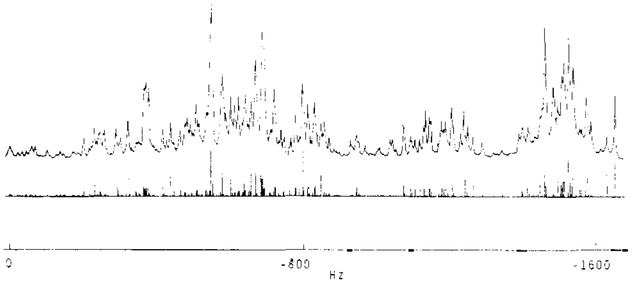


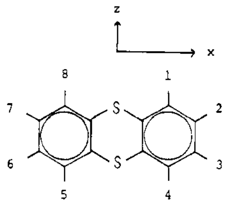
**Figure 1.** $^1H$ NMR spectra of thianthrene in nematic solution of ZLI1167. Only high-field half is shown.

**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: $\sigma^{b} = 0.06$ |
| $r_{18} = 5.131 \pm 0.009$ | angle, deg: $\theta^{c} = 141.6 \pm 0.2$ |

[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.

---

(11) Fronza, G.; Ragg, E. *J. Chem. Soc., Faraday Trans. 2*, **1982**, 291.

(12) Koga, Y.; Takahashi, H.; Higashi, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3359.

---

# 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*

*Received September 27, 1982*

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

---

(1) (a) Moss, R. A. *Acc. Chem. Res.* **1974**, 421. (b) Keating, J. T.; Skell, P. S. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Interscience: New York, 1970; Vol. II, pp 576 ff. (c) Friedman, L., in ref 1b, pp 656 ff.

(2) Snyder, J. K.; Stock, L. M. *J. Org. Chem.* **1980**, *45*, 1990.

(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.

(7) Woodward, R. B.; Hoffman, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim, 1970; p 72.

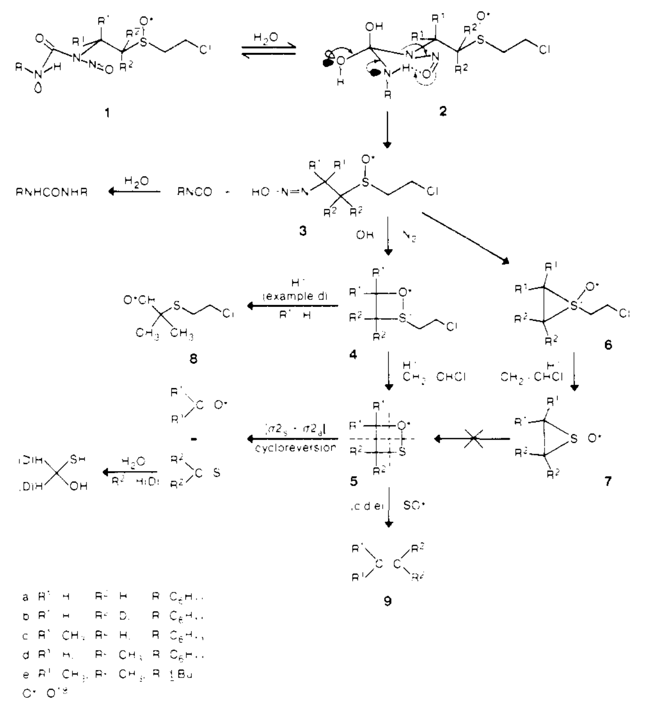
(8) Lown, J. W.; Koganty, R. R.; Joshua, A. V. *J. Org. Chem.* **1982**, *47*, 2027.

(9) Prepared by the general procedure given in ref 8.

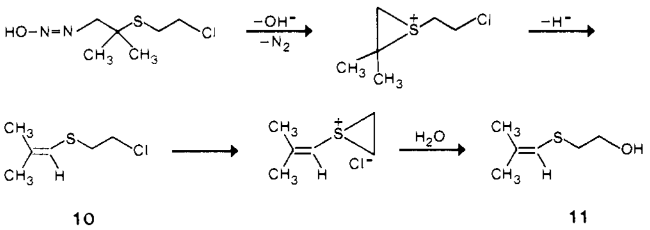
(10) Etienne, Y.; Soulas, R.; Lumbroso, H. In "The Chemistry of Heterocyclic Compounds"; Weissberger, A., Ed.; Interscience: New York, 1964; Vol. 1, Part 2, p 681.

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.

**Acknowledgment.** This work was supported by Grant 1R01 CA21488-01 awarded by the National Cancer Institute, DHEW, to J.W.L. and by a grant from the Alberta Provincial Cancer Hospitals Board.

---

[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.

[18] (a) Kopecky, K. R.; Filby, J. E., Mumford, C.; Lockwood, P. A.; Ding, J.-Y. *Can. J. Chem.* **1975**, *53*, 1103. (b) Richardson, W. H.; Montgomery, F. C.; Yelvington, H. E.; O'Neal, H. E. *J. Am. Chem. Soc.* **1974**, *96*, 7525. (c) Turro, N. J.; Lechtken, P. *Ibid.* **1972**, *94*, 2886. (d) White, E. H.; Wildes, P. D.; Weicko, J.; Doshan, H.; Wei, C. C. *Ibid.* **1973**, *95*, 7050 and references therein.

---

# 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*

*Received July 15, 1982*

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

---

[1] (a) Still, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 2493. (b) Still, W. C.; Galynker, I. *Tetrahedron* **1981**, *37*, 3981. (c) Still, W. C.; Galynker, I. *J. Am. Chem. Soc.* **1982**, *104*, 1774. (d) Doskotch, R. W.; Kelley, S. L., Jr.; Bufford, C. D. *J. Chem. Soc., Chem. Commun.* **1972**, 1137. (e) Corey, E. J.; Nicolaou, K. C.; Melvin, L. S., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 654.

[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.

[3] Vedejs, E.; Arnost, M. J.; Dolphin, J. M.; Eustache, J. *J. Org. Chem.* **1980**, *45*, 2601.

0002-7863/83/1505-0127$01.50/0