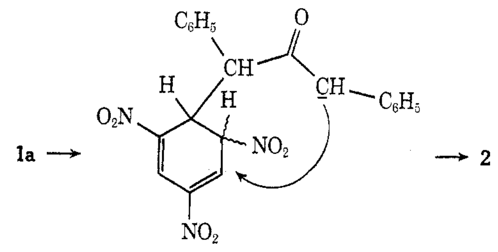
is shown in Figure 4, constructed from runs 25–30, Table I.

The remaining plots shown in Figure 3, runs 11–24, show the effects of NEt$_3$ and DBK concentration on rate. The slopes are 1.02 and 0.98, respectively. There is no effect observed upon mixing DBK and NEt$_3$ prior to injection, since the slope remains unchanged from those runs where DBK and TNB were premixed or where DBK and NEt$_3$ were premixed.

In addition to the above evidence substantiating a preequilibrium mechanism, variation of TNB concentration with all other component concentrations remaining constant did not yield a variation in k_{obsd} as would be expected if a mechanism corresponding to expression 2 were operative (runs 31–42, Table I).

Stage II. Formation of the Bicyclic Anion 2.—We have qualitatively studied cyclizations of a wide variety of σ complexes like **1**, in addition to cyclizations of complexes prepared from 1-carbomethoxy- and 1-cyano-3,5-dinitrobenzenes,[3,13] 1-carbomethoxy- and 1-methyl-2,4,6-trinitrobenzenes,[24] and 1,3-dinitro- and 1,3,6,8-tetranitronaphthalenes.[25] Many of these cyclizations quite probably are mechanistically similar to the cyclization of **1a** to **2**. In order to study this latter cyclization, we used NEt$_3$ and DBK concentrations approximately 10–100-fold greater than that of TNB. Under these conditions, Stage I was complete within several seconds, even when external triethylammonium bromide was added to the reaction solution. Under similar NEt$_3$ and HNEt$_3{}^+$ concentrations, a reaction rate measured in Stage I (run 25, Table I) has a half-life of about 7 sec, whereas the reaction rate measured for Stage II (run 55, Table II) has a half-life of about 50 min. In all the Stage II kinetic runs, Stage I was essentially complete before Stage II began. This point was checked by extrapolating the Stage II runs back to zero time to get the extinction coefficient of **1a** and confirming that all the TNB was converted to complex. This extinction coefficient could be determined from the TNB concentration and absorbance reading at t_∞ (over 8 half-lives) of the Stage I reaction under conditions where Stage II does not occur. The rate of Stage II was followed by measuring the diminishing absorbance of **1a** at 575 nm. The concentrations of DBK, NEt$_3$, HNEt$_3{}^+$, and NEt$_4{}^+$ were varied and the effect on rate was noted.

Prior to this study we proposed a "least contrived" mechanism in which proton transfer from the exocyclic ketonic moiety to the ring in **1a** was followed by intramolecular attack on the resultant dinitrodiene function of **8**.[3] Such a mechanism circumvented the necessity of proposing proton abstraction followed by intramolecular nucleophilic attack on a negatively charged species. This circumvention lead us to an incorrect conclusion, however (*vide infra*). Negative charge on the 2,4,6-trinitrocyclohexadienate function of **1a** resides primarily on the oxygens of the nitro groups (especially that nitro group para to the tetrahedral ring carbon) and the carbocyclic ring may in fact be slightly positive. These conclusions are based on the low field positions of H$_{b,c}$ in the pmr spectrum of **1a** and other similar complexes, as well as on molecular orbital calculations[26] and X-ray crystallographic data,[27] which indicate that structures like **1a** are the major contributors to the ground state of anionic σ complexes. The kinetic data we have generated are consistent with such a picture and show that intramolecular attack does occur in **4** to yield **5**.



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Effect of TNB Concentration.—Increasing the TNB concentration in the absence of any externally added

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[24] M. J. Strauss and S. P. B. Taylor, *J. Org. Chem.*, **38**, 1330 (1973).

[25] M. J. Strauss and S. P. B. Taylor, *J. Org. Chem.*, **38**, 856 (1973).

[26] H. Hosoya, S. Hosoya, and S. Nagakura, *Theor. Chim. Acta*, **12**, 117 (1968).

[27] R. Destro, C. Gramaccioli, and M. Simonetta, *Acta Crystallogr.*, **24**, 1369 (1968).

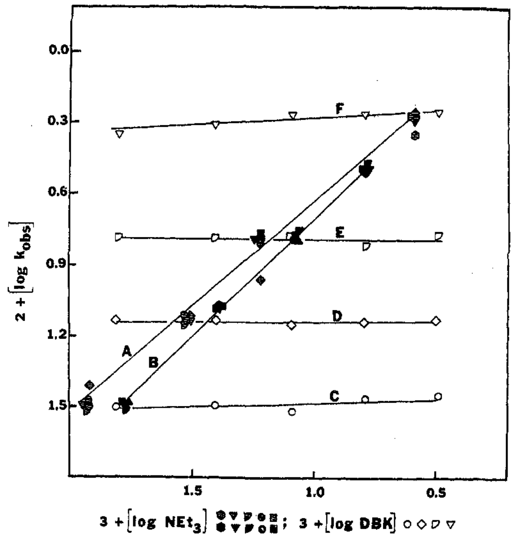

Figure 6.—Effect of NEt_3 and DBK concentrations on the rate of Stage II: A, runs 60–79; B, runs 80–95.

salts results in a dramatic decrease in k_{obsd}, shown in Figure 5, curve B (runs 43–48, Table II). This results from the rate-retarding effect on Stage II of increasing $HNEt_3^+$ which is formed in quantitative yield from the Stage I conversion of TNB to the $HNEt_3^+$ salt of **1a**. Superimposed upon this rate depression is a very slight rate increase caused by increasing ionic strength (*vide infra*), and a nonlinear relationship is thus not expected. If the ionic strength is held approximately constant by using a large excess of NEt_4^+, ClO_4^-, and in the presence of a constant excess amount of $HNEt_3^+$, Br^-, this rate depression disappears [Figure 5, line C (runs 55–59, Table II)]. There is in fact a very slight rate increase. The slope of the log–log plot of k_{obsd} *vs.* TNB concentration in this instance is about 0.06. The concentration of TNB thus has no significant effect on the rate of cyclization of **1a** to **2**. At approximately constant ionic strength, but with $HNEt_3^+$ production varying with initial TNB concentration, a rate depression is still observed at high concentrations [Figure 5, curve A (runs 49–54, Table II)].

TABLE II

EFFECT OF TNB CONCENTRATION ON THE STAGE II CYCLIZATION IN DMSO AT 20°

Run	Concn, mol/l.: TNB × 10^4	NEt₃ × 10^2	DBK × 10^2	k_{obsd}, min^{-1}
Absence of Added Salts				
43	3.516	2.412	2.410	0.0155
44	17.58	2.412	2.410	0.0152
45	35.16	2.412	2.410	0.0143
46	70.32	2.412	2.410	0.0123
47	135.80	2.412	2.410	0.0118
48	175.80	2.412	2.410	0.0101
Presence of 1.466 × 10^{-2} M NEt_4^+, ClO_4^-				
49	3.678	6.511	6.341	0.0508
50	7.357	6.511	6.341	0.0558
51	18.39	6.511	6.341	0.0562
52	36.79	6.511	6.341	0.0608
53	73.58	6.511	6.341	0.0600
54	183.90	6.511	6.341	0.0515
Presence of 2.875 × 10^{-3} M $HNEt_3^+$, Br^- and 1.274 × 10^{-2} M NEt_4^+, Br^-				
55	13.98	7.282	6.174	0.0132
56	34.95	7.282	6.174	0.0143
57	69.90	7.282	6.174	0.0142
58	139.80	7.282	6.174	0.0156
59	174.74	7.282	6.174	0.0159

Effect of NEt_3 and DBK Concentrations.—Log–log plots of NEt_3 concentrations *vs.* k_{obsd} for the Stage II reaction under a variety of different conditions have slopes very close to unity in the presence or absence of added salt (Figure 6, lines A and B). Log–log plots of DBK concentrations *vs.* k_{obsd}, each at differing but constant NEt_3 concentration, have slopes very close to zero in the presence or absence of added salt (Figure 6, lines C–F). These data are summarized in Tables III and IV. It is evident that the cyclization is catalyzed by NEt_3. This rules out a mechanism proceeding through **8**, since NEt_3 would not appear in the rate-limiting expression regardless of how the proton transfers were achieved. Assuming that the Stage II

TABLE III

EFFECTS OF DBK AND NEt₃ CONCENTRATION ON THE STAGE II CYCLIZATION IN DMSO AT 20°

Run	Concn, mol/l.: TNB × 10^4	NEt₃ × 10^2	DBK × 10^2	k_{obsd}, min^{-1}
Presence of 1.820 × 10^{-4} M $HNEt_3^+$, Br^-				
60	0.6939	8.313	0.308	0.0288
61	0.6939	8.313	0.615	0.0301
62	0.6939	8.313	1.230	0.0337
63	0.6939	8.313	2.552	0.0317
64	0.6939	8.313	6.447	0.0320
65	0.6939	3.325	0.308	0.0139
66	0.6939	3.325	0.615	0.0142
67	0.6939	3.325	1.230	0.0147
68	0.6939	3.325	2.552	0.0139
69	0.6939	3.325	6.447	0.0139
70	0.6939	1.663	0.308	0.00626
71	0.6939	1.663	0.615	0.00677
72	0.6939	1.663	1.230	0.00620
73	0.6939	1.663	2.552	0.00643
74	0.6939	1.663	6.447	0.00643
75	0.6939	0.381	0.308	0.00195
76	0.6939	0.381	0.615	0.00196
77	0.6939	0.381	1.230	0.00196
78	0.6939	0.381	2.552	0.00219
79	0.6939	0.381	6.447	0.00245
Absence of Added Salts				
80	1.358	6.033	6.024	0.0319
81	1.358	6.033	2.410	0.0321
82	1.358	6.033	1.205	0.0323
83	1.358	6.033	0.602	0.0330
84	1.358	2.413	6.024	0.0124
85	1.358	2.413	2.410	0.0128
86	1.358	2.413	1.205	0.0123
87	1.358	2.413	0.602	0.0130
88	1.358	1.207	6.024	0.00652
89	1.358	1.207	2.410	0.00653
90	1.358	1.207	1.205	0.00620
91	1.358	1.207	0.602	0.00604
92	1.358	0.603	6.024	0.00336
93	1.358	0.603	2.410	0.00335
94	1.358	0.603	1.205	0.00331
95	1.358	0.603	0.602	0.00303

TABLE IV

SALT EFFECTS IN THE STAGE II CYCLIZATION IN DMSO AT 20°

	Concn, mol/l.						
Run	TNB × 10^4	DBK × 10^2	NEt_3 × 10^2	$HNEt_3^+$, Br^- × 10^4	NEt_4^+, Br^- × 10^2	μ^a × 10	k_{obsd}, min^{-1}
96	0.6840	2.752	4.997	1.773		0.0260	0.02370
97	0.6840	2.752	4.997	3.546		0.0420	0.01710
98	0.6840	2.752	4.997	8.866		0.0950	0.01280
99	0.6840	2.752	4.997	17.732		0.1840	0.00838
100	0.6840	2.752	4.997	35.463		0.3610	0.00480
101	0.6990	6.174	7.282	1.917	1.2740	0.0130	0.04340
102	0.6990	6.174	7.282	3.833	1.2740	0.0130	0.03920
103	0.6990	6.174	7.282	9.583	1.2740	0.0140	0.02850
104	0.6990	6.174	7.282	11.979	1.2740	0.0140	0.01970
105	0.6990	6.174	7.282	28.750	1.2740	0.0160	0.01420
106	0.7358	6.341	2.605		0.0216	0.0030	0.02180
107	0.7358	6.341	2.605		0.0672	0.0075	0.02290
108	0.7358	6.341	2.605		0.3222	0.0329	0.02440
109	0.7358	6.341	2.605		0.7346	0.0742	0.02510
110	0.7358	6.341	2.605		1.5930	0.1600	0.02610

[a] (TNB + salt concentration) since all TNB is converted to triethylammonium salt of σ complex in Stage I.

Intramolecular abstraction of side-chain proton by ring nitronate carbon

$$\mathbf{1a} \overset{K_{eq}}{\rightleftharpoons} \mathbf{8}$$

$$\mathbf{8} \xrightarrow{k_s} \mathbf{5}$$

$$\mathrm{d}P/\mathrm{d}t = k_sK_{eq}[\mathbf{1a}] = k_{obsd}[\mathbf{1a}]$$

Intermolecular amine-catalyzed proton transfer from side chain to ring nitronate carbon

$$\mathbf{1a} + NEt_3 \overset{K_{eq}{}^1}{\rightleftharpoons} \mathbf{4} + H\overset{+}{N}Et_3$$

$$\mathbf{4} + H\overset{+}{N}Et_3 \overset{K_{eq}{}^2}{\rightleftharpoons} \mathbf{8} + NEt_3$$

$$\mathbf{8} \xrightarrow{k_s} \mathbf{2}$$

$$\mathrm{d}P/\mathrm{d}t = k_sK_{eq_1}K_{eq_2}[\mathbf{1a}] = k_{obsd}[\mathbf{1a}]$$

sequence outlined in Scheme III is applicable, two rate-limiting expressions can be derived, analogous to the steady-state and preequilibrium treatments of the Stage I formation of **1a**. A distinction between these

$$-\frac{\mathrm{d}[\mathbf{1a}]}{\mathrm{d}t} = +\frac{\mathrm{d}[\mathbf{2}]}{\mathrm{d}t} = \frac{k_4K_{eq}[\mathbf{1a}][NEt_3]}{[HNEt_3{}^+]} \tag{3}$$

$$-\frac{\mathrm{d}[\mathbf{1a}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathbf{2}]}{\mathrm{d}t} = \frac{k_3k_4[\mathbf{1a}][NEt_3]}{k_{-3}[H\overset{+}{N}Et_3] + k_4} \tag{4}$$

can be made by examining the effect of $HNEt_3{}^+$ concentration on the rate.

Effect of Salt Concentration.—Log–log plots of $HNEt_3{}^+$ and $NEt_4{}^+$ concentrations *vs.* k_{obsd} are shown in Figure 7. When $HNEt_3{}^+$ is constant (equal to initially added TNB) and $NEt_4{}^+$ is varied, little effect on the rate is seen (line C). 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 stablilization of increasing charge in the transition state leading to the dianionic intermediate. At constant ionic strength (maintained with an excess of $NEt_4{}^+$, Br^-) a log–log plot, B, of $HNEt_3{}^+$ *vs.* k_{obsd} is nonlinear with an approximated slope of about −0.4, consistent with eq 4 and not eq 3. A similar nonlinear curve is generated from an identical plot, A, in which the ionic strength was not kept constant. This differs little from B, except that the reaction is much slower at all $HNEt_3{}^+$ concentrations.

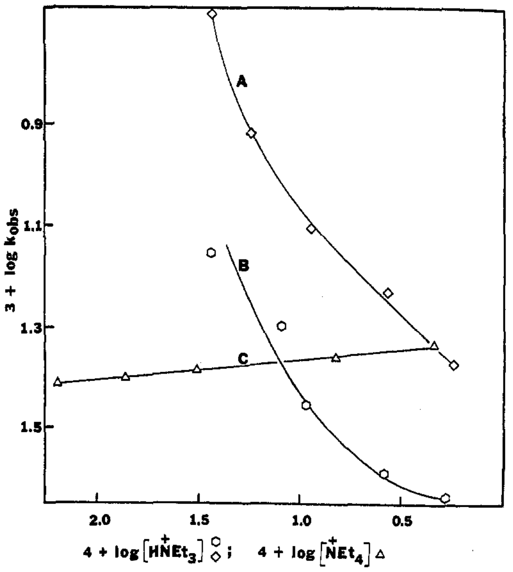

Figure 7.—Effect of $HNEt_3{}^+$ and $NEt_4{}^+$ concentrations on the rate of stage II: A, runs 96–100; B, runs 101–105; C, runs 106–110.

General Conclusions.—The short-lived intermediates **4** and **5** are quite reasonable structures, and are supported by the stable and isolable compound **7** and the characterization of bis-sulfite complexes of TNB.[19,28] In fact, we have found that **2** can be converted back to **5** in strong base. Addition of excess triethylamine to a solution of **2** (cis) in DMSO followed by aging this solution for several weeks causes broadening and loss of resolution of the $CHNO_2$ triplet in **2**, which strongly indicates nitronate formation at this bridge. Such changes occur more rapidly upon addition of NaOH. In addition, other changes in the pmr spectra of solutions of the cis or trans isomer occur. After a period of weeks in the presence of excess triethylamine, a partial decrease of resonances of cis adduct occurs concurrently with appearance of resonances attributable

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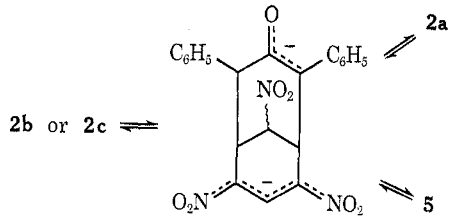
[28] M. R. Crampton, *J. Chem. Soc. B*, 1341 (1967).

to the trans isomer **2a**. This isomerization undoubtedly proceeds through the enolate of **2**, followed by reprotonation. The trans isomer **2a** is thus likely to be more thermodynamically stable than the cis. It is difficult to assess the detailed changes which are occurring owing to the complexity of the spectra which are generated upon aging a solution of **2** in base. No reversion to **1a** occurs, however, since the visible maximum of the aging solutions remains at 505 nm, showing no reappearance of absorption characteristic of **1a**.



Studies of cyclization mechanisms of carbanionic σ complexes to yield structures like **2** have been carried out in other laboratories.[19,20,29,30] Although the isolated crystalline bicyclic products have been correctly characterized in most of these studies, the specious mechanistic schemes proposed are for the most part conjecture, based on qualitative shifts in the uv-visible absorption maxima of reactant solutions. Such evidence is tenuous at best.[29,30]

Experimental Section[31]

Purification of Reagents.—Dimethyl sulfoxide (Mallinckrodt analytical reagent) was distilled from calcium hydride under vacuum on a spinning band column. It was stored under dry nitrogen until used. The specific conductance of DMSO purified in this fashion was less than 3×10^{-8} ohm^{-1} cm^{-1}, which is in excellent agreement with conductance values obtained for DMSO containing less than 4 ppm water.[32] Triethylamine (Baker) was distilled from small quantities of phenyl isocyanate.[33] The distillate was then redistilled from molecular sieves (4A) and the amine was collected at 89°. Only a single sharp peak was observed on chromatographic analysis using an HP-700 vpc (4 ft $\times$ 0.25 in. column, 30% Citroflex on Chromosorb W 60–80 mesh) at 65°. Dibenzyl ketone (Eastman) was recrystallized from pentane and dried under vacuum at room temperature for at least 8 hr. The crystals were then recrystallized from dry pentane, dried, and stored over P_2O_5 under nitrogen in a cold box to prevent melting (mp 34°, lit.[34] mp 35°). Triethylammonium bromide (Eastman) was recrystallized from anhydrous ethanol and dried at 110° (3 mm) for at least 8 hr. Tetraethylammonium bromide was recrystallized from a mixture of chloroform and benzene. The recrystallized salt was dried at 110° (3 mm) for at least 8 hr. Both the tri- and tetraethylammonium salts were stored in a drybox over P_2O_5. Tetraethylammonium perchlorate was purified as described previously.[35] Trinitrobenzene was repeatedly recrystallized from ethanol–water solutions which were decolorized with activated carbon. After three recrystallizations, colorless plates, mp 123° (lit.[36] mp 123°), were obtained. These were stored in a drybox at 0° until needed. In an alternate method of purification, TNB was sublimed at reduced pressure.[36] Crystals melting at 123° were obtained by this method.

Stage I Kinetic Runs.—Stock solutions of TNB, NEt_3, DBK, and the salts were prepared in DMSO and the required quantities for each run were pipetted into volumetric flasks and diluted to volume. Except where noted, the TNB and DBK were in one flask and NEt_3 and the salts were in another flask. Because of the low solubility of NEt_4^+, Br^- in DMSO, the required quantities of this salt were weighed separately for each run. In addition, because this salt is extremely hygroscopic, all weighings were done on an analytical balance in a dry bag under a dry nitrogen atmosphere.

After injection of the appropriate solutions into the reaction chamber of the spectrophotometer thermostated at 25°, the trace of absorbance at 575 nm *vs.* time recorded on the oscilloscope was copied with a Hewlett-Packard oscilloscope camera (Model 198-A). Two identical traces were recorded before a picture was taken. Absorbance and time values were taken from the curves with a circular film measuring device and were used for computation of pseudo-first-order rate constants in the region of 20–60% completion. Rate constants were obtained from the slopes of plots of ln $(A_\infty - A_t)$ *vs.* time. These plots were generated from a "LORDHELPUS" program[37] using a Xerox Sigma 6 computer. The program was designed specifically for analysis of a large amount of data, allowing job submittal from cards or terminal. It yields the rate constant and ln A_0 value (where A_0 is the absorbance at $t = 0$) from a series of absorbance and corresponding time values of a particular run. Runs with either increasing or decreasing absorbance as a function of time may be evaluated.

Stage II Kinetic Runs.—The Stage II kinetics were determined by mixing the appropriate solutions (preequilibrated to 20°) and transferring the reaction mixture to a thermostated cuvette in a Cary 14 spectrophotometer. The decrease in absorbance as a function of time was then recorded. The data were analyzed from the plot of absorbance *vs.* time as described for Stage I.

Acknowledgments.—The authors wish to thank the Army Research Office at Durham and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No.—**1a**, 26986-18-5; **2**, 12379-64-5; DBK, 102-04-5; TNB, 99-35-4.

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[31] All melting points and boiling points are uncorrected. Infrared, ultraviolet–visible, and pmr spectra were recorded using P-E 121 and 237-B (ir), Cary 14, P-E 402, Durrum-Gibson 110 stopped flow (uv-visible), and JEOL-MH-100 (pmr) instruments. Chemical shifts are reported in parts per million relative to internal TMS.

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[37] Program constructed by H. Schran and D. Frink, copies on request.