

81°<sup>30</sup>) are in close agreement with the experimentally determined value (77.7°).

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## Base-Induced Decomposition of $\beta$ -Nitroalkyl Nitrates

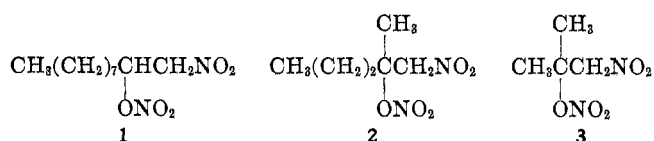
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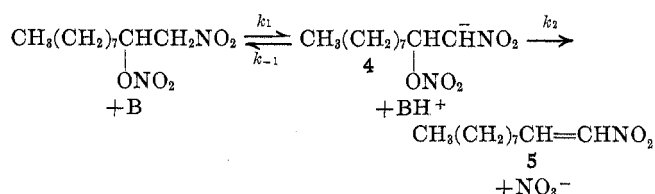
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The elimination of nitric acid from  $\beta$ -nitroalkyl nitrates proceeds *via* an E1cb type of mechanism when the nitro and nitrate groups are attached to primary and secondary carbon atoms, respectively. Where the nitrate function is on a tertiary carbon, it has not been unequivocally shown that an E2 mechanism is operative, although the evidence points in that direction. Previous interpretation of the relative rate differences ascribed to 1,2-dinitrooctadecane, 1-nitro-2-octadecyl nitrate, and 1-nitro-2-octadecyl nitrite as differences in leaving group abilities may require reconsideration. Most likely these eliminations depend both on the leaving group abilities and on the acidity of the nitromethylene protons.

The elimination of the elements of nitric acid by a base from  $\beta$ -nitroalkyl nitrates has been known for many years. Usually, the  $\beta$ -nitroalkyl nitrate was studied as a component of a mixture formed from the addition of nitrogen dioxide to an olefinic linkage.<sup>1</sup> This mixture, consisting of  $\beta$ -nitroalkyl nitrate,  $\beta$ -nitro alcohol,<sup>2</sup> and 1,2-dinitroalkanes, yielded the corresponding nitro olefin. Siefert,<sup>3</sup> working with pure materials, found the following order of reactivity with pyridine: 1,2-dinitrooctadecane > 1-nitro-2-octadecyl nitrite > 1-nitro-2-octadecyl nitrate. These results were interpreted in terms of leaving group effects. With such structures the activating effect of the nitro group on proton release might figure importantly, along with leaving group effects, in the elimination process. This communication reports some preliminary results of a study of the pyridine-induced decomposition of  $\beta$ -nitroalkyl nitrates to nitro olefins and sheds some further light on the mechanism of the reaction. 1-Nitro-2-decyl nitrate (1), 1-nitro-2-methyl-2-pentyl nitrate (2), and 1-nitro-2-methyl-2-propyl nitrate (3) were chosen as model compounds.



One possible reaction path would involve proton abstraction in an equilibrium step, followed by elimination of nitrate ion from the intermediate carbanion (E1cb type), *e.g.*, from 1.



(1) V. V. Perekalin, "Unsaturated Nitro Compounds," Daniel Davy, New York, N. Y., 1964.

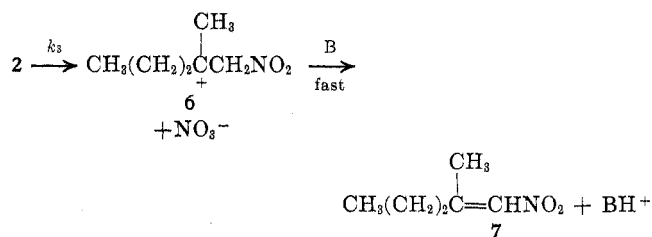
(2) Before treatment with base, the reaction mixture was hydrolyzed, converting the potentially explosive  $\beta$ -nitroalkyl nitrite to the  $\beta$ -nitro alcohol.

(3) W. K. Seifert, *J. Org. Chem.*, **28**, 125 (1963).

The steady-state approximation for such a process yields the rate expression of eq 1.

$$-\frac{d[1]}{dt} = \frac{k_1 k_2 [1][\text{B}]}{k_{-1}[\text{BH}^+] + k_2} \quad (1)$$

On the other hand, the nitro nitrate could lose nitrate ion in an unimolecular rate-determining step, forming a carbonium ion<sup>4</sup> which could eject a proton to form the nitro olefin (*e.g.*, from 2).



Between these two extremes, there can exist intermediate situations in which bond-breaking at the nitro methylene carbon acts in concert with double bond formation and bond-breaking of the leaving group, leading to an E2 type mechanism (*e.g.*, for 1).

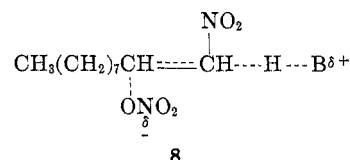


Table I gives the kinetic and product data for the decomposition of 1 and 2 in benzene and/or *m*-xylene in the presence of equimolar amounts of pyridine. For 1, the product obtained in near quantitative yield is 1-nitro-1-decene (5), identified by infrared [strong absorption at 6.55 and 7.3  $\mu$  (vinyl NO<sub>2</sub> asymmetric and symmetric stretch, respectively)] and by nuclear magnetic resonance [a two-proton multiplet at  $\delta$  2.25 (CH<sub>2</sub>-CH=CHNO<sub>2</sub>), a one-proton multiplet at 6.9 (CH<sub>2</sub>-CH=CHNO<sub>2</sub>), and a one-proton multiplet at 8.25 (CH<sub>2</sub>CH=CHNO<sub>2</sub>)]. The reaction is second order, first order in both 1 and pyridine, through two half-lives. Pyridinium nitrate precipitates from solution

(4) For a discussion of a tertiary nitrate which reacts *via* an E1 process, see D. N. Kevill and R. F. Sutthoff, *J. Chem. Soc. B*, 3366 (1969).

TABLE I  
 DECOMPOSITION OF  $\beta$ -NITROALKYL NITRATES IN AROMATIC SOLVENTS

Compd	Solvent	Initial concn, mol/l.		Temp, °C	$k \times 10^4$ , $M^{-1} \text{sec}^{-1}$ <sup>a</sup>	Nitro olefin yield <sup>b</sup>
		$\beta$ -Nitro nitrate	Pyridine			
1-Nitro-2-decyl nitrate	Benzene	0.11	0.11	33.5	1.7	95%
		0.11	0.11	51.8	5.4	
		0.11	0.11	60.0	10	
		0.067	0.067	60.0	10	
		0.13	0.13	60.0	11	
1-Nitro-2-methyl- 2-pentyl nitrate	Benzene	0.11	0.11	65.0	0.1	50% after one half-life
		<i>m</i> -Xylene	0.11	0.11	97.0	4.5
		0.11	0.11	114	14	
		0.11	0.11	120	22	
		0.22	0.22	97.0	4.5	

<sup>a</sup> Rate of reaction monitored by following the disappearance of the 7.8 and 11.6  $\mu$  infrared bands of the nitrate function ( $-\text{NO}_2$  sym str and  $-\text{ONO}_2$  str, respectively). The uncertainty of the rate constants is estimated at  $\pm 10\%$ . <sup>b</sup> Compounds isolated by column chromatography using silica gel as the substrate with hexane as the eluting solvent.

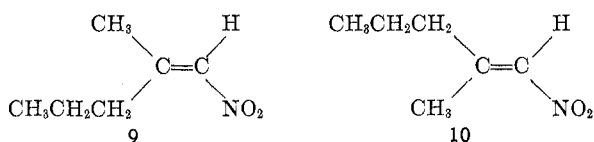
 TABLE II  
 DECOMPOSITION OF  $\beta$ -NITRO NITRATES IN THE PRESENCE OF DEUTERIUM OXIDE AND PYRIDINE<sup>a</sup>

Compd	Concn, <i>M</i>	Solvent	Temp, °C	Time, hr	Conversion, %	Deuterium incorpd into nitro olefin
1-Nitro-2-decyl nitrate	0.11	80% $\text{CH}_3\text{CN}$ - 20% $\text{D}_2\text{O}$	75	0.5	100	50% (nmr) at the 1 position
1-Nitro-1-decene	0.11		75	2.0		No (<5%) deuterium incorporation
	0.11 <sup>d</sup>		75	1.0		
1-Nitro-2-methyl- 2-propyl nitrate	0.11		75	2.0	80	7% (mass spectrum) <sup>b</sup>
	0.11		75	4.0	100	25% (nmr)
	0.11		25		60	No deuterium (nmr)
1-Nitro-2-methyl- 1-propene	0.11		75	2.0		33% (nmr) deute- rium incorporation

<sup>a</sup> Pyridine was present in the same molar quantities as the  $\beta$ -nitro alkyl nitrates. <sup>b</sup> The mass spectrum of 1-nitro-2-methyl-1-propene is complicated by a large  $M + 1$  peak. The presence of an ion-molecule process was confirmed by monitoring the ratio  $M/(M + 1)$  peak as a function of sample size. As sample increased,  $M/(M + 1)$  decreased. <sup>c</sup> Some isomerization to the unconjugate disomer 1-nitro-2-methyl-2-propene occurs as evidenced by ir absorption at 6.4  $\mu$  and nmr absorptions at  $\delta$  5.0. <sup>d</sup> 0.11 *M* pyridinium nitrate was present, no pyridine was present.

from the outset of the experiment. The temperature coefficient is small with an apparent energy of activation of *ca.* 12 kcal.

1-Nitro-2-methyl-2-pentyl nitrate (2) decomposes more slowly than 1 to give 1-nitro-2-methyl-1-pentene (7) having strong infrared absorption at 6.55 and 7.3  $\mu$ . The nuclear magnetic resonance spectrum (three allylic methyl hydrogens at  $\delta$  1.95 and three allylic hydrogens at 2.55) shows it to be a mixture of *cis* and *trans* isomers (9, 10).



In benzene at 65°, only 9 and 10 are formed when the decomposition is limited to one half-life. At higher temperatures ( $\sim 100^\circ$ ) after complete decomposition of 2, 9 and 10 are isolated in only 68% yield. The remaining material is a viscous, resinous substance. Since at these temperatures pyridinium nitrate begins to decompose, this resin formation is attributed to its oxidizing action. As with 1, the initial reaction is second order, with an indicated temperature coefficient ( $E_a$ ) of *ca.* 18 kcal.

When the decomposition of 1 and 2 was carried out in the more polar solvent, acetonitrile, the rates of decomposition were observed to increase significantly. Both followed approximate second-order kinetics through the first half-life. For 1 at 33° and for 2 at 65°, the in-

dicated specific rate constants were  $2.9 \times 10^{-3}$  and  $1.0 \times 10^{-3} M^{-1} \text{sec}^{-1}$ . Subsequent decomposition was slower than expected for a straightforward second-order process.<sup>5</sup> No precipitate was formed in these experiments.

These results indicate that the  $\beta$ -nitroalkyl nitrates reacted initially *via* an apparent bimolecular process. In all the solvents used in the study (benzene, *m*-xylene, acetonitrile, acetonitrile-deuterium oxide), 1 always reacted faster than 2, arguing against the possibility that both 1 and 2 are reacting *via* a concerted E2 type process. If such were the case, 2 might have been expected to react faster because of transition state stabilization by the additional alkyl group.<sup>6</sup> An E1cb type process is, however, a reasonable possibility for both 1 and 2. Carbanion mechanisms involving an initial equilibrium step can usually be detected by using as a reaction medium some compound which contains labile deuterium atoms. The intermediate carbanion abstracts the labile deuterium while reverting to starting material so that deuterium becomes incorporated into the latter and thence into the final product species.

Table II gives the results obtained when 1 and 3 were decomposed in acetonitrile in the presence of deuterium oxide. Deuterium incorporation was followed by nuclear magnetic resonance measurements. Compound 3 was chosen instead of 2 to simplify the nuclear

(5) Successive half-lives for 1 at 65° were 19 and 57 min, where  $[\text{NN}]_0 = [\text{B}]_0 = 0.11 M$ .

(6) D. V. Banthorpe, "Elimination Reactions," Elsevier, New York, N. Y., 1962, p 62.

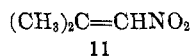
magnetic resonance spectra. Isomers such as **9** and **10** caused the spectra to be somewhat complex and difficult to analyze.

When **1** was completely decomposed in the presence of deuterium oxide, the nitro olefin formed (**5**) was found to contain deuterium at the 1 position (one-proton multiplet at  $\delta$  6.9 reduced in intensity to 50%). Subjecting unlabeled **5** to reaction conditions (see Table II) caused no deuterium (within limits of the nmr) to be incorporated into the molecule. This excludes the possibility of a subsequent equilibration with the nitro olefin and shows that deuterium is being incorporated into the molecules as the molecules are reacting with the base. An E1cb type mechanism is most likely operative in this case.

For an E1cb type of mechanism to follow good second-order kinetics through two half-lives (Table I, benzene data) is unusual. Normally as  $BH^+$  increases (eq 1) the rate decreases. However, as noted earlier, pyridinium nitrate precipitates immediately from benzene or xylene solution. The concentration of  $BH^+$  must therefore be constant and very small,<sup>7</sup> compared to the reactant concentrations used, throughout the measured reaction times. This accounts for the observed good second-order kinetics for these solvents, with the reaction rate constant approximating  $k_1$ .

$$-\frac{d[1]}{dt} = k_1[1][\text{pyridine}]$$

When **3** was completely decomposed in the presence of deuterium oxide at 75°, the nitro olefin isolated (**11**)



contained 25% deuterium at the 1 position. However, when unlabeled **11** was subjected to reaction conditions, 33% deuterium was incorporated into the molecule. Interruption of the decomposition of **3** at 80% conversion revealed that only 7% (mass spectra) deuterium had been incorporated into the nitro olefin. When **3** was decomposed at 25° (60% conversion) no deuterium could be detected (within the limits of nmr) in either recovered **3** or the product, 1-nitro-2-methyl-1-propene. Apparently little if any deuterium was incorporated into the molecule during decomposition, most if not all being incorporated after the formation of the nitro olefin.

Because of the sensitivity limits of the analytical method, it can not be unequivocally said that the reaction does not proceed by an E1cb type process. If it does proceed in this manner, the results show that during the first half-life, at least,  $k_1[BH^+]$  is small with respect to  $k_2[An^-]$  (that is, nitrate is being eliminated faster than deuterium is being incorporated), and the mechanism is approaching the E2 type.

Table III shows literature data<sup>8</sup> for the effect of  $\beta$ -methyl substitution upon proton removal from a series of nitro alkanes. Substitution of the  $\beta$  hydrogen by a methyl group causes a decrease in the rate of proton removal from the nitromethylene carbon by a factor near 2. Proton removal from **2** or **3** should be slower than from **1** since they differ by this  $\beta$  substitution. This

(7) The measured solubility of pyridinium nitrate in benzene at 25 and 65° was found to be  $\sim 10^{-4}$  and  $10^{-3}$  mol/l., respectively.

(8) A. T. Nielsen, "The Chemistry of the Nitro and Nitroso Groups," Part 1, H. Feuer, Ed., Interscience, New York, N. Y., 1969, p 368.

TABLE III  
RATE OF PROTON REMOVAL FROM NITRO ALKANES

Nitro alkane	$k_1$ $M^{-1} \text{ min}^{-1}$
$\text{CH}_3\text{NO}_2$	1026
$\text{CH}_3\text{CH}_2\text{NO}_2$	354
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$	195

decrease in  $k_1$ , coupled with the possibility that  $k_2$  may be larger for **2** or **3** (since nitrate is leaving from a tertiary center), makes reasonable the tentative conclusion that the E2 mechanism is favored by **2** (or **3**), while **1** decomposes by E1cb.

A similar effect, though less pronounced, has been seen in the reactions of  $\alpha$ - and  $\beta$ -methyl substituted  $\beta$ -phenylethyl tosylates and bromides with potassium *tert*-butoxide in *tert*-butyl alcohol and sodium ethoxide in ethanol.<sup>9</sup> These compounds have been shown to develop less carbanion character in their transition states in elimination reactions than those of  $\beta$ -phenylethyl tosylates and bromides.

### Experimental Section

The infrared spectra were obtained with a Perkin-Elmer 137B double beam recording spectrophotometer using thin films on sodium chloride disks, or differentially in solution in 0.1-mm sodium chloride cells. Nuclear magnetic resonance spectra were determined with a Varian Associates H-100 spectrometer at 100 MHz with tetramethylsilane as the internal standard. Mass spectra were determined with a CEC 21-104 mass spectrometer.

**General Preparation of  $\beta$ -Nitroalkyl Nitrates via  $\beta$ -Nitroalkyl Peroxynitrates.**<sup>10</sup> **A.  $\beta$ -Nitroalkyl Peroxynitrates.**—To 100 ml of a 1.3 M carbon tetrachloride solution of 1-alkene at 0° was added 8.0 ml (0.13 mol) of dinitrogen tetroxide over a period of 6 hr. The addition of the dinitrogen tetroxide was carried out by allowing a stream of oxygen (56 ml/min) to pass over the liquid dinitrogen tetroxide into the reaction vessel. After the dinitrogen tetroxide had been added, oxygen was allowed to flow through the reaction solution until the solution became colorless. Solution infrared showed that the  $\beta$ -nitroalkyl peroxynitrate has formed (strong absorptions at 5.8, 6.4, and 7.3  $\mu$ ).

**B.  $\beta$ -Nitroalkyl Nitrates.**—From the above solution the solvent was removed *in vacuo* at 20° and 100 ml of new solvent was added. This solution was chilled to  $-10^\circ$  and 0.13 mol of nitric oxide was added by passing nitric oxide through the solution at a flow rate of 60.8 ml/min. After two additions, the solution was kept at  $-10^\circ$  for 30 min and then allowed to warm to room temperature. The solvent was then removed, giving the  $\beta$ -nitroalkyl nitrate in near quantitative yield. These  $\beta$ -nitroalkyl nitrates were purified by chromatography on silica gel columns using hexane-methylene chloride (90:10) mixtures as the eluting solvent.

**Kinetic Experiments.**—Equimolar solutions of  $\beta$ -nitroalkyl nitrates and pyridine were mixed together and then the unstirred solutions were heated to the desired temperature. The decompositions of the  $\beta$ -nitroalkyl nitrates were followed by monitoring the disappearance of the 6.1, 7.8, and 11.6  $\mu$  infrared absorption bands. The solutions of  $\beta$ -nitroalkyl nitrates followed Beer's law in the concentration ranges studied (up to 0.22 M). The temperatures were maintained at  $\pm 0.5^\circ$ . Aliquots were withdrawn at timed intervals and their spectra were recorded differentially in 0.1-mm sodium chloride cells *vs.* the appropriate solvent. A base line, straddling the peak, technique was used to measure the absorbances of the band being monitored.<sup>11</sup> The rate constants were reproducible within  $\pm 3\%$ .

Isolation of the decomposition products was carried out by first filtering the precipitated pyridinium nitrate and then removing the reaction solvent. The crude product was chromatographed on silica gel using hexane as an eluent. In the cases

(9) C. H. DePuy, D. L. Storm, J. T. Frey, and C. G. Naylor, *J. Org. Chem.*, **35**, 2746 (1970).

(10) D. R. Lachowicz and K. L. Kreuz, *ibid.*, **32**, 3885 (1967); U. S. Patent 3,282,983 (1966).

(11) H. Morgan, R. M. Sherwood, and T. A. Washall, *Anal. Chem.*, **38**, 1009 (1966).

where pyridinium nitrate did not precipitate, the solvent was reduced to one-half its original size and four times that volume of ether was added. This solution was extracted three times with equal volumes of water and the ethereal layer was then separated and dried over sodium sulfate. The crude residue left after the ether was removed was chromatographed on silica gel using hexane as an eluent.

Inspection of all the crude reaction products was done by infrared and nuclear magnetic resonance spectra. The amount of deuterium incorporated was determined from nuclear magnetic resonance spectra or from mass spectra. 1-Nitro-2-methyl-2-pentyl nitrate, 1-nitro-2,4,4-trimethyl-2-pentyl nitrate,<sup>12</sup> and 1-nitro-2-methyl-2-propyl nitrate<sup>13</sup> have been described previ-

(12) J. M. Larkin and K. L. Kreuz, *J. Org. Chem.*, **37**, 3079 (1972).

(13) N. Levy, C. W. Scaife, and A. E. Wilder-Smith, *J. Chem. Soc.*, 52 (1948).

ously, as has 1-nitro-2-methyl-1-propene.<sup>14</sup> The elemental analysis for 1-nitro-1-decene and 1-nitro-2-methyl-1-pentene are given below.

		C	H	N
C <sub>10</sub> H <sub>18</sub> NO <sub>2</sub>	Calcd	64.9	10.4	7.57
	Obsd	64.5	10.5	7.30
C <sub>8</sub> H <sub>14</sub> NO <sub>2</sub>	Calcd	55.8	8.60	10.9
	Obsd	55.4	9.00	10.9

Registry No.—1, 36601-57-7; 2, 35223-51-9; 3, 14202-69-8; 5, 36601-60-2; 9, 36601-61-3; 10, 36601-62-4; 11, 1606-30-0.

(14) A. Lambert and A. Lowe, *ibid.*, 1517 (1947).

## The Use of an $\alpha$ -Fluorine Substituent as a Transition State Probe in Base-Catalyzed Nitrous Acid Eliminations

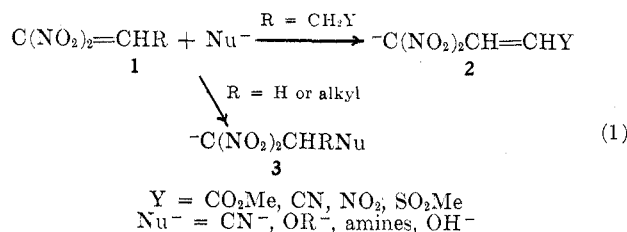
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The results of a study of the kinetics and mechanism of the reaction of 4,4,4-trinitrobutyronitrile and 4,4-dinitro-4-halobutyronitriles with base have shown that the isolated products are derived from an extremely reactive 1,1-dinitro- or 1-halo-1-nitroethylene intermediate. The  $\alpha$ -fluorine effect has been utilized as a transition state probe to show that the mechanism by which the olefin intermediate forms is a nonreversible, second-order carbanion  $\beta$  elimination of the elements of nitrous acid.

The reaction of 1,1,1-trinitroethyl compounds with bases<sup>1-6</sup> has been viewed as yielding a 1,1-dinitroethylene intermediate **1**.<sup>1</sup> The fate of this reactive intermediate depends upon the nature of the substituent attached to the carbon  $\alpha$  to the dinitromethyl group (eq 1). When R = CH<sub>2</sub>Y, where Y is a con-



jugatively electron-withdrawing substituent, the olefin **1** loses an  $\alpha$ -methylene proton to form the planar<sup>7</sup> carbanion **2**. When this path is not available, nucleophilic addition to the double bond occurs to form the adduct **3**. Though the olefin **1** has never been isolated from these base-catalyzed eliminations, its rate of formation might be expected to be slow relative to subsequent reactions. Thus, a combination of kinetic and trapping experiments should enable us to determine if **1** is the precursor of **2** and **3**.

We also planned to utilize the  $\alpha$ -fluorine effect<sup>8,9</sup>

(1) L. Zeldin and H. Shechter, *J. Amer. Chem. Soc.*, **79**, 4708 (1957).

(2) J. Meisenheimer and M. Schwarz, *Chem. Ber.*, **39**, 2546 (1906).

(3) J. Meisenheimer, *ibid.*, **36**, 434 (1903).

(4) M. J. Kamlet and J. C. Dacons, *J. Org. Chem.*, **26**, 3005 (1961).

(5) L. A. Kaplan, *ibid.*, **29**, 2256 (1964).

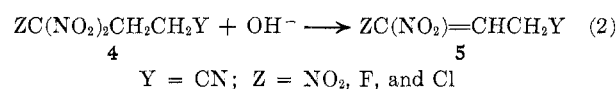
(6) M. J. Kamlet, J. C. Dacons, and J. C. Hoffsommer, *ibid.*, **26**, 4881 (1961).

(7) L. A. Kaplan, N. E. Burlinson, W. B. Moniz, and C. Poranski, *Chem. Commun.*, 140 (1970).

(8) L. A. Kaplan and H. B. Pickard, *ibid.*, 1500 (1969); L. A. Kaplan and H. B. Pickard, *J. Amer. Chem. Soc.*, **93**, 3447 (1971).

(9) J. Hine, L. G. Mahone, and C. L. Liotta, *J. Amer. Chem. Soc.*, **89**, 5911 (1967).

as a probe to determine the structure of the transition state for this nitrous acid elimination reaction (eq 2).



If the formation of **5** requires concerted C-H and C-NO<sub>2</sub> bond breaking in the transition state, then the  $\gamma$  carbon atom, ZC(NO<sub>2</sub>)<sub>2</sub><sup>-</sup>, has more s character in the transition state than in the ground state and  $\Delta H^*$ , but not necessarily  $\Delta F^*$ ,<sup>8</sup> for Z = F should be larger than for Z = NO<sub>2</sub> or Cl.<sup>8,9</sup> Alternatively, if only carbanion formation occurs in the rate-determining step,<sup>10</sup> then the hybridization of the  $\gamma$  carbon atom will be the same in the ground and transition states and  $\Delta H^*$  for Z = F and NO<sub>2</sub> should be essentially the same.<sup>11</sup> The twofold effect of the enhanced acidity of the  $\beta$  hydrogen atoms due to the strongly electron-withdrawing ZC(NO<sub>2</sub>)<sub>2</sub> function and the presence of a good leaving group, nitro departing as resonance-stabilized nitrite ion, might be expected to make the elimination of nitrous acid from the substrates **4** proceed by a nonreversible carbanion mechanism rather than an E2 or a reversible E1cB mechanism.

### Results and Discussion

**The Overall Reaction.**—Prior to making kinetic measurements, we carefully investigated the reaction of the substrates **4** with hydroxide. Since they have

(10) For a description of the various mechanisms for base-catalyzed  $\beta$  eliminations, see F. G. Bordwell, M. M. Vestling, and K. C. Yee, *J. Amer. Chem. Soc.*, **92**, 5950 (1970), and references cited therein.

(11) Since the  $\sigma^*$  values for FC(NO<sub>2</sub>)<sub>2</sub> and C(NO<sub>2</sub>)<sub>2</sub>, 4.4<sup>12</sup> and 4.5,<sup>13</sup> are about equal, large differences in  $\Delta H^*$  cannot be attributed to differences in C $\beta$ -H bond strengths.

(12) L. A. Kaplan and H. B. Pickard, *J. Org. Chem.*, **35**, 2044 (1970).

(13) J. Hine and W. C. Bailey, *ibid.*, **26**, 2098 (1961).