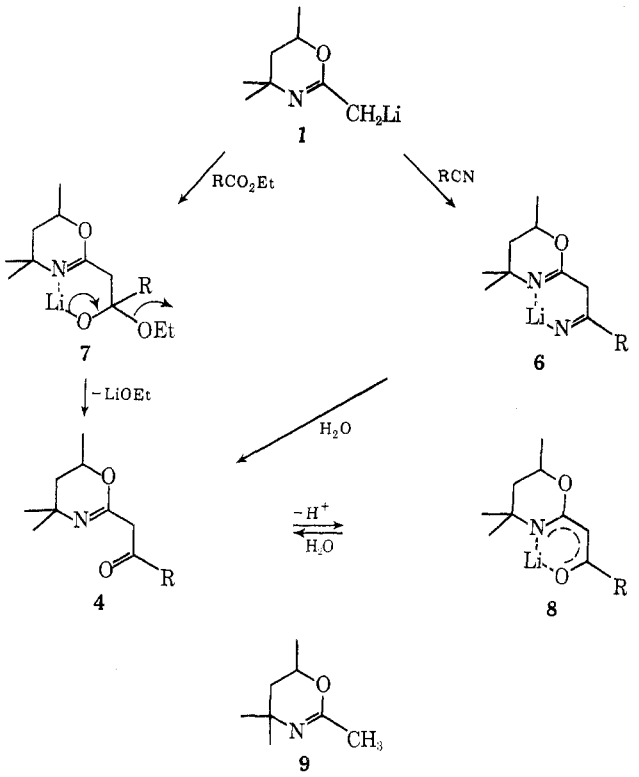
acylation must be due to proton abstraction from 4 generating the lithio salt 8. Hence, 4 must be formed directly in the reaction medium. When acylation was performed using the nitrile, the initial intermediate is probably 6 which is much less acidic than 4 and the latter is not produced until the reaction is quenched. It is, therefore, concluded that acylations of oxazine carbanions are more efficiently performed using nitriles as the acylating agent.




## Experimental Section[5]

**α-Ketoalkyloxazines 5. General Acylation Procedure.** A solution of 9 (0.02 mol) in 30 ml of tetrahydrofuran was cooled to −78° in Dry Ice–acetone and treated with 0.021 mol (1.6 *M*) of *n*-butyllithium (hexane). The system was under a nitrogen atmosphere throughout the addition. The anion 1 appeared within 1 hr as a yellow suspension and the ester or nitrile (0.21 mole) was added all at once. The reaction was allowed, while stirring, to warm to room temperature (8–15 hr) and then poured into water and acidified (1 *N* hydrochloric acid). The aqueous acid solution was extracted with ether–pentane (1:1) and the extracts were discarded. The aqueous solution was neutralized with 5% sodium bicarbonate and extracted with ether, dried ($Na_2SO_4$), and concentrated. The residue was recrystallized from petroleum ether to afford pure 5 (see Table I for physical constants).

**Acknowledgment.** The authors are grateful to the National Science Foundation (GP 22541), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health for financial support of this work. Generous supplies of organolithium reagents from the Lithium Corporation of America are also gratefully acknowledged.

**Registry No.** —1, 50311-32-5; **5aA**, 50311-33-6; **5aB**, 50311-34-7; **5bA**, 50311-35-8; **5bB**, 50311-36-9; **5cA**, 50311-37-0; **5cB**, 50311-38-1; 9, 26939-18-4; MeCN, 75-05-8; $MeCO_2Et$, 141-78-6; *n*-PrCN, 109-74-0; *n*-$PrCO_2Et$, 105-54-4; PhCN, 100-47-0; $PhCO_2Et$, 93-89-0.

## References and Notes

(1) Address all correspondence to this author at the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521.
(2) A. I. Meyers, A. Nabeya, H. W. Adickes, I. R. Politzer, G. R. Malone, A. C. Kovelesky, R. L. Nolen, and R. C. Portnoy, *J. Org. Chem.*, **38**, 36 (1973).
(3) R. Mondelli and L. Merlini, *Tetrahedron*, **22**, 3253 (1966).
(4) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, New York, N. Y., 1972, p 494.
(5) Melting points and boiling points are uncorrected. Analyses were performed by Midwest Microlabs, Indianapolis, Ind. Infrared, ultraviolet, and nmr spectra were recorded on Perkin-Elmer 257 and 202 and Varian T-60 instruments, respectively. Vapor phase chromatography was performed on a Hewlett-Packard 5750 using UCW-98 (80–100 mesh) columns.

# Thermal Decomposition of β-Nitroalkyl Nitrates in Olefinic Solvents

J. M. Larkin, W. M. Cummings,* and K. L. Kreuz

*Texaco Research Center, Beacon, New York 12508*

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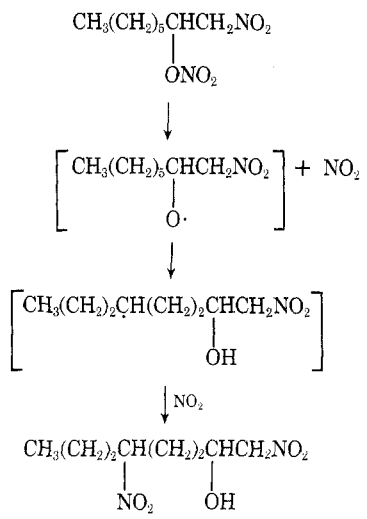
Kreuz and Larkin have shown that β-nitroalkyl nitrates decompose in paraffinic and aromatic solvents by a homolytic fission of the $O-NO_2$ bond, intramolecular rearrangement, and recombination to give dinitro alcohols.[1] Facile reaction requires somewhat higher temperatures for secondary (140–160°) than for tertiary (100–130°) nitrate structures.




Subsequent studies in our laboratories have demonstrated that a different decomposition path may be followed when olefinic solvents are employed. Thus, when 1-nitro-2-octyl nitrate was heated in dodecene-1 at 138°, a more rapid decomposition occurred than in dodecane ($T_{1/2}$ 20 min *vs.* 2300 min). In addition, infrared analysis showed that a conjugated nitro olefin was forming instead of a 1,5-dinitro alcohol.

Product isolation was facilitated when the nitro nitrate, *e.g.*, 1-nitro-2-decyl nitrate, was heated in octene-1 at 123° for an extended period (8 hr). After removal of the solvent under reduced pressure, followed by chromatography of the residue on silica gel with hexane as eluent, 1-nitro-1-decene was isolated in 90% yield. Also isolated was a mixture of nitrogen-containing materials and evidently (from nmr analysis) solvent derived. In order to determine the importance of solvent nitration as a source of nitro olefin, 1-nitro-2-octyl nitrate was decomposed in 2,4,4-trimethylpentene-1. No nitro olefin derived from the solvent could be detected by nmr analysis of the product [lack of broadening of one of the doublet lines centered at δ 7.86 and absence of a methyl absorption near δ 8.22 $[-C(CH_3)=CHNO_2]$.

Table I gives the products formed and their yield as determined by isolation or nmr analysis for the decomposition of various β-nitroalkyl nitrates. One sees that secon-

**Table I**
**Products Formed in the Decomposition of β-Nitroalkyl Nitrates in Octene-1 at 120°**

| β-Nitroalkyl nitrate | Registry no. | Nitro olefin | Registry no. | Yield,[a] % |
|---|---|---|---|---|
| 1-Nitro-2-pentyl nitrate | 49746-21-6 | 1-Nitro-1-pentene | 3156-72-7 | 90 (nmr) |
| 1-Nitro-2-hexyl nitrate | 14202-68-7 | 1-Nitro-1-hexene | 49746-23-8 | 90 (nmr) |
| 1-Nitro-2-octyl nitrate | 13434-64-5 | 1-Nitro-1-octene | 4550-05-4 | 90 (nmr) |
| 1-Nitro-2-decyl nitrate | 36601-57-7 | 1-Nitro-1-decene | 36601-60-2 | 90 (isolated)[b] |
| 1-Nitro-2-methyl-2-pentyl nitrate | 35223-51-9 | 1-Nitro-2-methyl-1-pentene | 49746-25-0 | 50 (nmr)[c] |
| 1-Nitro-2,4,4-trimethyl-2-pentyl nitrate | 32778-22-6 | 1-Nitro-2,4,4-trimethyl-1-pentene | 27838-96-6 | 15[d] |
| 2-Octyl nitrate | 7214-64-4 | No reaction | | |

[a] Yield was determined by comparing the nmr absorptions at δ 7.86 and 9.15 ($CH{=}CHNO_2$) to the absorptions at δ 4.68 ($CH_2NO_2$), or the absorptions at δ 7.85 [$C(CH_3){=}CHNO_2$] to the absorption at δ 4.82 ($CH_2NO_2$) in the crude product after the olefin was removed under vacuum. [b] 1-Nitro-1-decene typified 1-nitro 1-olefins in exhibiting two intense absorptions in the ir at 6.55 and 7.3 μ. The structure displayed below gives the proton assignments as determined by nuclear magnetic resonance.

$$\underset{1.30}{CH_3}(\underset{8.15}{CH_2})_6\underset{2.26}{CH_2}\underset{7.86}{CH{=}CHNO_2}$$

Saturation of the absorbing nuclei at δ 2.26 causes the absorption at δ 8.15 to become a doublet. [c] Other major product formed was 2-methyl-1,5-dinitro-2-pentanol in 50% yield (nmr). [d] Isolated in the combined chromatographic fractions containing the nitro olefin and 2,4,4-trimethyl-1,5-dinitro-2-pentanol. The overall yield is probably lower than 15% since some dinitro alcohol remains on the column.

**Table II**
**Kinetic Data for the Thermal Decomposition of 1-Nitro-2-Decyl Nitrate[a]**

| 1-Nitro-2-decyl nitrate | Solvent | Temp, °C | $k\psi \times 10^5$, $sec^{-1}$ [b] |
|---|---|---|---|
| 0.11 | Dodecene-1 | 116 | 1.7 |
| 0.11 | Dodecene-1 | 121 | 4.1 |
| 0.11 | Dodecene-1 | 140 | 58 |
| 0.16 | Dodecene-1 | 121 | 4.3 |
| 0.23 | Dodecene-1 | 121 | 4.6 |
| 0.11 | 50% dodecene-1 50% dodecane | 121 | 2.1 |

[a] Data obtained after induction period. [b] Pseudo-first-order rate constant. The decomposition was followed by monitoring the disappearance of the 11.6-μ band in the infrared. The reproducibility of the rate constant was ±5%.

**Table III**
**Variation of Pseudo-First-Order Rate Constants for the Decomposition of 0.11 *M* 1-Nitro-2-Decyl Nitrate at 123°**

| Olefin solvent | $k\psi \times 10^5$, $sec^{-1}$ |
|---|---|
| Hexachloropropylene | 0.38[a] |
| Dodecene-1 | 5.1 |
| *n*-Decyl vinyl ether | 23 |

[a] The rate of decomposition was so slow that an induction period was not detectable.

dary nitrates go cleanly to nitro olefins but that tertiary nitrate structures tend more to the rearrangement path which leads to dinitro alcohols. In fact, decomposition of 1-nitro-2,4,4-trimethyl-2-pentyl nitrate gives no more than 15% nitro olefin along with 85% of the radical rearrangement products, mostly 1,5-dinitro-2,4,4-trimethyl-2-pentanol. 1-Nitro-2-methyl-2-pentyl nitrate gives equal amounts of the nitro olefin along with 1,5-dinitro-2-methyl-2-pentanol. The importance of the nitro group is shown by the failure of 2-octyl nitrate to react under these conditions.

When a secondary β-nitroalkyl nitrate is heated, there is an induction period prior to decomposition.[2] This induction period is temperature dependent (being ~2 hr at 120° and ~10 min at 140°). There is no detectable change in the induction period when nitrobenzene is added to the reaction mixture, or when the reaction solution is deaerated with nitrogen. The induction period remains when *n*-decyl vinyl ether is used as a solvent in place of the hydrocarbon olefin. The cause of this inhibition is not known: no compositional changes were noted during the period by infrared monitoring. Since β-nitroalkyl nitrates are not amenable to the more conventional methods of purification[3] such as distillation and crystallization, there may be a small amount of impurity which is acting as an inhibitor and must be consumed before reaction can occur.

(For the tertiary systems, there is no apparent induction period, since the rearrangement reaction is also operative and is consuming nitrate.)

During the first half-life after the induction period, approximate first-order kinetics seem to be obeyed, as the half-life does not change appreciably with change in initial concentration of β-nitroalkyl nitrate. However, by halving the concentration of dodecene-1 (by diluting with an equal volume of dodecane, an inert solvent) the apparent rate constant is halved, indicating a dependency of the reaction on olefin concentration. See Table II. The rate of decomposition after the induction period is also affected by changes in the structure of the olefin solvent. This variation is given in Table III.

There seems to be a parallelism between the basicity of the olefin and the size of the rate constant, the largest value being associated with the strongest electron-donating solvent, *n*-decyl vinyl ether, and the smallest with the electron-poor solvent, hexachloropropylene. Decomposition of 1-nitro-2-decyl nitrate did not occur when heated with diphenyl ether under similar conditions. This indicates that the ether linkage *per se* is not sufficient to induce decomposition.

For the secondary systems (assuming that the induction period in the olefin-induced decomposition is due simply to some impurity causing inhibition) the overall data suggest that a bimolecular reaction is occurring which involves the solvent. The need for an activated hydrogen and apparent dependency upon the basicity of the olefin all lead to the thought that this elimination is proceeding by some type of acid–base sequence.

## 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 reasonance spectra were de-

termined with a Varian Associates H-100 spectrometer at 100 HMz with tetramethylsilane as the internal standard.

**β-Nitroalkyl Nitrates.** The compounds used in this study were prepared by the nitric oxide reduction of β-nitroalkyl peroxynitrates formed by the action of nitrogen dioxide and oxygen on the appropriate olefin according to the method of Lackowicz and Kreuz.[4]

**1-Nitro 1-Olefins.** A typical example for the preparation of 1-nitro 1-olefins is given below.[5] To 100 ml of octene was added 5.0 g of 1-nitro-2-decyl nitrate and this solution was heated at reflux for 12 hr. The solvent was removed under reduced pressure to give 4.7 g of a complex mixture. This mixture was transferred to a column containing 200 g of silica gel. Elution of the column with hexane gave in the initial fractions 3.4 g of 1-nitro-1-decene (90%). Subsequent elution with methanol gave 0.8 g of a solvent-derived nitrogen-containing mixture of compounds.

**Kinetics.** The appropriate amount of β-nitroalkyl nitrate was added to the olefin solution and the unstirred solutions were heated to the desired temperature. The decompositions of the β-nitroalkyl nitrates were followed by monitoring the disappearance of the 6.1-, 7.8-, and 11.6-μ infrared absorption bands. The solutions of β-nitroalkyl nitrates followed Beer's law in the concentration ranges studied (up to 0.22 *M*). The temperatures were maintained at ±0.5°. 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.[6] The rate constants were calculated from the slope of a log (β-nitroalkyl nitrate)/β-nitroalkyl nitrate *vs.* time plot and were reproducible within ±5%.

Inspection of all crude reaction mixtures was done by comparison of their infrared and nuclear magnetic resonance spectra with spectra of authentic samples of 1-nitro 1-olefins. The preparation and properties of the authentic 1-nitro 1-olefins is described by Cummings and Kreuz.[2]

**Registry No.**—2-Methyl-1,5-dinitro-2-pentanol, 49746-26-1.

## References and Notes


(1) J. M. Larkin and K. L. Kreuz, *J. Org. Chem.*, **37**, 3079 (1972).
(2) W. M. Cummings and K. L. Kreuz, *J. Org. Chem.*, **37**, 3929 (1972).
(3) They are purified by column chromatography on silica gel and the purity is established by chemical analysis, nmr, and ir. Therefore, small amounts of impurity could easily go undetected.
(4) D. R. Lachowicz and K. L. Kreuz, *J. Org. Chem.*, **32**, 3885 (1967); U. S. Patent 3,282,983 (1966).
(5) U. S. Patent 3,510,531 (1900).
(6) H. Morgan, R. M. Sherwood, and T. A. Washall, *Anal. Chem.*, **38**, 1009 (1966).


# On the Solvolysis Pathway for *exo*-3,3-Diaryltricyclo[3.2.1.0$^{2,4}$]oct-*exo*-6-yl Tosylates[1,2]


James W. Wilt* and John R. Flanyak

*Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626*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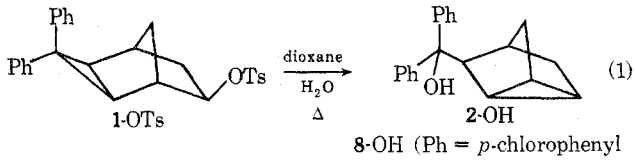
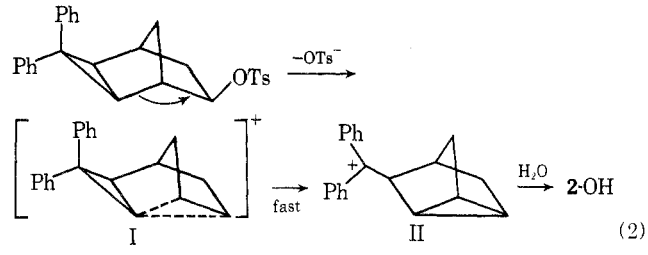
The solvolytic rearrangement of the parent title tosylate 1-OTs leads to a nortricyclyl product 2-OH (eq 1).[3] Two




1-OTs 2-OH 8-OH (Ph = *p*-chlorophenyl (1)

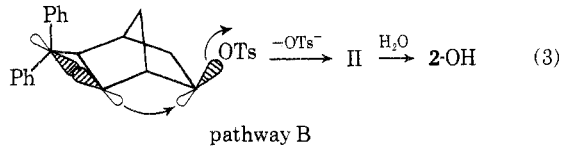
pathways were suggested[3] for this process. The first suggestion (pathway A) invoked a 1,2 σ-bond participation in the rate-determining step to produce ion I as an intermediate species (eq 2). It was further suggested that in a subsequent fast step, I was converted to the more stable benzhydrylic cation II, which then gave the alcohol product 2-OH. Such σ participation should be absent in the endo tosylate related to 1-OTs. Indeed, the exo/endo




(2)

pathway A

rate ratio for the epimeric tosylates was over 4000-fold at 25°.[3] A second suggested pathway (pathway B) invoked direct cyclopropyl ring participation *via* a "back-lobe" mechanism to produce ion II at once (eq 3). This idea would also accommodate a large exo/endo rate ratio. Moreover, such a notion has literature precedent,[4] as pathway A obviously has as well.

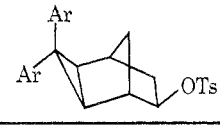



(3)

pathway B

It has now been found that pathway A seems to be in better accord with further results. Use of aryl groups in 1-OTs other than phenyl allowed a structure–reactivity study. Table I contains some of the results of that study.[5]

**Table I**
**Kinetic Data on Tricyclic Tosylates, 64.5° [a]**

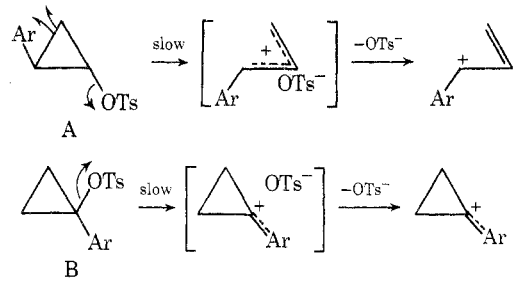



| Compd | Ar | $10^5 k_1$, sec$^{-1}$ | $k_{rel}$ |
|---|---|---|---|
| **3**-OTs | *p*-Anisyl | 28.85 | 27 |
| **4**-OTs | *p*-Tolyl | 15.97 | 15 |
| **5**-OTs | *p*-Chlorophenyl | 1.07 | 1 |

[a] In dioxane–water (80:20, v/v) containing 2,6-lutidine.

A plot of log $k_1$ *vs.* $2\sigma$[6] gave a value of $\rho = -1.44 \pm 0.04$. Use of $\sigma^+$[7] values gave a poor correlation with pronounced curvature. Clearly, the rate correlation with σ instead of $\sigma^+$ and the small spread in $k_{rel}$ are in better keeping with pathway A, wherein no appreciable cationic charge development on the aromatic ring; so the reaction wherein direct conjugation with the aryl groups exists in ion II.

A comparison might be made with the arylcyclopropyl systems shown in eq 4.[8] In A, solvolysis occurs with little




(4)

charge development on the aromatic ring, so the reaction follows σ and $\rho = -1.75$ (108°). In B, solvolysis occurs with extensive charge development on the aromatic ring; so the reaction follows $\sigma^+$ and $\rho = -4.31$ (108°). It is suggested that pathway A of the present study relates to A and pathway B relates to B.

As another point for investigation, one might note that a fundamental difference between the pathways lies in the