Three Types of Base-Initiated β-Elimination Reactions Involving Carbanion Intermediates

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Abstract: Comparison has been made between the methoxide ion initiated *anti* and *syn* β-eliminations of HOAc from nitroacetates **1** and **2** and the base-initiated elimination of HOMe from the corresponding methoxy compounds. The latter are shown to involve reversible carbanion (nitronate ion) formation with NaOMe–MeOH and nonreversible carbanion formation with *t*-BuOK–*t*-BuOH. Using comparisons of rate data, substituent effects, deuterium isotope effects, and activation parameters for acetoxy *vs.* methoxy compounds as criteria, the conclusion is drawn that the eliminations from **1** and **2** involve steady-state formation of carbanion intermediates. These studies therefore encompass all three possible types of carbanion elimination mechanisms. It is suggested that most β-eliminations involving activated β-protons proceed by carbanion mechanisms.

Base-initiated β-elimination reactions to form C=C bonds proceeding by way of carbanion intermediates can be divided into three types.[1] In type 1 rapid, complete, and essentially irreversible formation of a carbanion is followed by a rate-limiting, first-order expulsion of the leaving group (LG). An example of this relatively rare carbanion elimination was given in the preceding paper.[2] A second, more common type is that in which the carbanion is formed rapidly and reversibly; in such instances the presence of the carbanion can be detected by deuterium exchange.[3] A third type, which may be much more prevalent than commonly supposed, is one in which the carbanion is formed in only steady-state concentrations. Here carbanion formation is essentially irreversible because loss of the leaving group is much more rapid than protonation of the carbanion by the solvent. This, and the second type of elimination mentioned above, will follow second-order kinetics.[4]

Type 1, irreversible first-order carbanion elimination[4]

$$B^- + HCCLG \underset{\text{fast}}{\rightleftharpoons} BH + {}^-CCLG \xrightarrow{\text{slow}} C{=}C + LG^-$$

Type 2, reversible second-order carbanion elimination

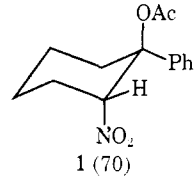
$$B^- + HCCLG \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} BH + {}^-CCLG \xrightarrow{\text{slow}} C{=}C + LG^-$$

Type 3, irreversible second-order carbanion elimination[4]

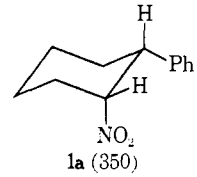
$$B^- + HCCLG \overset{\text{slow}}{\rightleftharpoons} BH + {}^-CCLG \xrightarrow{\text{fast}} C{=}C + LG^-$$

The most difficult type of carbanion elimination to identify is that in which the carbanion is formed in a steady-state concentration. The reason is that this mechanism merges imperceptibly into the concerted E2 mechanism. The two mechanisms are indistinguishable on stereochemical grounds or on the basis of the kinetic order of the reaction,[1] but differentiation can be made, in principle, by varying the nature of the leaving group.[1d] Using an approach of this type we believe that we have been successful in making this distinction, and that we have found an example of a carbanion mechanism of this type. In addition, further examples of reactions proceeding by type 1 and type 2 carbanion mechanisms are also described.

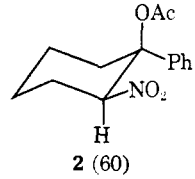
Several years ago we observed a piperidine- (in $CHCl_3$–EtOH) initiated elimination of HOAc from the nitroacetates **1** and **2** for which assignment of a carbanion mechanism seemed reasonably secure on the basis of (a) stereochemistry (*syn* elimination 3.5-fold faster than *anti* elimination), (b) solvent and salt effects (expected accelerations were observed in a more polar environment), and (c) the identity for *syn* and *anti* eliminations of the ρ values (+1.45) and k_H/k_D isotope effects (*ca.* 4.9).[5] Faith in this interpretation was shaken somewhat, however, by comparison of the methoxide-initiated rates of elimination for **1** and **2** with the methoxide-initiated rates of proton abstraction for the corresponding nitroalkanes, **1a** and **2a**[6] [the relative rates (NaOMe–MeOH at 25°) are given in parentheses].



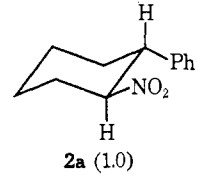
1 (70)



1a (350)



2 (60)



2a (1.0)

(1) See (a) D. V. Banthorpe, "Elimination Reactions," Elsevier, New York, N. Y., 1963, Chapter 4; (b) D. J. McLennan, *Quart. Rev., Chem. Soc.*, **21**, 490 (1967); (c) Z. Rappoport, *Tetrahedron Lett.*, 3601 (1968); and (d) J. F. Bunnett, *Surv. Progr. Chem.*, **5**, 53 (1969), for classifications of carbanion elimination mechanisms.

(2) F. G. Bordwell, K. C. Yee, and A. C. Knipe, *J. Amer. Chem. Soc.*, **92**, 5945 (1970).

(3) (a) J. Hine, R. Wiesboeck, and O. B. Ramsay, *ibid.*, **83**, 1222 (1961); (b) J. Hine, R. Wiesboeck, and R. G. Ghirardelli, *ibid.*, **83**, 1219 (1961); (c) D. J. Cram and A. S. Wingrove, *ibid.*, **86**, 5490 (1964); (d) J. Crosby and C. J. M. Stirling, *ibid.*, **90**, 6869 (1968); (e) L. R. Fedor, *ibid.*, **91**, 908 (1969).

(4) Although the term "irreversible" is not correct in an absolute sense, it is convenient to refer to these three types of eliminations as (1) irreversible first-order carbanion eliminations, (2) reversible second-order carbanion eliminations, and (3) irreversible second-order carbanion eliminations.[1]

(5) F. G. Bordwell, R. A. Arnold, and J. B. Biranowski, *J. Org. Chem.*, **28**, 2496 (1963).

(6) (a) F. G. Bordwell and M. M. Vestling, *J. Amer. Chem. Soc.*, **89**, 3906 (1967); (b) F. G. Bordwell and K. C. Yee, *ibid.*, **92**, 5933 (1970).

Table I. Rates of the Reaction of 2-Phenyl-*trans*-2-acetoxy-1-nitrocyclohexane (1) and Related Compounds with Sodium Methoxide in Methanol (Refer to Schemes I and III)

Substrate	Base concn, M	T, °C	k_1,[a] M^{-1} sec^{-1}	k_2,[b] M^{-1} sec^{-1}
2-Phenyl-*trans*-2-acetoxy-1-nitrocyclohexane (1)	0.0279	25.3	3.4×10^{-1}	
	0.0121	25.0	2.8×10^{-1}	
	0.0145	0.4		6.4×10^{-5}
	0.0144	24.8		5.9×10^{-3}
	0.056[c]	25.0		1.0×10^{-1} [c]
2-Phenyl-*trans*-2-acetoxy-1-nitrocyclohexane-1,3,3-d_3	0.0121	25.1	3.5×10^{-2}	
2-Phenyl-*cis*-2-acetoxy-1-nitrocyclohexane (2)	0.0279	25.3	3.0×10^{-1}	
	0.0121	25.1	3.0×10^{-1}	
	0.0144	24.8		6.1×10^{-3}
	0.0560[c]	25.0		1.0×10^{-1} [c]
2-Phenyl-*cis*-2-acetoxy-1-nitrocyclohexane-1,3,3-d_3	0.0121	25.0	3.8×10^{-2}	
2-*p*-Chlorophenyl-*trans*-2-acetoxy-1-nitrocyclohexane	0.0362	25.4	1.0	
2-*p*-Chlorophenyl-*cis*-2-acetoxy-1-nitrocyclohexane	0.0310	24.6	7.7×10^{-1}	
2-Phenyl-*trans*-2-bromoacetoxy-1-nitrocyclohexane	0.0355	25.8	9.0×10^{-1}	
2-Phenyl-1-nitrocyclohexene (3)	0.0144	24.8		5.9×10^{-3}
trans-4-Phenyl-1-nitrocyclohexane	0.0552	25.0	4.6×10^{-1}	
cis-4-Phenyl-1-nitrocyclohexane	0.0276	25.0	2.2	
2-Phenyl-*trans*-2-acetoxy-1-nitrocyclopentane (10)	0.00227	25.3	5.5	
	0.00309	24.8	5.6	
	0.00242	25.0	5.2	
	0.00121	20.5	3.6	
	0.00242	15.9	2.9	
	0.00536	0.30	7.1×10^{-1}	
2-Phenyl-*trans*-2-acetoxy-1-nitrocyclopentane-1,3,3-d_3	0.00242	25.0	8.3×10^{-1}	
2-*p*-Bromophenyl-*trans*-2-acetoxy-1-nitrocyclopentane	0.00138	25.1	12	
	0.00276	25.1	13	

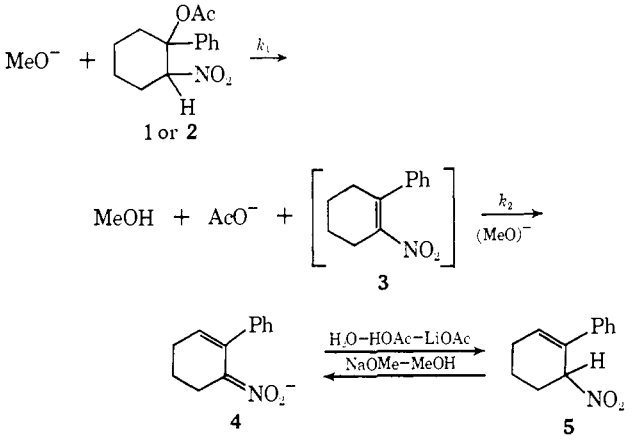
[a] Rate of formation of 3 (or its analog); average of two or more runs. For 1, 2, and their deuterio derivatives a calculated value for A_∞ of 3 was used and the reactions were followed to *ca.* two half-lives. [b] Rate of formation of 4 (or its analog); average of two or more runs followed by the increase in absorbance at 300 nm. [c] Potassium *t*-butoxide in *t*-butyl alcohol.

It will be observed that the methoxide ion promoted elimination reaction of 2 is 60 times as rapid as proton abstraction from the corresponding nitroalkane, 2a, whereas the elimination reaction for 1 is actually five times slower than proton abstraction from 1a. At first sight one might be tempted to ascribe the 60-fold rate acceleration of 2 over 2a to a concerted *anti* E2 elimination and the fivefold rate retardation to some factor disfavoring a nonconcerted *syn* elimination. But this analysis ignores the reason for the 350-fold difference in rates between 1a and 2a. Evidence has been presented in an earlier paper[6b] to show that this difference is caused by ring deformation in the *trans* isomer (2a), but not the *cis* isomer (1a), which leads to the marked retarding effect on proton abstraction. In 2 the presence of the acetoxy group might be expected to prevent ring deformation since the stabilization gained by moving the nitro group and phenyl groups away from one another could well be lost by forcing the nitro and acetoxy groups into closer proximity. Proton abstraction from 2 would not then be retarded relative to 1. To test this idea it was decided to examine the behavior of the methoxy analogs of 1 and 2 since these should react with methoxide ion by a carbanion mechanism,[2] and should therefore serve as models for this type of mechanism. It seemed likely that comparisons of rate and activation parameters for corresponding acetoxynitroalkanes, methoxynitroalkanes, and parent nitroalkanes would provide useful information. We also wished to examine deuterium isotope effects and the effect on the rates of substituents in the phenyl ring.

Results

Eliminations with β-Nitroacetates. Some difficulty was encountered in following the rate of formation of 2-phenyl-1-nitrocyclohexene (3) from 1 or 2 and methoxide ion spectrophotometrically because the rather weak absorbance of 3 (λ_{max} 280 nm, ϵ_{max} 1890) was swamped after about two half-lives by the appearance of the strongly absorbing nitronate ion 4 (ϵ 10,900 at λ_{max} 257 nm and ϵ 13,000 at λ_{max} 290 nm).

Scheme I



The identity of 4 was established by conversion to 6-nitro-1-phenylcyclohexene (5) with acetic acid–acetate buffer and by its generation from either synthetic 3 or 5 by the action of NaOMe (Scheme I). Rate data obtained with the *p*-Cl derivatives of 1 and 2 (Table I) are more reliable because the increase in rate of elimination (k_1) in this instance was not matched by a comparable increase in rate of proton abstraction from 3 (k_2). The rate of appearance of 4 was equal, within experimental error, starting from 1, 2, or 3 (Table I).

Eliminations with Nitro Methyl Ethers. It was anticipated that the reactions of 2-phenyl-*trans*-2-methoxy-

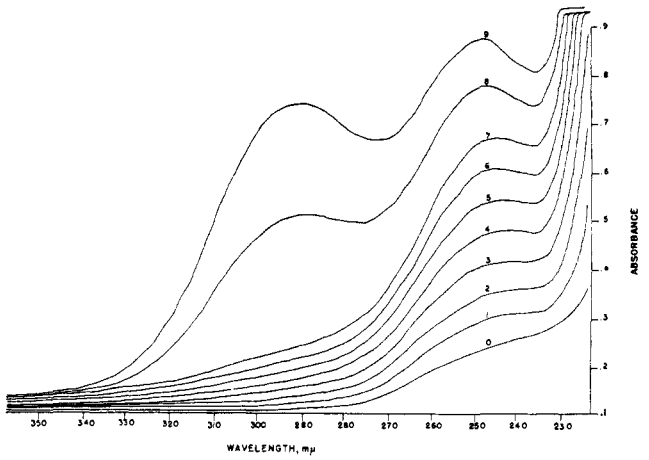


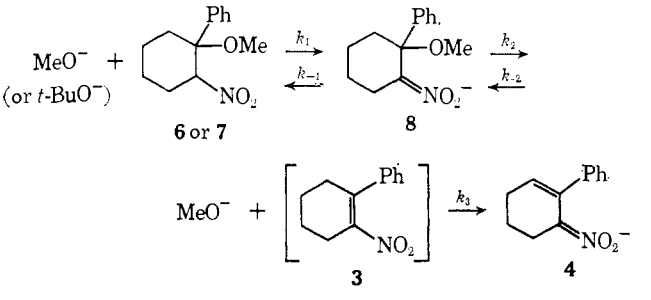
Figure 1. Changes in the ultraviolet absorption spectra of a solution formed by adding increments of 2 *M* NaOMe–MeOH to 2-phenyl-*cis*-2-methoxy-1-nitrocyclohexane (6.5×10^{-5} *M* in 3 ml of 0.0456 *M* NaOMe–MeOH) at 38.7°. Increments: curve 1, 31 μl; 2, 62 μl; 3, 102 μl; 4, 142 μl; 5, 182 μl; 6, 222 μl; 7, 262 μl; 8, 262 μl; 9, 262 μl (1.0-cm cell). Times: curves 0–7, about 1-min intervals; 0–8, 40 min; 0–9, 70 min.

1-nitrocyclohexane (**6**), or its *cis* isomer (**7**) with NaOMe–MeOH would rapidly produce a high concentration of the corresponding carbanion (nitronate ion) by analogy with the behavior of the corresponding five-membered ring compounds.[2] It was observed, however, that treatment of **6** with excess 0.1 *M* NaOMe gave only a low extinction maximum (ϵ_{max} 2310) in the region near 240 nm characteristic of nitronate ions.[2,6b] This could mean either (a) that the nitronate ion (**8**) is formed in high concentration, but has a much lower extinction coefficient than that of the corresponding five-membered ring nitronate ion (ϵ_{max} 11,000), or (b) that **8** is being formed in only low concentrations. The latter is the correct explanation because addition of increments of 2 *M* NaOMe–MeOH solution to a solution of **6** or **7** (*ca.* 10^{-5} *M*) in 3 ml of 0.0456 *M* NaOMe–MeOH caused successive increases in the absorbance at 240 nm (Figure 1).[7]

After about 5 min new absorption peaks at 253 and 292 nm began to appear in the reaction of NaOMe–MeOH with **6** or with **7**. These are due to the formation of nitronate ion **4**.

The sequence shown in Scheme II is analogous to

Scheme II



that demonstrated for the five-membered analog of **6** (or **7**), except that nitronate ion **8** is formed incompletely and reversibly, even in the presence of excess base (Figure 1). As a consequence, the rate of appearance of **4** is dependent on methoxide concentration (Table II), whereas for the five-membered ring analog of **6** (or **7**) the appearance of the nitronate ion corresponding to **4** is independent of methoxide ion concentration.[2]

When *t*-BuOK/*t*-BuOH was used in the reaction of **6** (or **7**), nitronate ion **8** was formed in high concentration (λ_{max} 252 nm, ϵ_{max} 10,000). The rate of appearance of **8** was first order in *t*-BuOK but the appearance of **4** was independent of base concentration (Table II). This behavior is analogous to that of the five-membered ring analog with NaOMe–MeOH.[2]

Activation Parameters. A comparison of activation parameters for proton abstractions and eliminations of HOAc and HOMe is shown in Table III.

Discussion

Reversible Second-Order Carbanion β-Eliminations. The reaction of 2-phenyl-*cis*-2-methoxy-1-nitrocyclohexane (**7**) with sodium methoxide in methanol provides an example of a second-order (overall) β-elimination involving the reversible formation of a carbanion (nitronate ion) intermediate (Scheme II). The appearance of the anion intermediate is rapid and demonstrably reversible (Figure 1).[8] Loss of methoxide ion from **8** (k_2) is slow, but is not likely to be rate limiting since it is probably reversible. This is at least the situation with the analogous five-membered ring compound,[2] and, since the rate of proton abstraction for 2-phenyl-1-nitrocyclopentene is *ca.* 5.7 times greater than that for 2-phenyl-1-nitrocyclohexene (**3**), it seems likely that addition of methoxide ion to the double bond of **3** will compete with proton abstraction from **3** just as happens in the five-membered ring series. If we assume that both of the first two steps are reversible (type 2 mechanism), *i.e.*, $k_{-1} \gg k_2$ and $k_{-2} \gg k_3$, then $k_{obsd} = [MeO^-]k_1k_2k_3/k_{-1}k_{-2} = 7.3 \times 10^{-4}\ M^{-1}\ sec^{-1}$ (Table II). The reaction will then be first order in methoxide, as observed (Table II). The first-order dependence on [NaOMe] is also consistent with a mechanism where k_2 is rate limiting (type 3 mechanism), *i.e.*, $k_{-1} \gg k_2$, but $k_3 \gg k_{-2}$. However, we feel this is a less likely mechanism, for the reasons just given.

In the presence of an excess of the stronger base, potassium *t*-butoxide, the **7** ⇄ **8** equilibrium is shifted strongly to the side of **8**. The rate of formation of **8** from **7** (or **6**) can be measured, and is first order in *t*-butoxide ion (Table II). This is then another example of a carbanion mechanism for β-elimination wherein the carbanion is formed in high concentration and the rate of appearance of the product is first order in substrate and zero order in base (type 1 mechanism, *i.e.*, irreversible first-order carbanion elimination).[2]

Irreversible Second-Order Carbanion Elimination. It will be recalled that the methoxy compounds **6** and **7** were prepared to serve as models for a carbanion mechanism of β-elimination. The data just presented show conclusively that they do indeed react by carbanion

(7) The difference in behavior of the five- and six-membered ring compounds is understandable inasmuch as nitrocyclopentane is about two pK_a units more acidic than nitrocyclohexane [see P. W. K. Flanagan, H. W. Amburn, H. W. Stone, J. G. Traynham, and H. Shechter, *J. Amer. Chem. Soc.*, **91**, 2797 (1969)]. If the pK_a of **6** and **7** in methanol approaches that of methanol, relatively low concentrations of **8** would be formed.

(8) Nitronate ion formation also occurs reversibly with 2-substituted nitrocyclohexanes.[6b] Even nitrocyclohexane itself forms the nitronate ion incompletely at methoxide concentrations below 0.05 *M*.[6b]

Table II. Rates of Reaction of 2-Phenyl-*trans*-2-methoxy-1-nitrocyclohexane (**6**) and Related Compounds with Potassium *t*-Butoxide in *t*-Butyl Alcohol (Refer to Scheme II)

Substrate	Base concn, *M*	*T*, °C	k_1,[a] M^{-1} sec^{-1}	k_2,[b] sec^{-1}	k_3,[c] M^{-1} sec^{-1}
2-Phenyl-*trans*-2-methoxy-1-nitrocyclohexane (**6**)	0.00183	38.4	21		
	0.00366	38.6	22		
	0.00183	38.6		2.7×10^{-4}	
	0.00366	38.6		3.4×10^{-4}	
	0.0273	38.8		3.2×10^{-4}	
	0.0545	38.8		2.7×10^{-4}	
2-Phenyl-*cis*-2-methoxy-1-nitrocyclohexane (**7**)	0.0456[d]	38.6			7.5×10^{-4} [d,e]
	0.0912[d]	38.4			7.1×10^{-4} [d,e]
	0.00183	38.8	29		
	0.00363	38.6	30		
	0.00183	38.6		3.2×10^{-4}	
	0.00273	38.8		3.2×10^{-4}	
	0.00366	38.6		3.6×10^{-4}	
	0.00545	38.8		2.8×10^{-4}	
cis-2-Phenyl-1-nitrocyclohexane (**1a**)	0.000912	25.2	460		
trans-2-Phenyl-1-nitrocyclohexane (**2a**)	0.00183	25.0	1.3		
2-Phenyl-1-nitrocyclohexene (**3**)	0.0545	38.6			2.4×10^{-1}
	0.0273	38.8			2.5×10^{-1}
	0.00366	38.6			3.0×10^{-1}
	(0.0456)[d]	38.7			2.8×10^{-2} [d]
2-Phenyl-*trans*-2-methoxy-1-nitrocyclopentane		25.0	2.6×10^{-1} [d]		
2-Phenyl-*trans*-2-methoxy-1-nitrocyclopentane-1,3,3-d_3		25.0	3.5×10^{-2} [d]		
1-Phenyl-2-nitropropane		25.0	5.0×10^{-1} [d]		
1-Phenyl-2-nitropropane-2-d_1		25.0	6.7×10^{-2} [d]		

[a] Rate of formation of nitronate ion **8** (or its analog); average of two or more runs (near 250 nm). [b] Apparent rate of elimination of methoxide ion from **8** (or its analog); average of two or more runs (near 300 nm). [c] Apparent rate of formation of **4**; average of two or more runs (near 300 nm). [d] Sodium methoxide in methanol. [e] This rate constant is complex; see Discussion.

Table III. Activation Parameters for Elimination Reactions and Related Proton Abstractions Initiated by Sodium Methoxide in Methanol

Substrate	*T*, °C	k,[a] M^{-1} sec^{-1}	E_a, kcal/mol	ΔS^*, eu	r[b]
2-Phenyl-*trans*-2-acetoxy-1-nitrocyclopentane (**10**)	0.3	7.03×10^{-1}			
	15.9	2.87			
	20.1	3.55			
	25.0	5.18	13.1	−13.4	0.999
2-Phenyl-*trans*-2-methoxy-1-nitrocyclopentane	25.0	2.64×10^{-1}	15.4	−11.7	0.998
	38.8	9.20×10^{-1}			
	50.0	1.44			
cis-2-Phenyl-1-nitrocyclopentane	14.4	5.10×10^{-1}			
	24.6	1.35	16.2	−5.4	
trans-2-Phenyl-1-nitrocyclopentane	13.7	1.25×10^{-1}			
	24.9	3.34×10^{-1}	14.8	−13.2	0.999
	36.9	8.85×10^{-1}			
	45.6	1.66			
2-Phenyl-1-nitrocyclopentene	24.8	4.91×10^{-2}	15.6	−14.0	
	38.6	1.58×10^{-1}			
2-Phenyl-*trans*-2-methoxy-1-nitrocyclopentane	25.0	7.60×10^{-6} [c]	25.0	−0.2	0.999
	38.8	4.44×10^{-5} [c]			
	49.5	1.89×10^{-4} [c]			

[a] Average of two or more runs. [b] Correlation coefficient for Arrhenius plots. [c] First-order rate for the appearance of the unsaturated nitronate ion.

mechanisms. It will be of interest, therefore, to compare their behavior with that of the corresponding acetoxy compounds. The parent nitroalkanes can also serve as models for the carbanion mechanism, except that for *trans*-2-phenyl-1-nitrocyclohexane there is a large rate-retarding effect caused by ring deformation and the attending lowering of ground-state energy.[6b] This is illustrated in Table II by the 350-fold faster rate of proton abstraction by *t*-BuOK from *cis*-2-phenyl-1-nitrocyclohexane than from the *trans* isomer.

Examination of Table II shows for the methoxy compounds **6** and **7**, that **7**, which has *trans*-diequatorial phenyl and nitro groups, actually reacts slightly faster (1.3-fold) than does **6** where these groups are *cis*. Furthermore, the relative ground-state energies for **6** and **7** are nearly the same.[6b] This contrasts sharply with the 2-phenyl-1-nitrocyclohexanes where ring deformation makes the *trans* isomer much more stable and much less reactive.[6b] Clearly the ring deformation effect has not carried over to **6** and **7**, and, therefore, would not be expected to appear in the corresponding acetoxy compounds, **1** and **2**. The nearly identical rates of β-elimination for **1** and **2** correspond to the nearly identical rates of formation of carbanions

(nitronate ions) from **6** and **7**. The data are entirely consistent with a carbanion mechanism for the elimination reactions of **1** and **2** (type 3 mechanism).

Examination of the spectrum near 250 nm, where nitronate ion **9** would be expected to have a high extinction maximum (compare **8**), during early stages of the reaction of **1** or **2** with NaOMe failed to give any evidence for the presence of **9**. This means that either **9** is being formed in only steady-state concentrations ($k_2' \gg k_{-1}$) or that breaking of the H–C and C–OAc bonds is concerted (E2 mechanism). We prefer the carbanion mechanism because of the near identity of the rates for *anti* and *syn* eliminations and on the basis of additional evidence cited below.

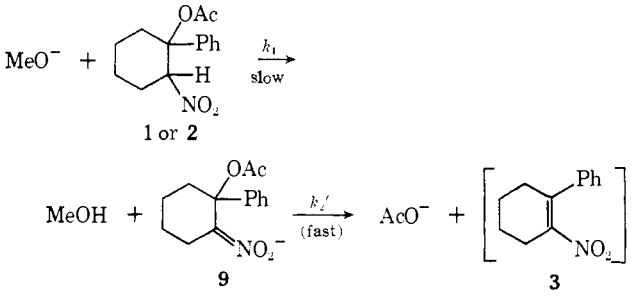
If the second-order rate constants recorded in Table I (k_1) represent rate of proton abstraction from **2** (equatorial Ph and equatorial NO_2) to form **9**, as we believe, then this rate should be comparable in magnitude to that for *trans*-4-phenyl-1-nitrocyclohexane (equatorial Ph and equatorial NO_2), except for the effect of the acetoxy group. Actually the elimination reaction is *ca.* 1.5-fold slower than the proton abstraction rate, and proton abstraction for *cis*-4-phenyl-1-nitrocyclohexane is *ca.* sevenfold faster than that for **1** (Table I). Similarly, proton abstraction from *cis*-2-phenyl-1-nitrocyclohexane is *ca.* fivefold faster than β-elimination from **1**.[9] On the other hand, methoxide ion initiated *syn* elimination from 2-phenyl-*trans*-2-acetoxy-1-nitrocyclopentane (**10**) is *ca.* 3.8-fold faster than is proton abstraction from *cis*-2-phenyl-1-nitrocyclopentane. This is about the acceleration expected for the inductive effect of an acetoxy group on the rate of abstraction of a β-proton. The slower rates produced by substitution of a β-acetoxy group in the cyclohexane series are anomalous. Possibly this substitution causes a lowering of ground-state energy, which overshadows the inductive effect.

Since the methoxy group is less electron withdrawing than the acetoxy group, one would expect substitution of the β-methoxy group into *cis*-2-phenyl-1-nitrocyclohexane to cause an even larger rate retardation. This is realized since **6** is *ca.* 21-fold less reactive than *cis*-2-phenyl-1-nitrocyclohexane toward *t*-BuOK and **7** is also less reactive (*ca.* 15-fold, see Table II). In this instance the retarding effect carries over to one of the five-membered ring analogs as well; 2-phenyl-*trans*-2-methoxy-1-nitrocyclopentane is *ca.* 5.8-fold less reactive than its parent, *cis*-2-phenyl-1-nitrocyclopentane, but 2-phenyl-*cis*-2-methoxy-1-nitrocyclopentane is *ca.* 5.6-fold more reactive than its parent, *trans*-2-phenyl-1-nitrocyclopentane.

If the elimination reactions of **1** and **2** are occurring by carbanion mechanisms, one would expect that substituents in the phenyl ring would have similar effects for the elimination reactions and for model reactions wherein carbanions are known to be formed. This is the case. Substitution of a *p*-Cl group into **1** increases the rate by 2.9-fold and similar substitution into **2** increases the rate by 2.6-fold. In the five-membered ring series a *p*-Br substituent causes a 2.4-fold increase in rate (Table I). The corresponding rate increases in the parent nitroalkanes (**1a**, **2a**, and *cis*-2-phenyl-1-nitrocyclopentane) are 1.8, 2.9, and 1.8, respectively. In the open-chain series 1-*p*-chlorophenyl-2-nitropropane reacts 2.0 times as rapidly as does 1-phenyl-2-nitropropane.

If the elimination reactions of **1** and **2** are occurring by Scheme III, as we believe, changing the leaving

Scheme III



group from acetoxy to bromoacetoxy should affect the rate only to the extent that the inductive effect of the bromine substituent accelerates proton abstraction. In practice this structural change caused a threefold acceleration of rate for *syn* elimination from **1** (Table I). This appears to be a reasonable value for the field effect of bromine on the rate of abstraction of the (*cis*) proton α to the nitro group. On the other hand, the effect is appreciably smaller than one might expect for a concerted E2 reaction. The reasoning here is as follows. The ratio of acidities of the conjugate acids of $BrCH_2CO_2^-$ and $HCH_2CO_2^-$ is about the same as that for the conjugate acids of Br^- and Cl^- (*ca.* 100/1). On this basis one might expect the leaving group effects, k_{Br}/k_{Cl} and $k_{BrCH_2CO_2}/k_{HCH_2CO_2}$ to be comparable in an E2 reaction. The k_{Br}/k_{Cl} ratios in the systems CH_3CH_2X and $PhCH_2CH_2X$ are 28 and 60, respectively;[10] these ratios are an order of magnitude larger than that observed for **1** and its bromoacetoxy analog.

Deuterium Isotope Effects. It is of interest to compare the deuterium isotope effect for the reactions of 2-phenyl-*trans*-2-methoxy-1-nitrocyclopentane (k_H/k_D = 7.4) and $PhCH_2CHMeNO_2$ (k_H/k_D = 7.5), where carbanions (nitronate ions) are unquestionably formed, with those for the elimination reactions of the nitroacetates **1**, **2**, and **10** where carbanions are postulated to be formed in steady-state concentrations as intermediates. The isotope effects should be similar for carbanion eliminations, but if proton abstraction is accompanied by formation of a C=C bond and by C—OAc bond breaking (E2 mechanism) one would expect a different, probably smaller, primary isotope effect. The observed k_H/k_D values for **1**, **2**, and **10** are 8.0, 8.0, and 6.3, respectively (Table I). Furthermore, the value of 4.9 obtained previously for the reaction of **1** or **2** with piperidine[5] is in line with data showing that in the formation of nitronate ions from nitroalkanes the k_H/k_D values decrease with decreasing basicity of the attacking base.[11]

(9) The eliminations are *ca.* 200-fold faster than proton abstraction from *trans*-2-phenyl-1-nitrocyclohexane, but this comparison is not valid because of ring deformation.[6b]

(10) (a) E. D. Hughes and V. G. Shapiro, *J. Chem. Soc.*, 1177 (1937); (b) C. H. DePuy and C. A. Bishop, *J. Amer. Chem. Soc.*, **82**, 2535 (1960).

(11) (a) O. Rietz, *Z. Phys. Chem. Abt. A*, **136**, 363 (1936); (b) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, **294**, 273 (1966). The latter authors give k_H/k_D ratios of 10.3, 6.5, 4.3, and 3.8 for the reactions of nitromethane with the bases HO^-, AcO^-, $ClCH_2CO_2^-$, and H_2O, respectively.

It has been suggested that the k_H/k_D values for carbanion eliminations should be low.[1b] This conclusion was apparently based on the expectation of a product-like transition state for carbanion formation. This would be unsymmetrical and, therefore, the primary deuterium isotope effect would presumably be small. The data presented herein show that this is *not* true when the carbanions formed are nitronate ions. We doubt that it will hold in other instances either.

Activation Parameters. Further support for the view that the elimination reaction of 2-phenyl-*trans*-2-acetoxy-1-nitrocyclopentane (**10**) is proceeding by carbanion formation comes from a comparison of its activation parameters with those of reactions known to give nitronate ions (Table III). Note particularly the close similarity of the parameters for the elimination of HOAc and the formation of the nitronate ion from the methoxy analog (E_a = 13.1 and 15.4, respectively, and ΔS^* = −13.4 and −11.7).

Conclusions

The failure of the nitroacetate **2** to avail itself of the *anti* E2 mechanism is worthy of special comment. The sizable k_H/k_D ratio indicates appreciable H—C bond breaking in the transition state. An appreciable negative charge must be building up on carbon, but this negative charge is not delocalized to any very large extent to the oxygen atoms of the nitro group since the rate in other instances has been found *not* to parallel nitronate ion stability.[6b,12] It is surprising, then, that the negative charge is not dissipated by ejection of acetate ion and simultaneous formation of a C=C bond (E2 mechanism). That it is not must mean that this process is energetically unfavorable. It is evidently more favorable energetically to form the nitronate ion, which subsequently ejects the acetate ion. In other words, it is energetically more economical to convert the two adjacent sp^3 carbon atoms to sp^2 carbon atoms in separate steps rather than in a concerted fashion. This seems to indicate that structural reorganization is the costly factor and that *the preferred mechanism will be that requiring the least structural reorganization* (principle of least motion[13]).

According to this picture the nitro group exerts its activating influence in promoting elimination reactions primarily *by an inductive effect.* This view is supported by qualitative evidence in the literature which suggests that the effects of strongly activating groups (NO_2, CN, SO_2R, NMe_3^+, COR, SOR) on elimination reactions do not differ greatly,[14] despite differences in pK_a's of the corresponding carbon acids that range over 20 powers of ten. It now seems likely that *all* base-initiated elimination reactions wherein the proton is activated by groups of this type *proceed by carbanion mechanisms.* Carried to its extreme the principle of least motion predicts that most base- (or solvent-) initiated elimination reactions will proceed by two-stage mechanisms and that the E2 mechanism will be relatively rare. It appears to be worthwhile to at least consider β-elimination reactions from this point of view; this is the approach we are presently taking.

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(12) F. G. Bordwell, W. J. Boyle, Jr., and K. C. Yee, *J. Amer. Chem. Soc.*, **92**, 5926 (1970).

(13) See J. Hine, *J. Org. Chem.*, **31**, 1236 (1966).

(14) This is true also of proton abstraction from these carbon acids by bases. Note, for example, that the relative rates of deprotonation of the carbon acids by hydroxide ion at 25° in the series CH_3NO_2, CH_3COCH_3, $CH_3SO_2CH_3$ are *ca.* $10^4:10^2:1.0$,[15] whereas the relative K_a's (in water) are *ca.* $10^{18}:10^8:1.0$.[16] Another example is the more rapid removal of protons from phenylacetylene than from nitroethane, despite the 10^{11} stronger acidity of the latter.[13]

(15) (a) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, **294**, 273 (1966); (b) R. P. Bell, G. R. Hillier, J. W. Mansfield, and D. G. Streit, *J. Chem. Soc. B*, 379 (1967); (c) J. Hockberg and K. F. Bonhoeffer, *Z. Phys. Chem., Abt. A*, **184**, 419 (1939).

(16) F. G. Bordwell, R. H. Imes, and E. C. Steiner, *J. Amer. Chem. Soc.*, **89**, 3905 (1967).