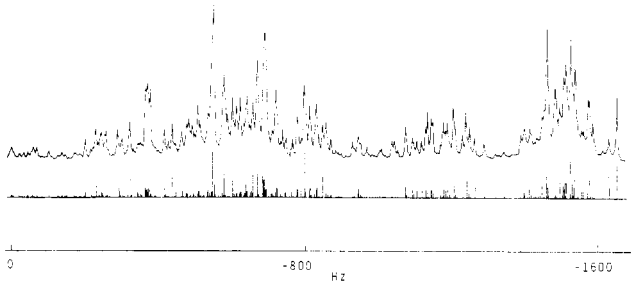


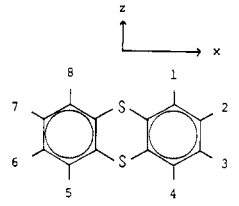
Figure 1. ^1H NMR spectra of thianthrene in nematic solution of ZLI1167. Only high-field half is shown.

Table I. NMR Spectral Parameters of Thianthrene in Nematic Solution of ZLI1167[a]

direct couplings	$D_{26} = 14.73 \pm 0.05$
$D_{12} = 565.98 \pm 0.02$[b]	$D_{27} = 16.90 \pm 0.04$
$D_{13} = 96.60 \pm 0.02$	chemical shift
$D_{14} = 58.87 \pm 0.04$	$\nu_1 - \nu_2 = 20.84 \pm 0.08$
$D_{15} = 29.09 \pm 0.04$	indirect coupling[c]
$D_{16} = 22.20 \pm 0.03$	$J_{12} = 7.71$
$D_{17} = 33.06 \pm 0.03$	$J_{13} = 1.63$
$D_{18} = 101.58 \pm 0.04$	$J_{14} = 0.11$
$D_{23} = 456.89 \pm 0.04$	$J_{23} = 7.54$

[a] In units of hertz at 90 MHz. [b] Probable errors. [c] Cited from ref 9.

Table II. Structural Parameters and Order Parameters of Thianthrene



bond length, Å	$r_{23} = 2.482$[a]
$r_{12} = 2.536 \pm 0.003$	$r_{26} = 9.654 \pm 0.014$
$r_{13} = 4.316 \pm 0.002$	$r_{27} = 9.329 \pm 0.015$
$r_{14} = 4.913 \pm 0.001$	order parameter:
$r_{15} = 7.104 \pm 0.007$	$S_{xx} = -0.11429 \pm 0.00055$
$r_{16} = 8.154 \pm 0.010$	$S_{zz} = -0.05818 \pm 0.00001$
$r_{17} = 7.369 \pm 0.011$	rms dev, Hz: σ[b] $= 0.06$
$r_{18} = 5.131 \pm 0.009$	angle, deg: θ[c] $= 141.6 \pm 0.2$

[a] Assumed from ref 3. [b] Root-mean-square deviation between observed and recalculated direct couplings. [c] Dihedral angle between the two benzene rings.

is not included in the present communication, considering the high inversion barrier for the molecules, i.e., ~25 kJ/mol.[12] The dihedral angle is 141.6 ± 0.2° and evidently differs from those in the gaseous and crystalline states. This angle is also being tested in a liquid-crystal of carboxylic acid (140.2 ± 0.2°) in a detailed study of this solvent dependency now under way. In conclusion, the significant dependency of the angle on the environment of the molecule has been revealed.

r_{12}/r_{23} is 1.022 ± 0.001, and r_{12} is shown to be longer than r_{23} in the benzene ring. This tendency is also observable in the recently reported case of dibenzo-*p*-dioxin.[11] These facts support a distorted hexagon for the ring protons, although the gas electron diffraction study of thianthrene[3] has failed to detect such distortion.

Acknowledgment. H.F. is grateful to Professor P. Diehl (Basel University) for making the program SHAPE available to him.

Registry No. Thianthrene, 92-85-3.

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Formation of 1,2-Oxathietanes and Their Formal [$_\sigma 2_s$ + $_\sigma 2_a$] Cycloreversion during the Stereoelectronically Controlled Aqueous Decomposition of Sulfoxide-Substituted Nitrosoureas

J. William Lown* and R. Rao Koganty

Department of Chemistry, University of Alberta
Edmonton, Alberta, T6G 2G2 Canada

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Ambient-temperature aqueous decomposition of nitrosoureas and nitrosourethanes provides a convenient source of alkanediazohydroxides[1-3] to explore neighboring group effects on incipient carbenium ions. We have exploited this approach in the controlled aqueous decomposition of certain nitrosourea sulfoxides that leads to the hitherto elusive 1,2-oxathietanes, which are inter alia subject to formal [$_\sigma 2_s$ + $_\sigma 2_a$] cycloreversion or rearrangement. 1-[2-[(2-Chloroethyl)sulfinyl]ethyl]-3-cyclohexyl-1-nitrosourea (**1a**)[4] was allowed to decompose in aqueous potassium phosphate buffer pH 7.0 at 37 °C. The volatile products that were detected and identified by GC and GC–MS were formaldehyde, thioformaldehyde hydrate, and vinyl chloride.[5] The nonvolatile products that were isolated and identified were cyclohexyl isocyanate and dicyclohexylurea. The results are in accord with the decomposition pathway outlined in Scheme I.

The initial step involves a rotation about the N–N bond followed by hydration of the amide carbonyl group.[2,3] Subsequent stereoelectronically controlled collapse of the tetrahedral intermediate **2**[2,3] in which the hetero atom lone pairs are aligned antiperiplanar to the breaking CO–N_1 bond[6] releases the alkane diazohydroxide **3** and the isocyanate. Participation of the sulfoxide oxygen at the demand of the incipient cationic center in the diazohydroxide forms 1,2-oxathietane **4**. The latter eliminates vinyl chloride to give the parent 1,2-oxathietane **5**, which is then subject to cycloreversion (formally of the type [$_\sigma 2_s$ + $_\sigma 2_a$][7] or possibly a stepwise diradical pathway) to formaldehyde and thioformaldehyde, the latter of which is identified as the hydrate.

The alternative pathway to the carbonyl products via the thiirane *S*-oxides **6** and **7** may be eliminated since 1-[2-[(2-chloroethyl)sulfinyl]ethyl-*2*-d_2]-3-cyclohexyl-1-nitrosourea (**1b**)[8] affords formaldehyde and thioformaldehyde-d_2 hydrate with no label scrambling, although it is conceivable that **7** may give rise to **9** (which see). The aqueous decomposition of 1-[2-[(2-chloroethyl)sulfinyl]-1,1-dimethylethyl]-3-cyclohexyl-1-nitrosourea (**1c**)[9] afforded acetone, thioformaldehyde hydrate, vinyl chloride, cyclohexyl isocyanate, and dicyclohexylurea. The relative yields of the cycloreversion products from 1,2-oxathietane **4c** are increased compared with **4a**, in qualitative agreement with the easier ring closure as a result of the buttressing effects of the geminal methyl groups.[10] Similar aqueous decomposition of 1-[2-[(2-chloroethyl)sulfinyl-^{18}O]-1,1-dimethylethyl]-3-cyclohexyl-1-nitrosourea (**1a**-^{18}O)[11] afforded acetone-^{18}O and thioformaldehyde

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(3) Lown, J. W.; Chauhan, S. M. S. *J. Org. Chem.* **1981**, *46*, 5309.
(4) Lown, J. W.; Joshua, A. V.; McLaughlin, L. W. *J. Med. Chem.* **1980**, *23*, 798.
(5) Hewlett-Packard 5840A gas chromatograph with 10% carbowax column, helium flow rate of 22 mL/min at 60 °C. Compound retention times: vinyl chloride, 0.5 min; thioformaldehyde hydrate, 1.31 min; acetone 3.4 min; thioacetone, 4.2 min; 3,3,4,4-tetramethyl-1,2-oxathietane, 5.3 min; 2,3-dimethyl-2-butene, 1.24 min; 2-methyl-2-propene, 1.1 min.
(6) Deslongchamps, P. *Tetrahedron* **1975**, *31*, 2463.
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(9) Prepared by the general procedure given in ref 8.
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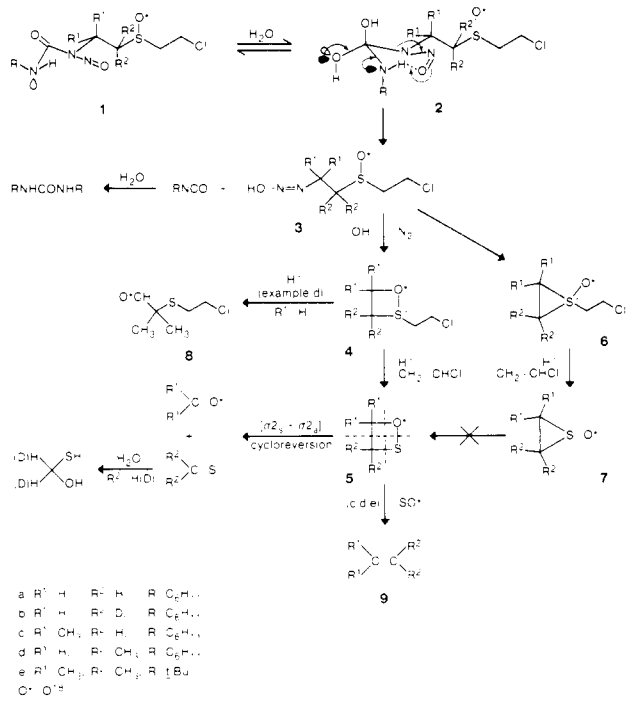
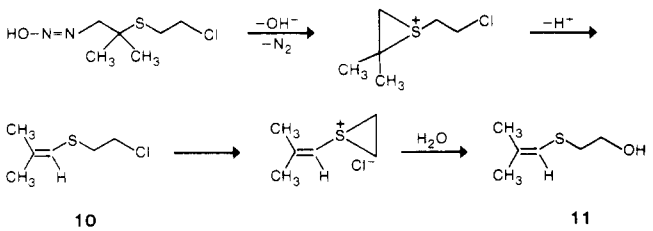
0002-7863/83/1505-0126$01.50/0

Scheme I



Scheme II



hydrate among the volatile products. Thus the reaction proceeds by intramolecular transfer of ^{18}O via a four-membered-ring intermediate.

The isomeric 1-[2-[(2-chloroethyl)sulfinyl]-2,2-dimethylethyl]-3-cyclohexyl-1-nitrosourea (**1d**)[12] decomposes in pH 7.0 buffer to give 2-[(2-chloroethyl)thio]-2-methylpropanal (**8**) and small amounts of 1-[(2-chloroethyl)thio]-2-methylpropene (**10**),[13] 1-[(2-hydroxyethyl)thio]-2-methylpropene (**11**),[13] cyclohexyl isocyanate, and dicyclohexylurea. Isolation of aldehyde **8** is in accord with the generation of the sulfoxide-substituted diazohydroxide **3d** and then formation from the latter of a 3,3-dimethyl-2-(2-chloroethyl)-1,2-oxathietanium (**4d**), which undergoes proton loss at position 4 and breakage of the O–S bond with formation of the propanal **8**. The corresponding reaction of 1-[2-[(2-chloroethyl)sulfinyl-^{18}O]-2,2-dimethylethyl]-3-cyclohexyl-1-nitrosourea (**1d**-^{18}O)[11] to afford 2-[(2-chloroethyl)-thio]-2-methylpropanal-^{18}O (**8**-^{18}O) is in accord with the suggested pathway.

Controlled aqueous decomposition of 1-[2-[2-chloroethyl)-sulfinyl]-1,1,2,2-tetramethylethyl]-3-*tert*-butyl-1-nitrosourea (**1e**)[14] at pH 7.0 and 38 °C afforded acetone, thioacetone, *tert*-butyl isocyanate, and di-*tert*-butylurea. GC analysis[5,15] of the reaction mixture permitted detection of the labile 3,3,4,4-tetramethyl-1,2-oxathietane (retention time 5.3 min), GC–MS analysis of which gave the corresponding correct m/e of 132.[16] The GC analysis also detected 2,3-dimethyl-2-butene (**9e**) from the extrusion of SO from the 1,2-oxathietane.[15] This alternative mode of cleavage has a counterpart in the fragmentation of the m/e 132 molecular ion of **5e**.[16]

Evidence for the existence of 1,2-oxathietane has not, to our knowledge, been hitherto reported. Only one report claiming the intermediacy of such a species in the pyrolysis of 1,2,3-oxadithiolane 2-oxide and thiirane 1-oxide at 1043–1404 K has been made;[17] however, no evidence was obtained for what now appears to be the characteristic (2 + 2) cycloreversion. The latter reaction is anticipated by analogy with the 1,2-dioxetanes.[18] Attempts to isolate 1,2-oxathietanes and to examine their possible chemiluminiscent behavior are in progress.

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(11) Prepared by the methylene blue sensitized photooxidation of **1a**, **1d**, or **1e** in methanol in the presence of $^{18}O_2$ (99% isotopic enrichment), **1a**-^{18}O; m/e 312, 249 (100), $M^+ - CH_2CH_2Cl \equiv C_{11}H_{23}N_2OS\ ^{18}O$.

(12) Prepared as described in ref 8 from (2-hydroxy-2-methylpropyl)-amine.

(13) These products arise from a competing minor deoxygenation pathway of the parent sulfoxide giving rise, in each case, to traces of aqueous decomposition products characteristic of the corresponding thioether nitrosourea[8] (Scheme II).

(14) Prepared from tetramethylaziridine (Closs, G. L.; Brois, S. J. *J. Am. Chem. Soc.* **1960**, *82*, 6068) as described in footnote 9. The *tert*-butyl group ensures the desired regiochemistry in the nitrosation step.

(15) Integrated GC peak areas of components given as percent relative to the *tert*-butyl isocyanate peak: vinyl chloride (14.5); thioacetone (7.0); 2,3-dimethyl-2-butene (53); acetone (22); 3,3,4,4-tetramethyl-1,2-oxathietane (2.0).

(16) m/e (%) 132.15904 (10) M^+ (measured for $C_6H_{12}SO$), 117 (4) ($M^+ - CH_3$), 116 (17) ($M^+ - O$), 84 (100) ($M^+ - SO$), 74 (8) ($(CH_3)_2C{=}S^+$).

(17) Carlsen, L.; Egsgaard, H. *J. Chem. Soc., Perkin Trans. 2* **1982**, 279. Semiempirical CNDO/B calculations predict a planar configuration for 1,2-oxathietane at least in the gas phase (Snyder, J. N.; Carlsen, L. *J. Am. Chem. Soc.* **1977**, *99*, 2931.

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Stereocontrolled Osmylation of Medium-Ring Alkenes: Synthesis of a C_1–C_9 Erythronolide Fragment

E. Vedejs,* J. M. Dolphin, and H. Mastalerz

S. M. McElvain Laboratory of Organic Chemistry
Chemistry Department, University of Wisconsin
Madison, Wisconsin

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We are interested in the stereochemistry of medium- and large-ring alkene addition reactions, many of which occur with high selectivity.[1] The goal is to identify dominant conformational factors that might have predictive value in synthesis. In this communication we report that osmylation of the nine-membered-ring alkene **1** can be used for stereocontrolled synthesis of an erythronolide fragment having the correct C_2–C_6 stereochemistry.[2] For comparison, two isomeric ten-membered-ring alkenes **2** and **3** have also been studied.

Syntheses of alkenes **1–3** are outlined in Scheme I. The α-oxo dithioester Diels–Alder reaction occurs with normal regiochemistry[3] to give **4**, which is efficiently desulfenylated to **5**.[4] After

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(2) For total synthesis of erythronolide A, see: Corey, E. J.; Hopkins, P. B.; Kim, S.; Yoo, S.; Nambiar, K. P.; Falck, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 7131.

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