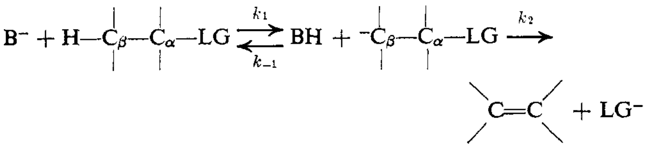
A First-Order Base-Initiated β-Elimination Reaction Involving a Carbanion Intermediate

F. G. Bordwell, K. C. Yee,[1] and A. C. Knipe

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received October 17, 1969*

Abstract: A kinetic analysis of the methoxide ion initiated elimination of MeOH from 2-phenyl-*trans*-2-methoxy-1-nitrocyclopentane (**1**) or its *cis* isomer (**2**) has shown that it proceeds by a rapid second-order reaction to form a nitronate ion (**3**, common to **1** and **2**) followed by a slow, rate-limiting first-order loss of methoxide ion from **3** to give 2-phenyl-1-nitrocyclopentene (**4**). The latter step is reversible, and the equilibrium favors **3** over **4** by a factor of 530/1 at 1 *M* [MeO$^-$]. Under the conditions of the reaction, **4** is formed in only a steady-state concentration because it undergoes a further rapid reaction with methoxide ion to give nitronate ion **5**. The overall reaction **1** (or **2**) to **4** is an example of a first-order β elimination involving a carbanion (nitronate ion) intermediate. Examination of deuterium isotope effects for **1** and for **4** has allowed evaluation of the rate constants for both the forward and reverse steps in the reaction sequence **1** $\rightleftarrows$ **3** $\rightleftarrows$ **4** $\rightarrow$ **5**. The proposed kinetic scheme was subjected to an analog computer analysis which showed the formation of steady-state concentrations of **4** and provided a pictorial representation of the rate phenomena starting from **3** and from **4**.

Base-initiated E2 elimination reactions for H–C$_\beta$–C$_\alpha$–LG systems are believed to occur by a spectrum of mechanisms with varying degrees of H–C and C–LG bond breaking.[2,3] As the β-hydrogen atom is made more acidic the mechanism changes imperceptibly to one where an intermediate carbonion is formed in a nonreversible manner.[4] If the β-hydrogen is made more acidic and at the same time the leaving group (LG) is made poorer, the mechanism may change to one where the carbanion is formed reversibly (E1cb mechanism).



$$\mathrm{B^- + H{-}C_\beta{-}C_\alpha{-}LG \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} BH + {}^-C_\beta{-}C_\alpha{-}LG \xrightarrow{k_2} {>}C{=}C{<} + LG^-}$$

In the nonreversible carbanion mechanism $k_2 \gg k_{-1}$, but in the reversible carbanion mechanism $k_{-1} > k_2$, and the existence of a preequilibrium can be detected by means of deuterium isotope effects.[5,6] Particularly clearcut examples of this mechanism have been obtained recently with phenoxy[7] and methoxy[8] leaving groups. For base-initiated elimination of methanol from β-methoxy ketones the $k_{\mathrm{exch}}/k_{\mathrm{elim}}$ ratio was of the order of 225/1.[8]

With a poor leaving group and a particularly stable carbanion it is possible to have a third type of carbanion mechanism, one in which carbanion formation is in theory reversible, but in practice is nonreversible because it is essentially complete before elimination occurs ($k_1 \gg k_{-1}$ or k_2). This carbanion elimination can be distinguished from the other two kinetically because, in the presence of excess base, it will be independent of the base concentration, whereas the other two will be first order in base concentration. Examples of this type of elimination are rare.[4c,9] Only the nitro group is a strong enough electron-withdrawing group to render the β-hydrogen atom sufficiently acidic to make this mechanism feasible with a *single* activating group. Using the nitro group to activate the β-hydrogen atom we have, in fact, been able to find examples not only of this type of mechanism, but also of the other two types of mechanisms mentioned above. These will be discussed in this and the succeeding paper.

Results

Reaction of 2-phenyl-*trans*-2-methoxy-1-nitrocyclopentane (**1**) or its *cis* isomer (**2**) with excess sodium methoxide in methanol resulted in the formation, at different rates, of a common nitronate ion (**3**, $\lambda_{\max}$ 246 nm; $\epsilon_{\max}$ 11,000). The rates were of the same order of magnitude as those for the formation of a comparable nitronate ion from the corresponding nitroalkanes, *cis*- and *trans*-2-phenyl-1-nitrocyclopentanes,[10] and were first order in methoxide ion and, presumably, in substrate (**1** or **2**). After about 5 min (at 0.1 *M* NaOMe) a new absorption peak at 296 nm began to appear slowly and the absorbance at 246 nm began to drop very slowly. The rate of appearance of the 296 nm peak was found to be *independent* of methoxide ion concentration in the presence of excess base. It was the same, within experimental error, starting with either **1** or **2**. The final product was nitronate ion **5** with maxima at 249 ($\epsilon_{\max}$ 8900) and 296 nm ($\epsilon_{\max}$ 8650). The identity of **5** was established by protonation with acetic acid–acetate buffer solution to give 5-nitro-1-phenylcyclopentene (**6**), and the demonstration that

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[1] Abstracted in part from the Ph.D. Dissertation of K. C. Yee, Northwestern University, Evanston, Ill., Aug 1969.

[2] D. J. Cram, F. D. Greene, and C. H. DePuy, *J. Amer. Chem. Soc.*, **78**, 790 (1956).

[3] J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, **1**, 225 (1962); *Surv. Progr. Chem.*, **5**, 53 (1969).

[4] See: (a) D. V. Banthorpe, "Elimination Reactions," Elsevier, Amsterdam, 1963, Chapter 4; (b) D. J. McLennan, *Quart. Rev. Chem. Soc.*, **21**, 490 (1967); and (c) Z. Rappoport, *Tetrahedron Lett.*, 3601 (1968), for classifications of carbanion elimination mechanisms.

[5] J. Hine, R. Wiesboeck, and O. B. Ramsay, *J. Amer. Chem. Soc.*, **83**, 1222 (1961); J. Hine, R. Wiesboeck, and R. G. Ghirardelli, *ibid.*, **83**, 1219 (1961).

[6] D. J. Cram and A. S. Wingrove, *ibid.*, **86**, 5490 (1964).

[7] J. Crosby and C. J. M. Stirling, *ibid.*, **90**, 6869 (1968).

[8] L. R. Fedor, *ibid.*, **91**, 908 (1969).

[9] Z. Rappoport and E. Shohany, *Isr. J. Chem. Proc.*, **6**, 15 (1968), have recently described the amine-initiated elimination of HCN from $\mathrm{(CN_2)CHC(CN)_2NHC_6H_3Me_3}$ as being the first example of this type of mechanism.

[10] F. G. Bordwell and K. C. Yee, *J. Amer. Chem. Soc.*, **92**, 5933 (1970) (paper II in this series).

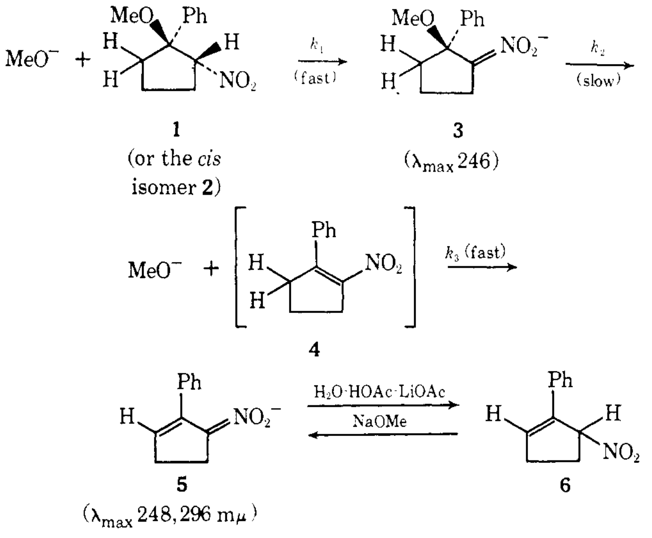
Table I. Rates of Reaction of 2-Phenyl-*trans*-2-methoxy-1-nitrocyclopentane (**1**), and Related Compounds with Sodium Methoxide in Methanol

Compound	T, °C	k_1,[a] M^{-1} sec^{-1}	k_2,[b] sec^{-1}
cis-2-Phenyl-1-nitrocyclopentane	25	$(1.4)^c$	
trans-2-Phenyl-1-nitrocyclopentane	25	$(3.3 \times 10^{-1})^c$	
2-Phenyl-*trans*-2-methoxy-1-nitrocyclopentane (**1**)	25.0	2.64×10^{-1}	
	38.8	9.20×10^{-1}	
	25.0		7.6×10^{-6}
	38.8		$(4.4 \times 10^{-5})^d$
	38.6		$(4.5 \times 10^{-5})^e$
	49.5		1.9×10^{-4}
2-Phenyl-*trans*-2-methoxy-1-nitrocyclopentane (**1**)-1,3,3-d_3	25.0	3.5×10^{-2}	
	38.8	1.5×10^{-1}	$(2.6 \times 10^{-5})^d$
	38.8		$(2.7 \times 10^{-5})^e$
2-Phenyl-*cis*-2-methoxy-1-nitrocyclopentane (**2**)	25.0	$(6.9 \times 10^{-1})^f$	
	25.1	$(7.1 \times 10^{-1})^g$	
	25.6		9.0×10^{-6}
2-Phenyl-1-nitrocyclopentene (**4**)	24.8	$(4.9 \times 10^{-2})^h$	
	38.6	$(1.6 \times 10^{-1})^h$	
	38.6	$(1.3 \times 10^{-1})^i$	$(7.2 \times 10^{-3})^j$
2-Phenyl-1-nitrocyclopentene (**4**)-3,3-d_2	38.6		$(2.1 \times 10^{-5})^k$

[a] Second-order rate constant for the appearance of nitronate ion **3** (or an analog) at 246 nm (by deprotonation unless otherwise noted); obtained by dividing the pseudo-first-order rate constant by the base concentration (average of two or more runs).[10] [b] First-order rate constant for the appearance of nitronate ion **5** (from **3** unless otherwise noted) at 296 nm (average of two or more runs). [c] Reference 10. [d] 0.0912 *M* NaOMe. [e] 0.0456 *M* NaOMe. [f] 0.0242 *M* NaOMe. [g] 0.0485 *M* NaOMe. [h] Second-order constant for the appearance of both **3** and **5** (see text). [i] Second-order contant for the deprotonation of **4** corrected for the formation of **3** (see text). [j] Approximate pseudo-first-order constant for deprotonation of **4** with 0.0456 *M* NaOMe (see text). [k] Approximate first-order constant for the formation of **5** *via* **3** (see text).

5 could be generated from **6** or from its isomer, 2-nitro-1-phenylcyclopentene (**4**) in separate experiments. The rate data are given in Table I.

A plausible reaction scheme based on the observations discussed above and one additional fact, namely, that the conversion of the presumed intermediate, 2-phenyl-1-nitrocyclopentene (**4**), to **5** is much faster than the conversion of **3** to **5** (Table I), is outlined below.



1 (or the *cis* isomer **2**)

3 (λ_{max} 246)

4

5 (λ_{max} 248, 296 mμ)

6

The rate of reaction of **1**-1,3,3-d_3 to give **3** was 7.5-fold slower at 25° than that for **1**, which is about the expected value. The rate of conversion of **1**-1,3,3-d_3 to **5** was about 1.7-fold slower than that of the parent hydrogen compound. The latter result is not expected on the basis of the scheme presented since there should be no deuterium isotope effect for the conversion of **1**-1,3,3-d_3 to **5** if k_2 is rate limiting and step 2 is irreversible. In seeking a cause for this isotope effect the rate of conversion of **4**-3,3-d_2 to **5** by methoxide ion was examined by following the change in absorbance at 296 nm. This reaction appeared to be 340-fold slower than that of the parent hydrogen compound (Table I; compare the last two entries in the right-hand column). Since $k_H/k_D = 340$ is far beyond the theoretical maximum, it was clear that the reaction of **4** with methoxide ion invoved more than simple proton abstraction. (The k_H/k_D for proton abstraction from **6** is *ca.* 8.[11]) Examination of the reaction of **4**-3,3-d_2 with methoxide ion by measuring the rate of change of absorbance over the region of 240–350 nm by repetitive scan showed a rapid buildup at 246 nm within the first 5 min, after which the absorbance in this region increased very slowly and shifted gradually to a peak with an absorption maximum at 249 nm (ϵ_{max} 9000), which is characteristic of **5**. A slower increase in absorbance at 296 nm, where **5** has its second maximum, was observed during the first 5 min; this peak continued to grow slowly with time.[12] The rapid appearance of the 246-nm peak was accompanied by the complete disappearance of the absorption due to **4** in the region near 350 nm. This same pattern of behavior was observed for the parent hydrogen compound except that the difference between the rates of absorbancy increases at 246 nm and 296 nm was much smaller.

The initial burst in absorbance in the 246-nm region just described with **4**-3,3-d_2 must be due not only to deprotonation of **4**-3,3-d_2 to form **5**, but also to addition of methoxide ion to the double bond of **4**-3,3-d_2 to form **3**. The subsequent slow appearance of the 296-nm peak corresponds to the formation of **5** from **3**. The ratio of the first-order rate of appearance of the 296-nm peak from nondeuterated **4** and deuterated **4** is *ca.* 340/1 (see above), but this is not k_H/k_D. The major component of the rate for nondeuterated **4** is a pseudo-first-order deprotonation rate constant, whereas the

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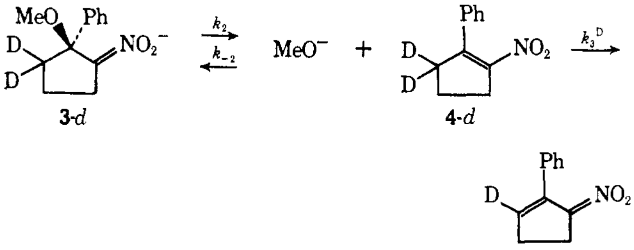
(11) K. C. Yee, Ph.D. Dissertation, Northwestern University, Evanston, Ill., Aug 1969.

(12) It was later established (see below) that the apparent discrepancy of having the 246- and 296-nm peaks increase at different rates was caused by formation of two products absorbing at 246 nm (**3** and **5**) *vs.* only one at 296 nm (**5**). This illustrates the importance of measuring rates at more than one wavelength.

major component of the rate for deuterated **4** is the rate constant for the first-order loss of methoxide ion from **3**. These rate constants are subjected to a more detailed analysis in the Discussion.

Discussion

The data on hand provide a clear picture of the mechanism for the conversion of **1** or **2** to **5** by methoxide ion. The first step (k_1) is rapid proton abstraction to form nitronate ion **3**. Protonation of **3** by the solvent in the reverse step (k_{-1}) is very slow, and the equilibrium strongly favors **3**.[13] Loss of methoxide ion from **3** is slow, but not quite as slow as the first-order rate for **1** recorded in Table I. This rate needs to be corrected for the amount of return of **4** to **3** caused by its reversal. A correction of this kind can be made by an analysis of the rates of reaction of **4** and **4**-3,3-d_2 (**4**-*d*) with sodium methoxide.



Reaction of **4**-*d* with sodium methoxide results in competition between addition (k_{-2}) and deuterium abstraction (k_3^D). Since **4**-*d* had disappeared completely within 5 min, the amount of **5**-*d* formed in that time interval (as judged by the absorbancy at 296 nm) when divided by that formed at infinity gives the fraction of **5**-*d* formed by direct deuteron abstraction. This amounted to 48%. In other words, $k_3^D/(k_3^D + k_{-2}) = 0.48$ and $k_{-2}/(k_{-2} + k_3^D) = 0.52$. Therefore, the ratio of $k_{-2}/k_3^D = 1.1$.

If we return now to our original reaction scheme, but take into account the reversibility of the loss of methoxide ion from **3**, we can assume that **4**-*d* is formed in a steady-state concentration during the reaction of **1**-1,3,3-d_3. Then

$$\mathrm{d}(\mathbf{4}\text{-}d)/\mathrm{d}t = k_2[\mathbf{3}] - k_{-2}[\mathbf{4}\text{-}d][\mathrm{MeO^-}] - k_3^D[\mathbf{4}\text{-}d][\mathrm{MeO^-}] = 0 \quad (1)$$

Therefore

$$[\mathbf{4}\text{-}d] = k_2[\mathbf{3}]/\{(k_{-2} + k_3^D)[\mathrm{MeO^-}]\} \quad (2)$$

and

$$-\mathrm{d}(\mathbf{3})/\mathrm{d}t = \mathrm{d}[\mathbf{5}\text{-}d]/\mathrm{d}t = k_3^D[\mathbf{4}\text{-}d][\mathrm{MeO^-}] \quad (3)$$

or

$$\mathrm{d}(\mathbf{5}\text{-}d)/\mathrm{d}t = k_2k_3^D[\mathbf{3}]/(k_{-2} + k_3^D) \quad (4)$$

Since k_2 and k_{-2} are essentially the same for the hydrogen and deuterium compounds

$$\frac{\mathrm{d}(\mathbf{5})/\mathrm{d}t}{\mathrm{d}(\mathbf{5}\text{-}d)/\mathrm{d}t} = \frac{k_3^H(k_{-2} + k_3^D)}{k_3^D(k_{-2} + k_3^H)} \quad (5)$$

Equation 4 shows that conversion of **3** to **5** should be independent of methoxide ion concentration as was observed (see above). Since **1** is rapidly and completely converted to **3** by MeO⁻, the conversion of **1** → **5** is also independent of methoxide.

Equation 5 allows us to estimate the magnitude of the deuterium isotope effect that can be expected for the conversion of **1** to **5** according to this scheme. On one extreme k_3^H and $k_3^D \gg k_{-2}$ and $k_H/k_D = 1.0$. (This was the first scheme assumed—see above.) On the other extreme $k_{-2} \gg k_3^H$ and k_3^D, and k_H/k_D is equal to the deuterium isotope effect for the final proton abstraction step.

Since we know that $k_{-2} = 1.1k_3^D$, this can be used in eq 5, together with the value of the observed overall isotope effect (1.7) to calculate k_3^H/k_3^D.

$$\frac{k_3^H(1.1k_3^D + k_3^D)}{k_3^D(1.1k_3^D + k_3^H)} = 1.72 \text{ and } k_3^H/k_3^D \cong 5$$

Since $k_3^H/k_3^D \cong 5$ and $k_{-2}/k_3^D \cong 1.1$, treatment of **4** with methoxide ion should give *ca.* 5/6 of **5** and *ca.* 1/6 of **3**, both at relatively fast rates. Note that for **4**-*d* the rates to form **3** and **5** are about equal so the rate of increase in absorbancy near 246 nm (due to both **3** and **5**) is about double that at 296 nm (due to **5** alone). For the hydrogen analog, **4**, formation of **5** is *ca.* fivefold faster than formation of **3** making the rate of increase in absorbancy at 246 nm less than that at 296 nm. A slow conversion of **3** to **5** should follow the initial rapid reaction of **4** with methoxide, and the infinity absorbance at 296 nm should be increased, in time, by about one-sixth the total absorbance recorded after **4** has completely disappeared. Examination showed that in this reaction there was a rapid increase in absorbance in the first 25 min. After this time the shape of the curve and the size of the absorbance reading at 296 nm ($A = 0.79$ with the base line at $A = 0.10$) remained essentially unchanged on further scanning (Figure 1). After 22 hr (*ca.* 97% completion), however, the absorbance reading at 296 nm had increased from 0.79 to 0.92. This increase in absorbance (1/6.4) is in good agreement with the estimated increase.

The corrected rate constants for k_2, k_{-2}, and k_3 in the reaction sequence

$$\mathbf{1} \xrightarrow{k_1} \mathbf{3} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{MeO^-} + \mathbf{4} \xrightarrow{k_3} \mathbf{5}$$

were calculated as follows.

Since $k_{-2}/k_3 = 1.1/5$, $k_3(\text{corr}) = (5/6.1)k_3(\text{obsd}) = 1.30 \times 10^{-1}\ M^{-1}\ \text{sec}^{-1}$ [$k_3(\text{obsd}) = 1.6 \times 10^{-1}$ at 38.6°—see Table I] and $k_{-2}(\text{corr}) = (1.1/6.1)k_3(\text{obsd}) = 2.85 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$. Also $k_2(\text{obsd}) = k_3^Hk_2/(k_3^H + k_{-2}) = 5/6.1k_2(\text{corr})$; $k_2(\text{corr}) = 6.1/5 \times 4.4 \times 10^{-5} = 5.38 \times 10^{-5}\ \text{sec}^{-1}$ at 38.8°.

It is possible, then, to calculate the equilibrium constant for the addition of methoxide ion to 2-phenyl-1-nitrocyclopentene (**4**).

$$\mathbf{4} + \mathrm{MeO^-} \underset{k_2}{\overset{k_{-2}}{\rightleftarrows}} \mathbf{3};\ K_{\text{eq}}(1\ M\ \text{NaOMe}) = (2.85 \times 10^{-2})/(5.38 \times 10^{-5}) = 5.3 \times 10^2$$

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[13] A pK_a in methanol for **1** or **2** below 14, which seems reasonable, would place the equilibrium constant for the reaction with methoxide ion at above 10^4.

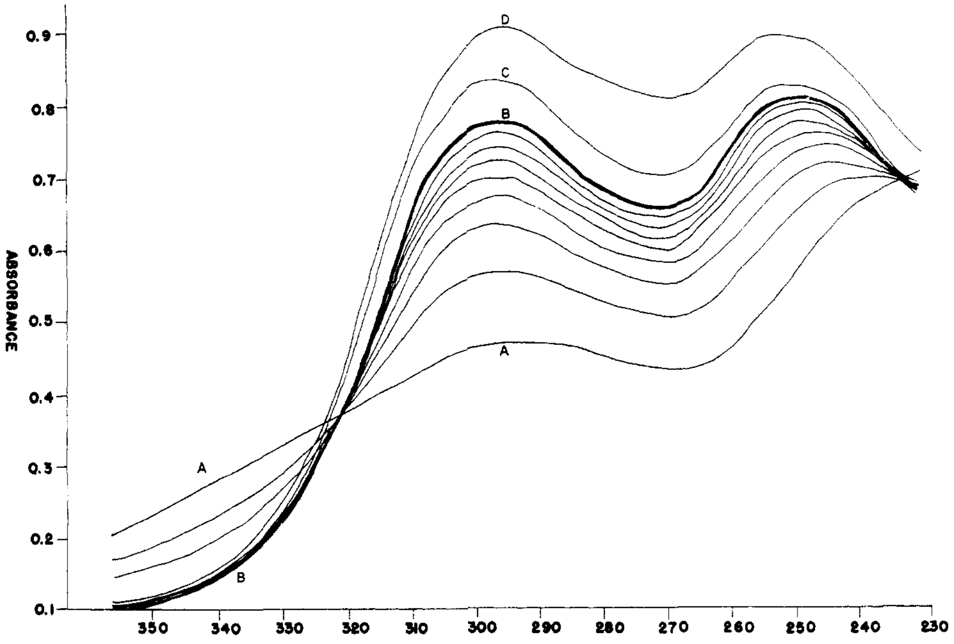

Figure 1. Repetitive scan of the reaction of 0.0456 M NaOMe in MeOH with 2-phenyl-1-nitrocyclopentene (**4**, *ca.* 10^{-5} M) at 38.7°. The time intervals are: curve A to the first curve above, 1 min; A–B, 25 min; A–C, 3.5 hr; A–D, 21.5 hr.

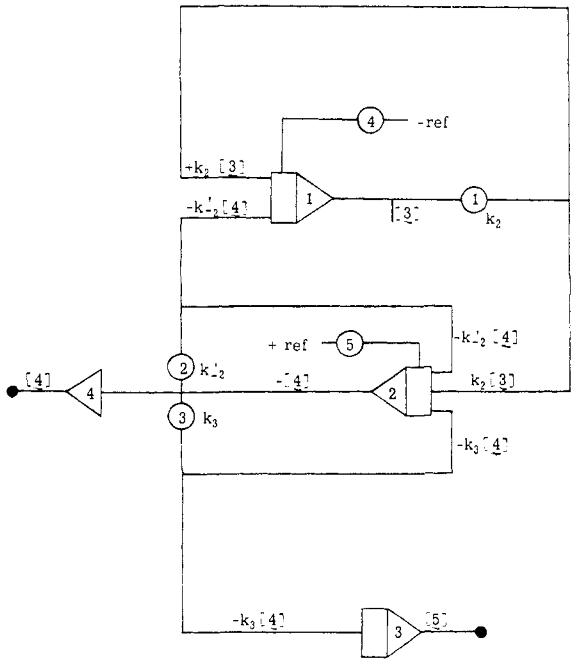

Figure 2. Analog computer program for simultaneous solution of eq 6, 7, and 8.[14,15] The rate constants and concentration terms refer to the reaction scheme presented above; $k_{-2}' = k_{-2}[\mathrm{MeO^-}]$ and $k_3' = k_3[\mathrm{MeO^-}]$.

Analog Computer Simulation of the Kinetics.[14,15] The kinetic scheme outlined above was checked by analog computer simulation, which permits simultaneous solution of the differential equations and allows visualization of the formation and disappearance of the transient intermediates **4** and **4**-*d* without recourse to the steady-state approximation. Differential eq 6, 7, and 8 governing the variation of the concentrations of **3**, **4**, and **5** (or their deuterio analogs) with time, *t*, in terms of the rate constants, k_2, k_{-2}, and k_3 were derived, and an analog circuit (Figure 2) was constructed using an Electronics Associates, Inc., Analog Computer Model TR20.[14,15]

$$d[\mathbf{3}]/dt = k_{-2}[\mathbf{4}][\mathrm{MeO^-}] - k_2[\mathbf{3}] \tag{6}$$

$$d[\mathbf{4}]/dt = k_2[\mathbf{3}] - k_{-2}[\mathbf{4}][\mathrm{MeO^-}] - k_3[\mathbf{4}][\mathrm{MeO^-}] \tag{7}$$

$$d[\mathbf{5}]/dt = k_3[\mathbf{4}][\mathrm{MeO^-}] \tag{8}$$

The computer analysis simulates the reaction of methoxide ion with: (a) **3**, (b) **3**-*d*, (c) **4**, and (d) **4**-*d*. Figure 3 depicts with solid lines the analog simulation of the changes in the percentage composition of **3**, **4**, and **5** with time for the reaction of 0.01 M NaOMe with **3** at 38.8° using the rate constants $k_2 = 5.38 \times 10^{-5}$ sec^{-1}, $k_{-2} = 2.86 \times 10^{-2}\ M^{-1}$ sec^{-1}, and $k_3 = 1.30 \times 10^{-1}\ M^{-1}$ sec^{-1}. The dashed lines represent the course of the same reaction with the deuterio analog, **3**-*d*, for the same base concentration and with the same values of k_2 and k_{-2}, but using $k_3^{\mathrm{D}} = 2.60 \times 10^{-2}$ M^{-1} sec^{-1}. Figure 4 depicts in a similar manner the reaction of methoxide ion with **4** and with **4**-*d* under the same conditions.

Note in Figure 3 that steady-state concentrations of **4** and **4**-*d* build up to different degrees and, as a consequence, the rate of formation of **5** is faster than that of **5**-*d*. This accords with the experimental observation of a $k_{\mathrm{H}}/k_{\mathrm{D}}$ value of 1.7 for the conversion of **1** to **5**, which was rationalized by assuming formation of a steady-state concentration of **4** (see above).[16]

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(14) We are greatly indebted to Robert Hershfield, not only for writing the computer program, but also for guiding us in its use.

(15) See R. Griswold and J. F. Haugh, *J. Chem. Educ.*, **45**, 576 (1968), for a discussion of the use of the analog computer in simulating complex chemical reactions.

(16) For reason of clarity, representations of reactions in 0.01 M NaOMe have been given in Figure 3 instead of 0.10 M (the experimental conditions). The effect of a tenfold decrease in base concentration is to increase the steady-state concentration of **4** by tenfold (Figures 3 and 4) and to decrease by tenfold the initial rate of loss of **4** and the rates of formation of **3** and **5** (Figure 4).

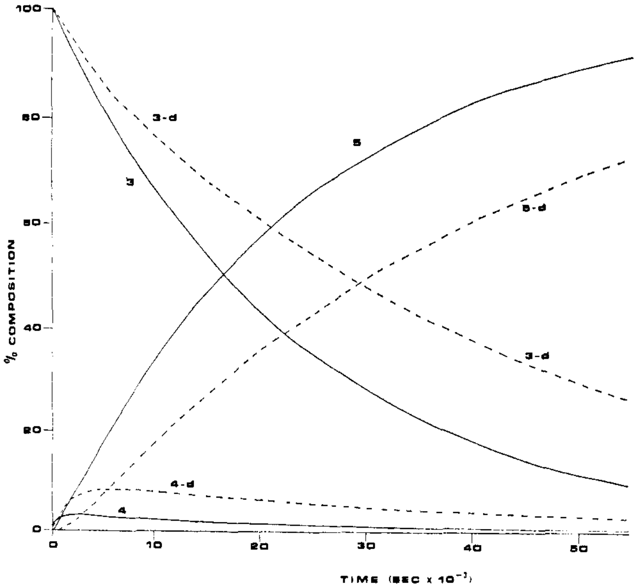

Figure 3. Simulation of the reaction of 0.01 *M* NaOMe–MeOH at 38.8° with **3** (solid lines) and with **3**-*d* (dashed lines).

Figure 4 shows the rapid initial conversion of **4** to **3** and **5** by methoxide ion (solid lines). This is followed by slow formation of **5** from **3** through intermediate **4**, which remains at a low steady-state concentration. The dashed lines represent the course of formation of **5**-*d* from **4**-*d*, once again simulated by replacement of k_3 by k_3^D. Figure 4 provides a pictorial explanation of the, at first, puzzling observation that reaction of NaOMe with **4**-*d* resulted in a rapid increase in the absorbance at 246 nm corresponding with the production of **5**-*d*, but a much smaller change in the absorbancy at 296 nm, where **5**-*d* also has a high intensity maximum. During the first 5 min **4**-*d* will be almost completely consumed, there being formed *ca.* 45% of **3**-*d* and *ca.* 55% of **5**-*d*. The increase in absorbance at 246 nm during this time brought about by the appearance of **3**-*d* and **5**-*d*, both of which absorb strongly in this region, will be about double that at 296 nm, which is due to **5**-*d* alone.

Conclusions

From the foregoing analyses of the kinetic data we have seen that in the methoxide-initiated elimination of MeOH from 2-phenyl-*trans*(or *cis*)-2-methoxy-1-nitrocyclopentane, **1** (or **2**), the rate-limiting step is a first-order elimination of methoxide ion from nitronate ion **3**. This constitutes one of the few known examples of a base-initiated β-elimination reaction involving a carbanion (nitronate ion) intermediate that follows first-order kinetics.[9]

Experimental Section

***cis*- and *trans*-1-Methoxy-2-nitro-1-phenylcyclopentanes.** A 7.5-g (0.030 mol) sample of 1-acetoxy-*trans*-2-nitro-1-phenylcyclopentane[17] was dissolved in a solution prepared from 500 ml of methanol and 80 ml of concentrated sulfuric acid. After 21 hr at 25° the solution was poured into 600 ml of saturated aqueous sodium bicarbonate. The organic material was removed by extraction with ether and dissolved in a minimum of chloroform.

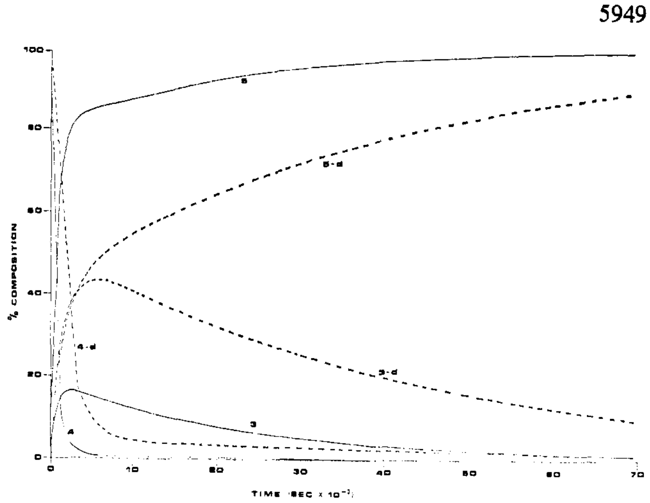

Figure 4. Simulation of the reaction of 0.01 *M* NaOMe–MeOH at 38.8° with **4** (solid lines) and with **4**-*d* (dashed lines).

Chromatography was carried out on a column (3.8 × 64 cm) slurry packed with silica gel (430 g) and 4% ether–hexane (600 ml). The column was eluted in 500-ml fractions with 6 l. of 15% ether–hexane and 2 l. of 50% ether–hexane. Fractions 5–11 gave 3.58 g (54%) of methoxy compounds with the *trans* isomer predominating. The isomers were finally separated by crystallization at low temperature from hexane; the *trans* isomer greatly predominated. Fractions 21–22 gave an unidentified by-product, mp 68–68.5° (ether–hexane).

1-Methoxy-*trans*-2-nitro-1-phenylcyclopentane melted at 73–74°: ir $\lambda_{\max}^{\text{KBr}}$ 3.30, 3.40, 3.46, 3.50, 3.60, 6.50 (NO_2), 6.70, 6.86, 6.92, 7.15, 7.32 (NO_2), 7.50, 7.65, 7.75, 8.04, 8.25, 8.50, 9.15 (OMe), 9.40, 9.54, 9.95, 10.20, 10.30, 10.45, 10.90, 11.05, 11.35, 11.65, 12.35, 13.00, 14.35; nmr $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.40 (m, Ar–H), 5.09 (m, C*H*NO₂, W_H = 12 Hz) 2.95 (s, methoxy H), 2.7–1.8 (m, methylene H).

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83. Found: C, 65.32; H, 6.93.

1-Methoxy-*cis*-2-nitro-1-phenylcyclopentane melted at 65.0–65.6°; ir $\lambda_{\max}^{\text{KBr}}$ μ 3.40, 3.46, 3.50, 3.60, 6.50 (NO_2), 6.70, 6.80, 6.92, 7.32 (NO_2), 7.58, 7.84, 8.05, 8.26, 8.36, 8.66, 8.90, 9.34 (OCH_3), 9.65, 9.86, 9.95, 10.50, 10.90, 11.94, 13.10, 14.30; nmr $\delta_{\text{TMS}}^{\text{CDCl}}$ 7.50 (s, Ar–H), 5.00 (apparent quartet, C*H*NO₂, W_H = 10 Hz), 3.05 (s, methoxy H), 1.67–2.63 (m, methylene).

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83. Found: C, 65.07; H, 6.83.

The structures were assigned from the nmr spectra by analogy to 1-methoxy-*cis*- and 1-methoxy-*trans*-2-nitro-1-phenylcyclohexanes. In the latter the chemical shift for the MeO group for the *trans* isomer was upfield relative to the *cis* isomer, whereas the C*H*NO₂, signal came downfield for the *trans* isomer.[18]

2-Phenyl-1-nitrocyclopentene-3,3-d_2 and 2-Phenyl-*trans*-2-methoxy-1-nitrocyclopentane-1,3,3-d_3. Addition of 12 g (0.137 mol) of cyclopentanone-2,2,5,5-d_4[19] in 30 ml of ether to phenylmagnesium bromide (0.15 mol) in 80 ml of ether gave crude 1-phenylcyclopentanol-2,2,5,5-d_4, which was dehydrated, without purification by the method of Garbisch[20] to give 1-phenylcyclopentene-2,5,5-d_3. Addition of acetyl nitrate[17] gave 2-phenyl-*trans*-2-acetoxy-1-nitrocyclopentene-1,3,3-d_3, which was converted to 2-phenyl-*trans*-2-methoxy-1-nitrocyclopentane-1,3,3-d_3 by the method described above and to 2-phenyl-1-nitrocyclopentene-3,3-d_2 by the method of Bordwell and Garbisch.[17]

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