I. THE SYNTHESIS, STRUCTURE AND CHEMISTRY OF α,α-DICYANO N-(p-DIMETHYLAMINOPHENYL)NITRONE

II. THE SYNTHESIS AND STABILITY OF CUMULENES DERIVED FROM DI-t-BUTYL THIOKETONE

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Approved:

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GLOSSARY OF ABBREVIATIONS

DMSO	dimethylsulfoxide
HOMO	highest occupied molecular orbital
Hz	Hertz
ir	infrared
LUMO	lowest unoccupied molecular orbital
m-CPBA	meta-chlorobenzoic acid
NIH	National Institute of Health
MINDO/3	modified incomplete neglect of differential overlap /3
nm	nanometer
nmr	nuclear magnetic resonance
ppm	parts per million
TCNQ	7,7,8,8-tetracyanoquinodimethane
THF	tetrahydrofuran
TLC	thin-layer chromatography
TMS	tetramethylsilane
UV	ultraviolet

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SUMMARY PART I

The synthesis and chemistry of α,α-dicyano N-(p-dimethylaminophenyl)nitrone (1) was described. SCF semiempirical calculations suggested an explanation for the deoxygenation of 1 and an x-ray structure of 1 agreed favorably with the structure predicted by the molecular orbital calculations.

The thermal and photochemical deoxygenation of 1 was investigated. Although 1 deoxygenated readily at its melting point, no oxygen atom transfer to substrates was observed. A novel cycloadduct (4) resulted from the thermal reaction of 1 with norbornylene. A mechanism for the formation of 4 was postulated. The photochemical deoxygenation of 1 in an olefin solvent resulted in a low yield of the corresponding epoxide.

SUMMARY PART II

The purpose of the research described herein was to investigate the synthesis and stability of sulfur heterocumulenes derived from di-t-butylthioketone. A new and general synthesis of di-t-butylthione S-imides was described and the reaction of di-t-butylthioketone with diazo compounds was investigated as a possible route to stable thione S-methylides.

The thermal and photochemical decomposition of di-t-butylsulfine (8) was investigated. While the thermal decomposition afforded a temperature dependent mixture of products via a first order process, the photochemical decomposition proceeded cleanly to a single product. A mechanism was offered for these reactions based on the formation of an intermediate oxathiirane.

Reaction of di-t-butylthioketone with chlorine yielded 2,2,4,4-tetramethylpentane-3-chloro-3-sulfenyl chloride (10) whose reaction with primary amides afforded imines. The reaction of 10 with hindered alkyl primary amines afforded thione S-imides. Carbon-13 nmr shifts were calculated for two unsubstituted model compounds, 17 and 18 and based on these calculations it is predicted that the valence angle at sulfur is approximately 80° for 15. SCF semiempirical calculations suggested a possible mechanism for the desulfurization reaction of sulfines and thione S-imides. An x-ray crystal structure was done on the cycloadduct

of **15** with TCNQ.

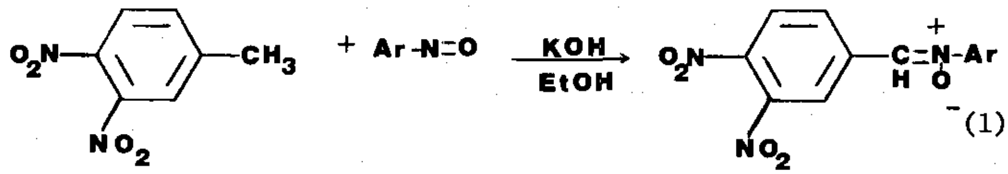
The reaction of di-*t*-butylthioketone with a series of diazo compounds was investigated. While diphenyl diazomethane and ethyl diazoacetate yielded 1:1 cycloadducts; diazofluorene afforded an azine derived from desulfurization of the intermediate cycloadduct. Diethyl diazomalonate and di-*t*-butyl diazomalonate yielded products derived from cyclization of the intermediate thione *S*-methylide.

I. THE SYNTHESIS, STRUCTURE AND CHEMISTRY OF α,α-DICYANO N-(p-DIMETHYLAMINOPHENYL)NITRONE

CHAPTER I

INTRODUCTION

The synthesis and chemistry of nitrones has been the subject of several reviews.[1,2,3] It is sufficient to mention that nitrones have been synthesized from aromatic nitroso compounds by four different general methods, (eq 1-4)[1] and based on the availability of starting



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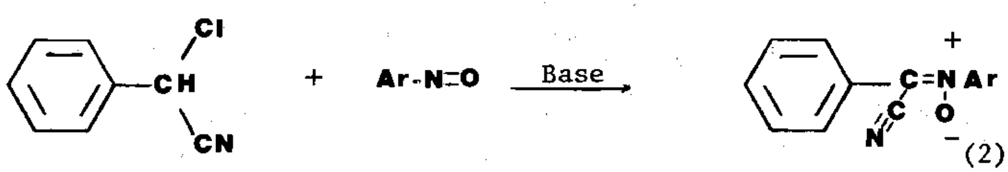

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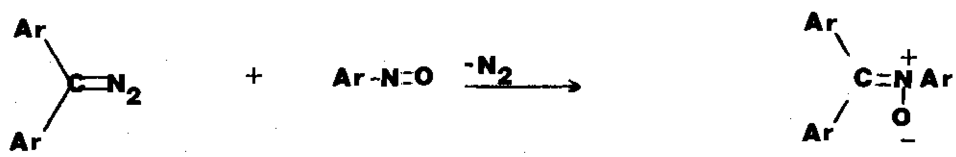

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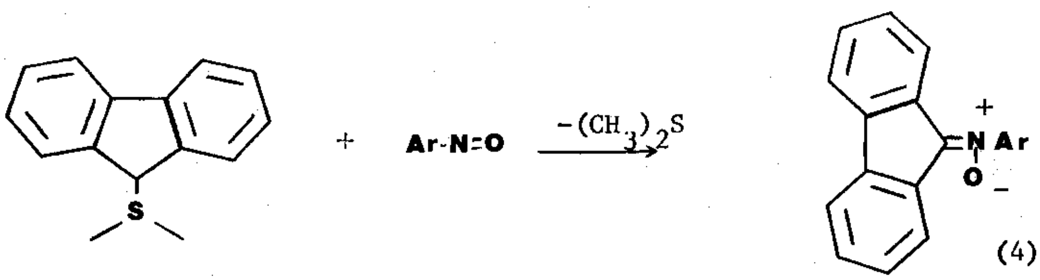

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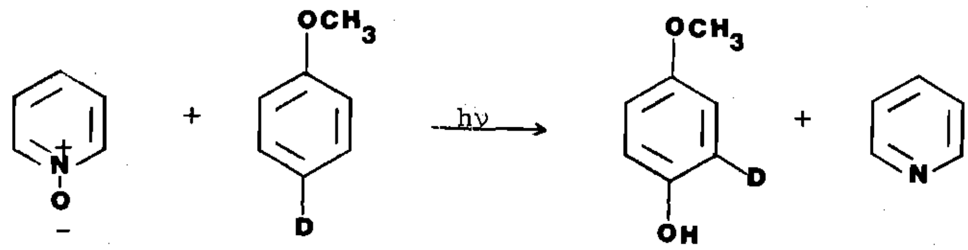
materials, a route patterned after equation 2 was employed for the synthesis of the title compound.



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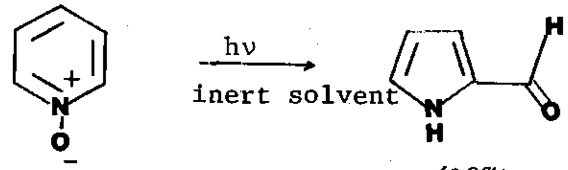

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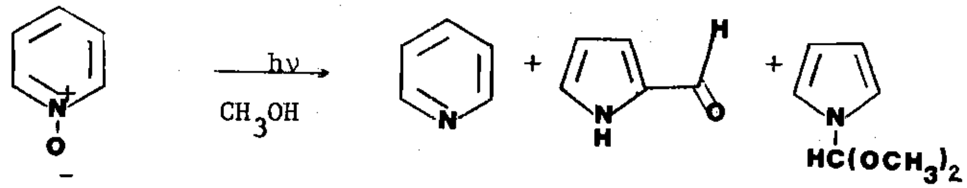

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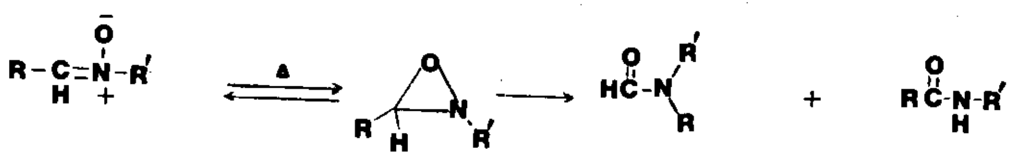
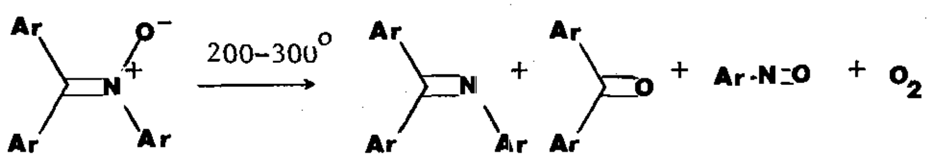


(8)

The deoxygenation of nitrones is of theoretical interest as an oxygen atom transfer model for enzymatic oxygenation; for example, Boyd has observed an NIH shift when anisole and pyridine N-oxide were photolyzed in methylene chloride, (eq. 5).[4] The photolytic deoxygenation of pyridine N-oxide has been assumed by other workers to proceed through a transient oxaziridine to liberate atomic oxygen[5] and one of the characteristics of the reported photolyses of pyridine-N-oxides is the poor material balance, (eq. 6 and 7).[2]

The photolytic conversion of nitrones to oxaziridines is well documented (eq. 8);[1,2] however, in some cases irradiation of nitrones causes deoxygenation to the corresponding imines. The mechanism of the deoxygenation has not been elucidated, but it may be due to reduction of primary product, an oxaziridine.[2]

Simple alkyl substituted oxaziridines show no ultraviolet or visible spectra and therefore are photochemically inert. Oxaziridines however, are relatively unstable species and thermal ring opening proceeds easily to give either isomeric nitrones or rearrangement to amides. Oxaziridines with an aryl group on carbon isomerize thermally to the corresponding nitrones, while C-alkyl oxaziridines are isomerized to amides. Oxaziridines which carry an aryl group on nitrogen rearrange at room temperature and cannot be isolated.[6] The pyrolysis of nitrones has not been subjected to a detailed systematic study; however, the pyrolysis of α,α,N-triphenylnitrone at 200-300° results in partial deoxygenation, (eq. 9).[1,8] The isomerization of α,α-diphenyl N-(diphenyl-



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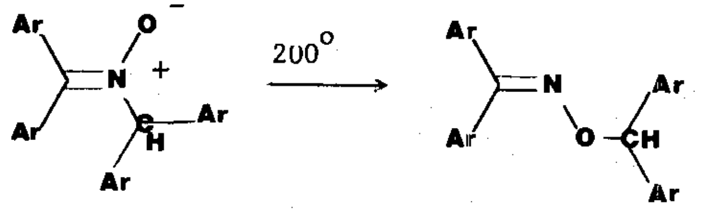
methyl)nitrone at 200° results in an N-to O-alkyl transfer, (eq 10)[3]; however, this rearrangement has only been observed for N-(diphenylmethyl)nitrones.



(10)

The reduction of nitrones often leads to simple deoxygenation. Deoxygenation of nitrones has been accomplished by zinc, tin, or iron dust, phosphines, sulfur dioxide, sulfur, and catalytic hydrogenation, while treatment with either lithium aluminum hydride or sodium borohydride provide in high yield the corresponding hydroxylamines, presumably by a 1,3-addition mechanism.[1]

The reduction of oxaziridines, like nitrones, is reported to lead to deoxygenated products and has been accomplished by lithium aluminum hydride, phosphines, and tertiary amines.[7,8]

Investigations into the deoxygenation of nitrones with the possible intermediacy of an oxaziridine species might provide a new general method of oxygenating selective substrates. Thus, it was the goal of the research described herein to synthesize α,α-dicyano N-(p-dimethylaminophenyl)nitrone and investigate its thermal and photolytic deoxygenation.

CHAPTER II

INSTRUMENTATION AND EQUIPMENT

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Hexane and pentane were washed with concentrated sulfuric acid, distilled and then redistilled from sodium metal. Triethylamine, and methylene chloride were fractionally distilled and stored over 4 Å molecular sieves. Anhydrous ether was purchased commercially in one pound cans and used without further purification. Methanol, acetonitrile, and ethanol were distilled from calcium hydride. Purification of all other organic reagents was achieved by established procedures.[9]

Anhydrous reaction conditions were established by drying the necessary glassware in an oven maintained at 150°. An inert atmosphere was provided by purified argon which had been dried by passing through a coiled glass tube immersed in a dry ice-isopropanol bath.

Concentration or evaporation of solvents was performed under reduced pressure (ca 20 mm) using a Buchi rotary evaporator. Thin layer chromatography was performed using Eastman Chromagram sheets. Column chromotographies were performed using Silica gel (80-100 mesh) or Florosil (80-100 mesh) as indicated.

Whenerver two solvents were indicated for a column chromatography, a general procedure was employed. The column was loaded with a 30:1 ratio of adsorbent to substrate using the adsorbent indicated in each case. The substrate was eluted with 2-5 column volumes of hexane followed by 5 column volumes of 90% hexane:10% methylene chloride. Successive lots of 5 column volumes were eluted using 80/20, 60/40, 40/60, 20/80, and 100/0 ratios of hexane to methylene chloride. The elutant was analyzed by TLC and column volumes of equivalent composition were combined for further work-up.

Proton nuclear magnetic resonance spectra (nmr) were recorded on a Varian Associates Model T-60A or A-60 spectrometer in the solvent specified in each case. Chemical shifts were reported versus an internal tetramethylsilane (TMS) standard and the abbreviations s, d, t, q, and m refer to singlet, doublet, triplet, quartet, and multiplet, respectively. Carbon-13 nuclear magnetic resonance spectra were obtained on a JOEL Model PFT-100 Fourier transform nmr spectrometer and the chemical shifts were reported versus a tetramethylsilane standard in the same manner as proton nmr. Infrared spectra were obtained on a Perkin-Elmer Model 457 recording spectrophotometer using either 0.1 mm sodium chloride cells or potassium bromide pellets as indicated. Ultraviolet and visible spectra were recorded on a Cary-14 spectrophotometer using one centimeter balanced quartz cells. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-7L high resolution mass spectrometer or a Varian Associates Model M-66 medium resolution mass spectrometer. Melting points were determined on a Thomas Hoover capillary melting point apparatus. Melting points are reported in degrees centigrade and are uncorrected. Gas-liquid chromatography separations were performed on a Hewlett-Packard model 402 high efficiency gas chromatograph using either 6 ft 10% SE-30, 6 ft 5% Carbowax 20 M, 10 ft 10% QF1 or 30 ft 10% TCEP columns.

Thermolyses were performed at the specified temperature using an oil bath. The temperature was maintained (±2°) using an I^2R Thermo-Watch controller. The progress of each thermolysis reaction was monitored using proton nmr spectrometer and the percentage of each constitutent was determined by peak integration of the spectra.

Data for the x-ray structure was collected on a Syntex $P2_1$ four circle diffractometer. For the solution and refinement of the structure, computations were performed using standard programs[13] and were carried out with a CDC 6600-6800 computer.

Geometry optimized molecular orbital calculations were performed using MINDO/3 program,[14] and the computations were carried out on a CDC 6600-6800 computer.

Elemental analyses (C, H, and N) were performed by Atlantic Microlab, Inc., Atlanta, Georgia.

CHAPTER III

EXPERIMENTAL

α,α-Dicyano,N-(p-dimethylaminophenyl)nitrone (1)

Bromomalononitrile (1.45 g, 0.01 mol) in 50 ml anhydrous diethyl ether was added dropwise over a period of 20 min. to N,N-dimethyl p-nitrosoaniline (1.50 g, 0.01 mol) and triethylamine (1.0 g, 0.01 mol) in 100 ml anhydrous ether maintained at 0°C. When the addition was complete the cooling bath was removed and the reaction was allowed to stir for an additional 30 min. at 25°. The mixture was filtered with suction and washed with 100 ml anhydrous ether. The dark solid precipitate collected was placed in a soxhlet extractor and continuously extracted with 1000 ml anhydrous ether for 5 hr. On cooling the combined ether solutions to -78°, crystals of the crude nitrone separated and were collected by filtration. The crude nitrone was recrystallized from ether to yield 0.61 g (35%) of 1 as purple needles: mp 139-140°; proton nmr ($CDCl_3$) δ 3.10 (s, 6H), 7.8 (dd, 4H); ir (KBr) 2225, 2210 (C≡N), 1605 (C=N), 1410, 1335, 1255, 1160 cm^{-1}; UV max (hexane) 460 nm (ε 1.96×10^6); mass spectrum (70 eV) m/e (rel. intensity) 214 (94), 198 (74), 197 (100), 184 (50), 136 (43).

Anal. Calculated for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.70; N, 26.16. Found: C, 61.53; H, 4.76; N, 26.08.

N,N-Dimethyl-N′-(dicyanomethylene)-p-phenylenediamine (3)

N,N-Dimethyl-N -(dicyanomethylene)-p-phenylenediamine was prepared by a modification of the procedure of Sachs.[10] N,N-dimethyl-p-nitrosoaniline (1.5 g, 0.01 mol), anhydrous potassium carbonate (2.75 g, 0.02 mol), and malonitrile (0.73 g, 0.01 mol) were suspended in 150 ml anhydrous ether and the mixture was stirred at 27°. After 8 hr the reaction mixture was filtered, and the precipitate washed with 50 ml anhydrous ether. The combined filtrate was concentrated with rotary evaporator under reduced pressure to give a red solid. The solid was sublimed at 100° (0.5 mm) to yield 0.7 g (35%) of pure 3: mp 160° (lit.[10] mp 167°); proton nmr δ3.19 (s, 6H), 7.16 (dd, 4H), ir (KBr) 2220, 2200 (C≡N), 1620 (C=N), 1470, 1390, 1200 m^{-1}, UV max (EtOH) 460 nm (ε 3,960), 364 (6,420), 318 (5,460), 248 (1,460); mass spectrum (70 ev) m/e (rel intensity) 198 (73), 197 (100), 182 (11), 181 (10), 118 (7).

Thermal Decomposition of Nitrone 1

Nitrone 1 (750 mg, .035 mol) was heated to 140° in a sublimator under an argon atmosphere. After 2 hr a vacuum was applied and imine 3 was sublimed (105 mg, 15%) at 140° (0.5 mm). The sublimand consisted of 620 mg of black insoluble tar.

In order to detect evolved oxygen, the thermal decomposition was also carried out in several solvents: refluxing anhydrous pyridine (115°), anhydrous dimethyl sulfoxide (150°), diphenyl sulfoxide (150°), naphtahalene (150°), diphenyl sulfide (150°); however, no pyridine N-oxide, dimethyl sulfone, diphenyl sulfone, naphthol, or diphenyl sulfoxide, respectively, were detectable by GLC.[11]

Reaction of Triphenyl Phosphine with Nitrone **1**

Nitrone **1** (21.4 mg, 0.10 mmol) and triphenylphosphine (52.5 mg, 0.2 mmol) were dissolved in 25 ml anhydrous benzene and were refluxed for 5 hours under an inert atmosphere. The reaction was cooled and concentrated with a rotary evaporator under reduced pressure. Chromatography on silica gel using methylene chloride/hexane as the elutant afforded 10 mg of imine 3 (75%) and triphenyl phosphine oxide.[12]

Reaction of Tris-(dimethylamino)phosphine with Nitrone **1**

Tris-(dimethylamino)phosphine (TDMAP) (0.1 g, 0.6 mmol) in 0.2 ml dry benzene was added in 4 portions to a solution of **1** (73 mg, 0.3 mmol) in 0.5 ml dry chloroform maintained at 27° under an inert atmosphere. The reaction was monitored by nmr at each of the intermediate stages and rapid and stoichiometric conversion to imine **3** and tris-(dimethylamino)phosphine oxide(TDMAPO) was observed. After the addition of the final portion of TDMAP the reaction was concentrated with a rotary evaporator under reduced pressure. Chromotography on silica gel using methylene chloride/hexane as the elutant afforded 50 mg of imine **3** (74%) and TDMAPO.[12]

Reaction of Norbornylene with Nitrone **1**

Norbornylene (1.0 g, 10 mmol) and nitrone **1** (0.22 g, 1 mmol) were heated in an oil bath to 95° for 5 hrs under an inert atmosphere. The reaction was cooled to room temperature and chromotographed on silica gel using methylene chloride/hexane as the elutant afforded the cycloadduct 4. Recrystallization from ether yielded 0.3 g (90%) of pure cycloadduct 4 as a yellow solid: mp 145-146°, proton nmr (CCl_4) δ 1.25-1.60 (m, 6H), 2.60 (s, 2H), 3.00 (s, 6H), 3.20 (d, sH, J=7Hz), 4.70 (d, 2H, J=7Hz), 6.95 (d, 1H, J=3Hz), 7.12 (dd, 1H, J=3, 9Hz), 7.83 (d, 1H, J=9Hz); ir (CH_2Cl_2) 3045, 2980, 1632, 1604, 1574, 1527; UV max (EtOH) 397 nm (ε 13200), 282 (15000), 260 (17200), 226 (32800); carbon-13 nmr ($CDCl_3$) δ 23.24 (t), 27.79 (t), 32.22 (t), 40.16 (q), 41.68 (d), 41.92 (d), 49.51 (d), 86.40 (d), 105.32 (d), 113.82 (d), 128.02 (d), 131.96 (s), 141.73 (s), 145.06 (s), 150.34 (s), 161.63 (s); mass spectrum (70 ev m/e (rel. intensity) 281 (100), 214 (16), 202 (16), 141 (26).

Anal. Calculated for $C_{18}H_{20}N_4O$: C, 72.56; H, 6.81; N, 14.94. Found: C, 72.73; H, 6.83; N, 14.92.

Kinetics of Nitrone 1 Thermal Decomposition

All decomposition reactions were run at 150° in DMSO-d_6 under an inert atmosphere. The disappearance of starting material was monitored by proton nmr through at least the first 60% of the course of the reaction. The only detected product was imine 3.[12] The results of these reactions are shown in Table 5.

Attempt to Detect Evolved O_2 in the Thermal Decomposition of Nitrone 1

Nitrone 1 (214 mg, 1 mmol) in 10 ml dry DMSO was heated to 150° under an atmosphere of prepurified N_2. Nitrogen was bubbled through the reaction and swept into a solution of 0.5 g pyrogallol in 15 ml of 45% aqueous potassium hydroxide in order to detect the evolution of oxygen. After 1 hr of reaction, no significant color change of the pyrogallol solution had occurred. A control blank reaction was run as above and after 1 hr no oxygen had been detected. A third experiment using 0.5 g pyrogallol in 15 ml of 45% aqueous potassium hydroxide indicated that 0.1 ml of oxygen could be easily detected; therefore, the upper limit on the detection of oxygen evolved in the original experiment is ∿1%.

Attempted Oxidation of Imine **3**

m-Chloroperbenzoic acid (34 mg, 0.2 mmol) in 15 ml dry methylene chloride was added dropwise over a 5 min period to a solution of imine **3** (20 mg, 0.1 mmol) in 15 ml dry methylene chloride maintained at 25°. The reaction was allowed to stir for 24 hr after the addition was complete at which time T.L.C. showed no reaction.

The reaction was repeated using glacial acetic acid as the solvent with the same final results. The oxidation was also attempted using 2 equivalents of 50% hydrogen peroxide in ethanol, but no reaction was observed.

Photolytic Decomposition of Nitrone **1**

Nitrone **1** (22 mg, 0.1 mmol) in 30 ml THF was photolyzed with a low pressure Hg-discharge lamp in a quartz vessel under an inert atmosphere. After 3 hr photolysis was stopped and the THF was removed on a rotary evaporator under reduced pressure. The crude reaction mixture was sublimed at 120° (0.02 mm) to yield 15 mg imine **3**.[12]

Photolysis of Nitrone 1 in Cyclohexene

A quartz photolysis vessel was dried at 150° and allowed to cool to 27° under an argon atmosphere. The vessel was charged with 150 mg nitrone 1 (0.7 mmol) and 250 ml of freshly distilled cyclohexene. The mixture was stirred for 30 min under an argon flush to remove oxygen and then irradiated with a 150 watt high pressure Hg-discharge lamp for 2 hr. The reaction was fractionally distilled and yielded 10 mg (10%) cyclohexene oxide, identified by nmr comparison with an authentic sample.

Photolysis of Nitrone 1 in Benzene

A quartz photolysis vessel was dried at 150° and allowed to cool to 27° under an argon flush. The vessel was charged with 2.15 g (0.01 mole) nitrone 1 and 2000 ml of freshly distilled benzene. The mixture was stirred for 45 min under an argon flush to remove oxygen and then irradiated with a 450 watt high pressure Hg-discharge lamp for 250 hr. The benzene was then removed under vacuum. Proton nmr of the red-brown solid showed 80% conversion of nitrone 1 to imine 3. The red-brown solid was extracted with 2X50 ml of 10% sodium hydroxide, filtered, acidifed with 10% sulfuric acid and extracted with 5X100 ml of methylene chloride. The methylene chloride was dried with magnesium sulfate, filtered, and concentrated with a rotary evaporator under reduced pressure to give a red solid which was chromatographed on Porosil C_{18} and eluted with cyclohexane and yielded a mixture of nitrone 1 and imine 3 but no phenol.

CHAPTER IV

X-RAY STRUCTURE

X-Ray Structure Of α,α-Dicyano N-(p-Dimethylaminophenyl)nitrone (1)

A purple crystal with approximate dimensions 0.05 x 0.1 x 1.0 mm was mounted on a glass fiber using epoxy cement such that the longest crystal dimension was approximately parallel to the fiber axis.

Unit cell parameters and orientation matrix were determined on a Syntex $P2_1$ four circle diffractometer equipped with a graphite monochromator (Bragg 2θ angle 12.2°) using MoKα radiation at a takeoff angle of 6.5° . Fifteen reflections of various 2θ value were machine-centered and used in least-squares refinement of the lattice parameters and orientation matrix. Unit cell parameters obtained were a=5.12(1)Å, b=12.10(1)Å, c=19.1(1)Å, α=γ=90.00(1)°, β=110.09(1)°. Omega scans of three low 2θ angle reflections gave peak widths at half-height of less than 0.3° indicating a satisfactory mosaic spread for the crystal.

Intensity data were collected using θ-2θ scans with x-ray and monochromator settings identical to those used for determination of the unit cell parameters. A variable scan rate of from 2.0° to 29.3° per minute was used. No significant fluctuations were observed in the intensities of three standard reflections monitored every 97 reflections. A total of 726 reflections were accepted as statistically above the background on the basis that I was greater than 2 sigma.

The space group was determined to be $P2_{1/c}$ on the basis of systematic abscences, h01, when l=2n + 1, 0k0, when k=2n + 1. The structure was solved by direct methods using program MULTAN. One solution contained all 16 atoms in a chemically reasonable arrangement. The coordinates and isotropic temperature factors of these atoms were refined by full matrix least squares.

The four aromatic hydrogen atoms were placed using program FINDH and all non-hydrogen atoms were refined anisotropically until convergence was reached at R = 0.23 with the weighed R_w = 0.13. The highest peak in the final E map was 0.93. Structure factor tables are listed in the appendix.

Using the numbering system indicated below, the atomic fractional coordinates are listed in Table 1.

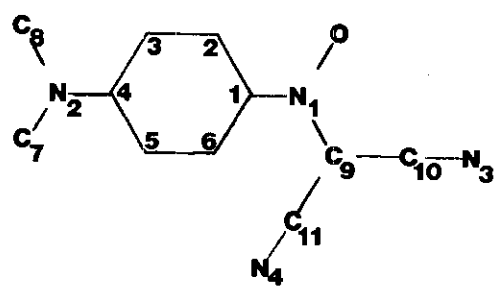


Table 1. Atomic Fractional Cell Coodinates Of Nitrone 1

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O	-.014(4)	-.065(1)	.222(1)	.09(1)	.001(1)	.021(2)	-.006(3)	.017(4)	-.004(1)
N_1	.024(5)	.035(2)	.214(1)	4.7(5)					
N_2	1.039(6)	.183(2)	.420(1)	.106(2)	.018(3)	.002(9)	-.010(7)	.005(3)	-.003(1)
N_3	-.079(5)	.277(3)	.112(1)	.098(2)	.026(4)	.003(1)	.018(7)	-.003(3)	-.001(1)
N_4	-.626(6)	.013(2)	.092(1)	.110(20)	.009(2)	.005(1)	-.003(5)	.008(4)	-.005(1)
C_1	.273(5)	.070(2)	.254(1)	.101(19)	.012(3)	-.0037(4)	.010(6)	.0002(24)	.0019(10)
C_2	.305(5)	.188(2)	.278(9)	.060(9)	.005(2)	.005(1)	.006(5)	.006(3)	-.001(1)
C_3	.583(4)	.222(1)	.340(1)	.022(9)	.006(2)	-.0006(6)	.008(4)	-.002(2)	.0014(9)
C_4	.799(7)	.152(2)	.365(2)	.060(20)	.004(2)	.013(2)	.002(5)	.013(6)	-.005(2)
C_5	.752(5)	.043(3)	.344(2)	.026(14)	.004(2)	.009(2)	-.004(5)	-.009(4)	-.0004(15)
C_6	.513(7)	-.001(2)	.306(2)	.120(20)	.004(2)	.007(2)	.003(6)	.021(6)	-.0009(15)
C_7	1.123(7)	.309(2)	.447(1)	.220(30)	.0002(16)	.005(1)	.018(6)	-.006(5)	.0015(12)
C_8	1.284(6)	.114(2)	.468(1)	.080(20)	.013(2)	.0005(7)	-.006(6)	-.003(3)	.003(1)
C_9	-.143(5)	.100(2)	.164(1)	.060(20)	.004(2)	.0018(9)	.0007(51)	-.013(3)	-.002(1)
C_{10}	-.044(8)	.197(2)	.148(2)	.190(40)	.007(2)	.008(2)	.022(7)	.017(7)	.009(2)
C_{11}	-.424(5)	.057(2)	.108(2)	.030(10)	.009(3)	.011(2)	.007(6)	.0002(50)	.003(2)

Table 2. Selected Bond Lengths And Angles Of Nitrone 1

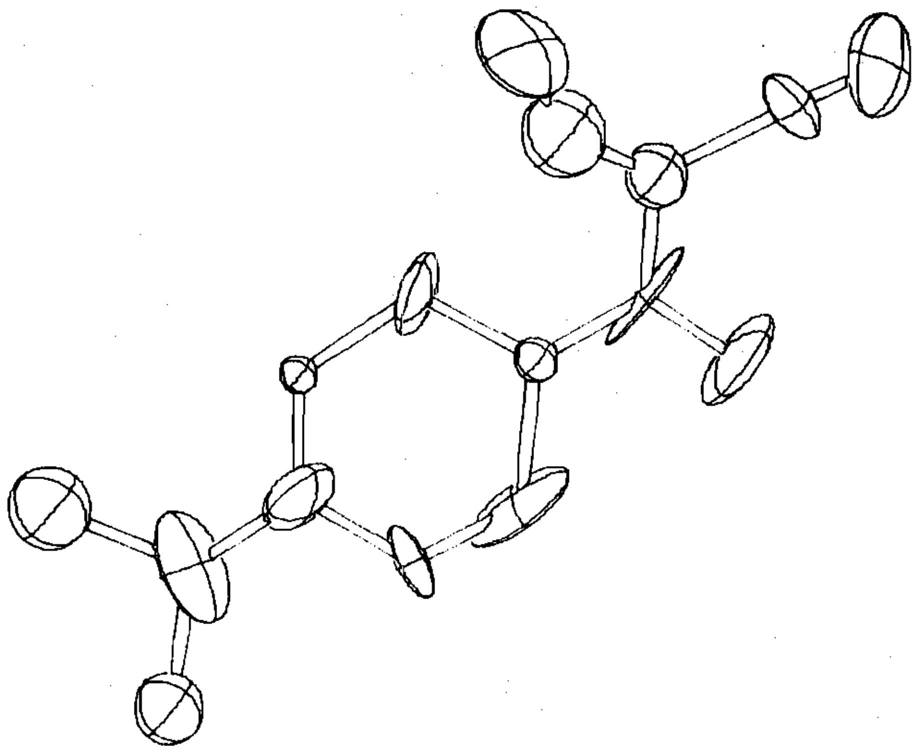
	Bond Length, Å	Angle, Degrees
$O-N_1$	1.266(18)	
N_1-C_1	1.309(26)	
N_1-C_9	1.297(23)	
C_1-N_1-O		114.6(2.5)
C_9-N_1-O		123.8(2.5)
$C_1-N_1-C_9$		120.8(2.1)
C_1-C_2	1.477(28)	
C_2-C_3	1.564(26)	
C_3-C_4	1.364(28)	
C_4-C_5	1.370(31)	
C_5-C_6	1.284(31)	
C_6-C_1	1.567(33)	
C_4-N_2	1.366(30)	
C_7-N_2	1.627(28)	
C_8-N_2	1.505(28)	
C_9-C_{10}	1.372(36)	
C_9-C_{11}	1.570(33)	
$N_1-C_9-C_{10}$		117.9(2.4)
$N_1-C_9-C_{11}$		123.0(2.2)
N_3-C_{10}	1.177(29)	

Table 2. Selected Bond Lengths And Angles Of Nitrone 1 (Continued)

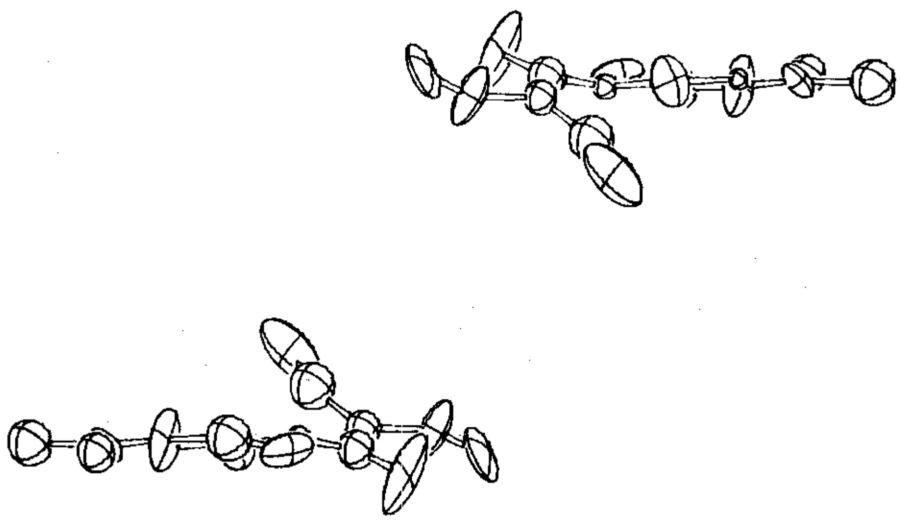
	Bond Length, Å	Angle, Degrees
N_4-C_{11}	1.101(23)	
C_9-C_{10}-N_3		151.1(3.8)
C_9-C_{11}-N_4		154.5(3.2)

Table 3. Dihedral Angles Of Nitrone 1

	Dihedral Angle, Degrees
$(ON_1C_1)(C_2C_1N_1)$	28.4(1.9)
$(C_{10}C_9N_1)(C_{11}C_9C_{10})$	16.2(3.9)
$(C_{11}C_9N_1)(C_{11}C_9C_{10})$	163.4(4.1)



ORTEP Drawing Of Nitrone 1



ORTEP Drawing Of 1/2 A Unit Cell Of Nitrone 1

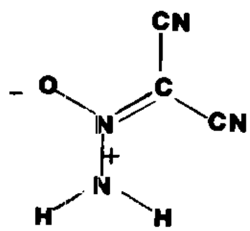
Showing Deviation From Planarity

CHAPTER V

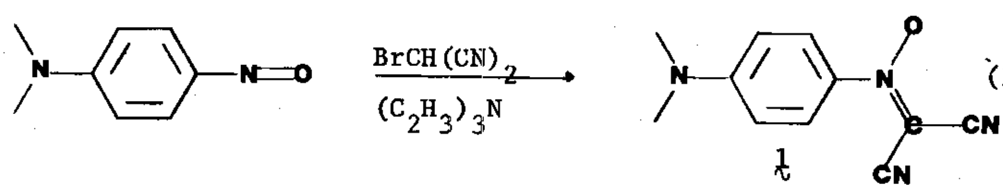
DISCUSSION OF RESULTS

α,α-Dicyano N-(p-dimethylaminophenyl)nitrone (1) was synthesized and characterized. Investigation of its thermal and photochemical reactions was performed. An x-ray structure of 1 was done and was found to agree with the geometry-energy optimized structure of a model compound (2) as calculated using MINDO/3.[14]

The synthesis of α,α-dicyano N-(p-dimethylaminophenyl)nitrone was accomplished by the reaction of equimolar amounts of bromomalononit-



2



(1)

rile with N,N-dimethyl-p-nitrosoaniline in the presence of triethylamine (eq. 1).

Nitrone **1** was characterized by its absorption in the infrared at 2225, 2210 (C≡N) and 1605 (C=N) and by its mass spectrum fragmentation pattern of M^{+} at 214 and M^{+} -O at 198.

Using an energy-geometry optimized SCF-MINDO/3 molecular orbital calculation, the potential energy minima structure of a model nitrone **2** was calculated. The large number of π electrons of **2** results in the highest occupied molecular orbital (HOMO) being antibonding and noded between N_2-O, C_3-N_5 and C_3-N_7 (Figure 1). Occupation of antibonding molecular orbitals with large contributions on the atoms of the C=N(O)-N system causes a pyramidalization of these atoms from electron-electron replusion terms, and consequently, deviation from planarity is particularly evident in **2** (Figure 2). The net atomic charge density at N_2 (+.865), O (-.591), and C_3 (-.285) indicates a considerable electron delocalization from oxygen onto the dicyanomethylene group. The lowest unoccupied molecular orbital (LUMO) of **2** places the additional node between N_2-C_3 with a large coefficient on oxygen (Figure 3). Two conclusions can be drawn from these calculations: first, deoxygenation of **2** would reduce the number of antibonding π electrons; and second, nucleophilic attack on oxygen should be facilitated by the large LUMO coefficient on oxygen.

The x-ray structure of **1** agrees favorably with the structure calculated for **2** (Figures 2 and 4). A comparison of bond lengths is shown in Table 4. Since **2** is a good model for **1**, the conclusions reached above should be valid for **1**.

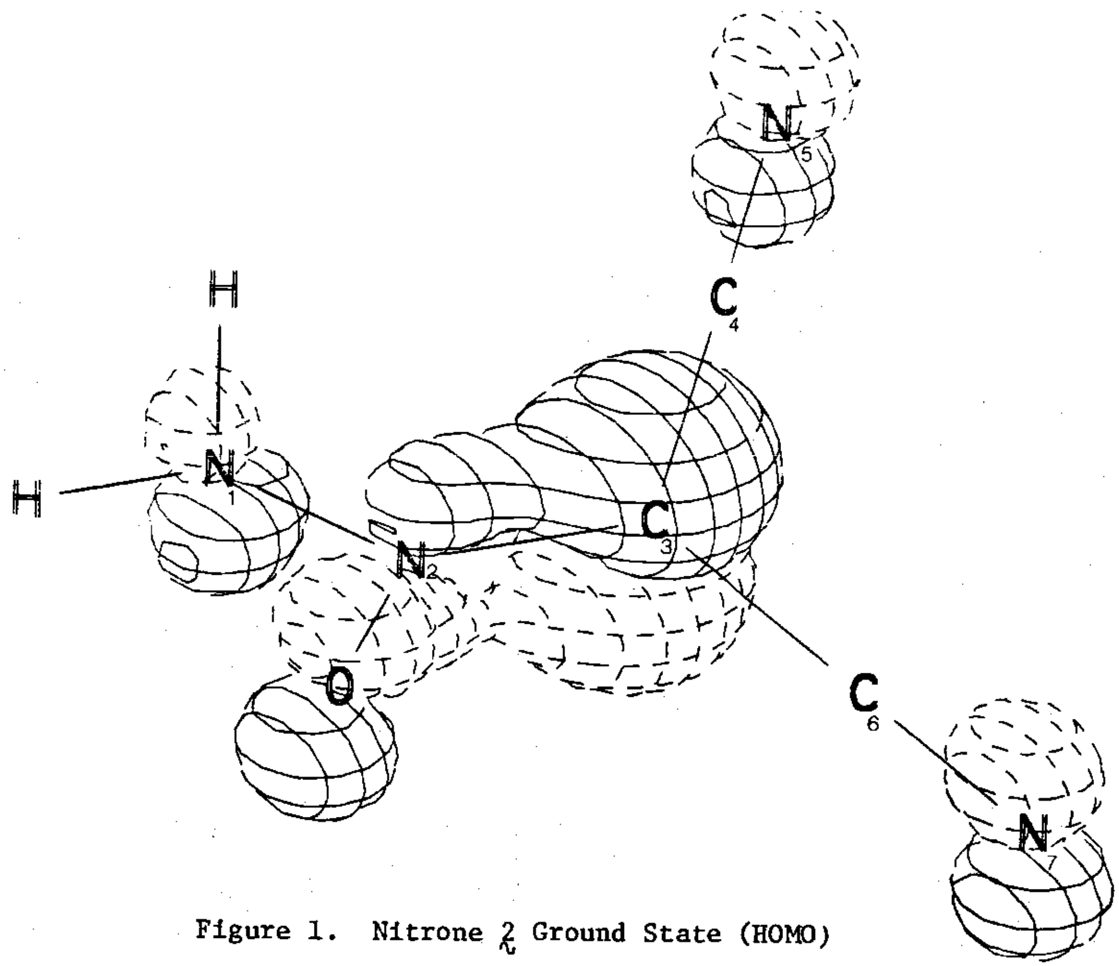


Figure 1. Nitrone 2 Ground State (HOMO)

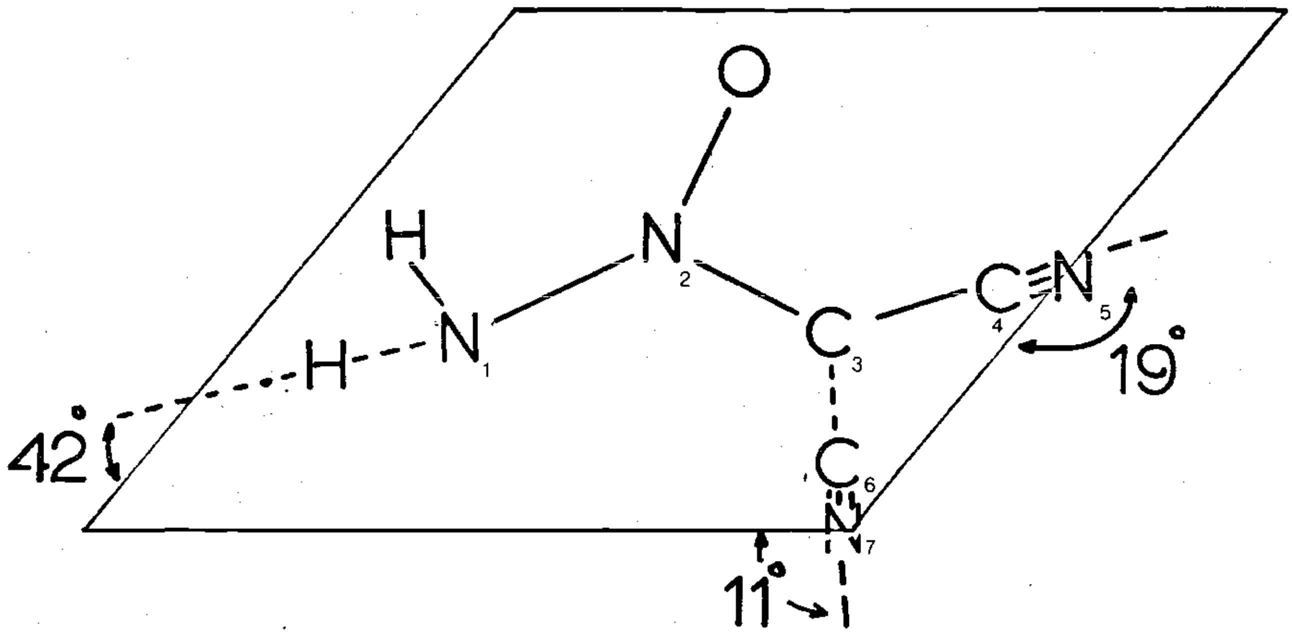


Figure 2. Deviation from Planarity of Nitrone 2

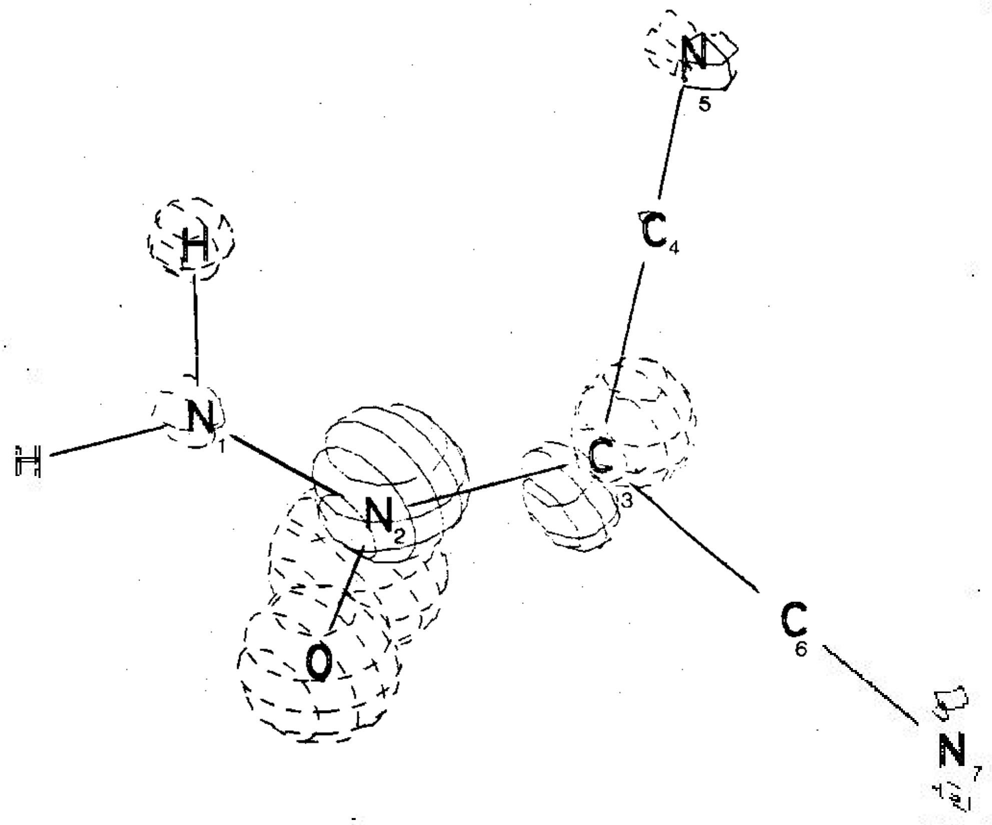


Figure 3. Nitrone 2 Ground State (LUMO)

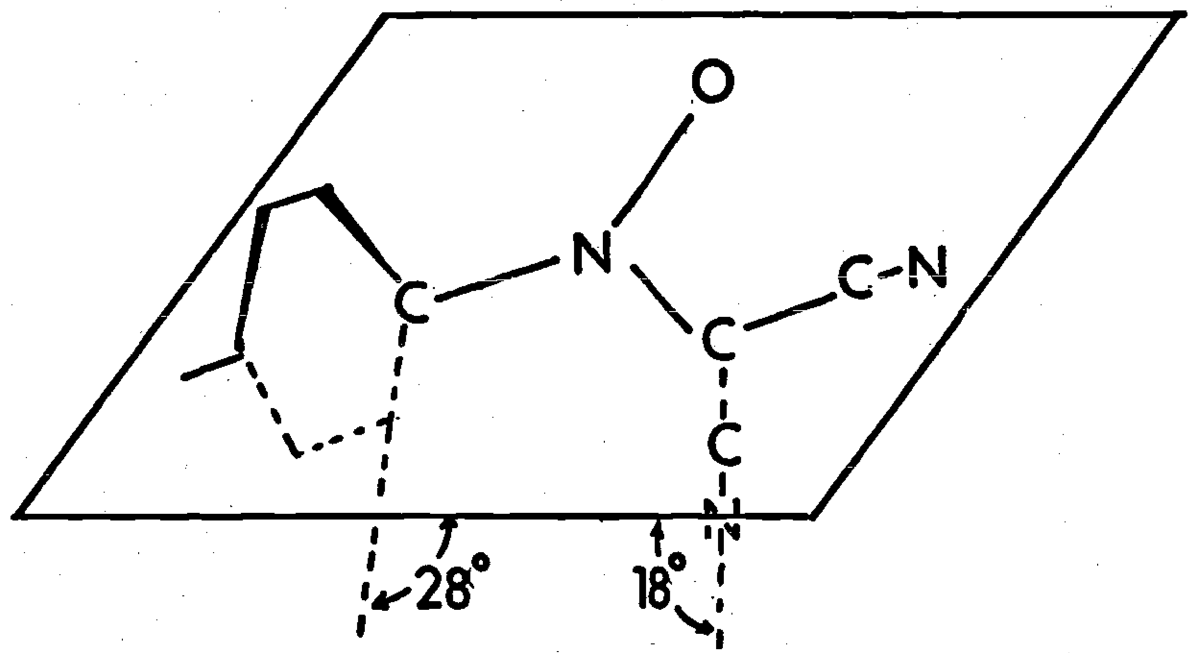
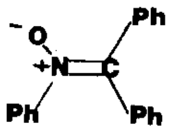
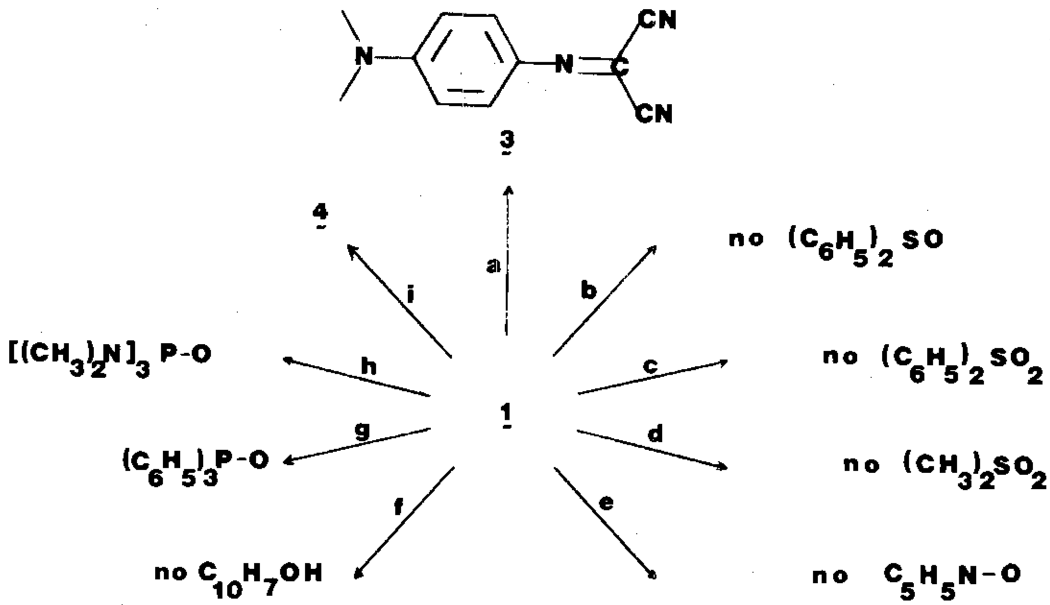


Figure 4. Deviation from Planarity of Nitrone 1

Table 4. Comparison Of N-O Bond Length

	Bond Distance (Å)
	1.30
1	1.266
2	1.240

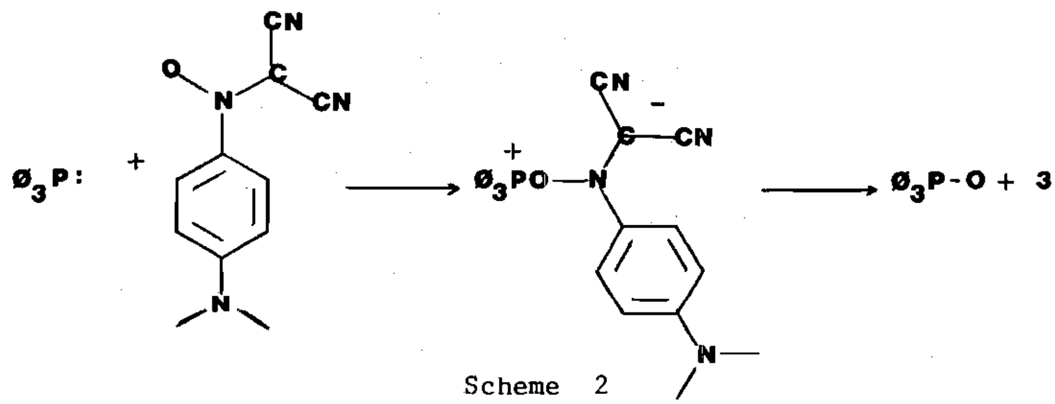


a) neat, 130°-200°; b) $(C_6H_5)_2S$, 150°; c) $(C_6H_5)SO$, 150°; d) $(CH_3)_2SO$, 150°; e) excess pyridine, 115°; f) excess naphthalene, 150°; g) 1 eq. $(C_6H_5)_3P$ in benzene, 80°; h) 1 eq. $[(CH_3)_2N]_3PO$ in $CHCl_3$, 25°; i) excess norbornylene, 95°

Scheme 1

Nitrone 1 decomposes to N,N-dimethyl-N′-(dicyanomethylene)-p-phenylenediamine (3) at its melting point (140°); thus the ability of 1 to transfer an oxygen atom thermally was investigated by the thermolysis of 1 with various potential substrates (Scheme 1).

Phosphine reagents react with 1 at temperatures below its decomposition temperature possibly by the mechanism shown in Scheme 2. Thermolysis of 1 in the presence of sulfides, sulfoxides, amines and aromatic hydrocarbons resulted in the formation of 3 without the formation of the respective sulfoxide, sulfone, amine-N-oxide, or



Scheme 2

Table 5. Kinetics Of Nitrone 1 Decomposition In Dimethylsulfoxide

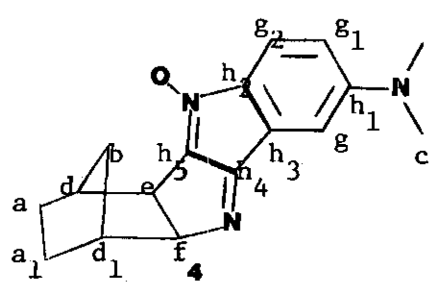
C(M)	T(C^o)	k(min^{-1})
0.075	150	0.008
0.280	150	0.009

naphthol. The possibility of a mechanism shown in equation 2 was investigated and the reaction kinetics were determined in dimethyl

$$1 \longrightarrow 1/2\ O_2 + 3 \qquad (2)$$

sulfoxide at 150° and found to be first order in nitrone 1 (Table 5). No oxygen was detected in the decomposition of 1 with an alkaline solution of pyrogallol. The above efforts proved fruitless in determining the mechanism and other final products in the decomposition of 1.

The reaction of 1 with an olefin could potentially produce an epoxide or a cycloadduct. An excess of norbornylene was reacted with 1 at 95°, and the elemental analysis of the product showed that the reaction had yielded a cycloadduct which had eliminated one equivalent of hydrogen cyanide. The ir showed no OH, NH or C≡N absorptions; however, two distinct C=N bands were present (1632, 1604 cm^{-1}). The proton nmr showed only three aromatic protons with a splitting pattern consistent with a 1,2,4-trisubstituted aromatic ring (meta coupling J = 9Hz, ortho coupling J = 3Hz, para coupling J = 0Hz).[15] Two broad doublets at δ 3.20 and 4.70 (J = 7Hz) were consistent with two axial protons on the norbornylene ring system, and the bridgehead protons appear as a broad singlet at δ 2.60 while the methylene protons appear as a complex multiplet (δ 1.25-1.60). The methyl protons appear as a singlet at δ 3.00. The Carbon-13 nmr (Table 6) contains three triplets, one quartet, seven doublets and five singlets and is consistent with tentative structure 4: a mechanism which explains the formation of this adduct is shown in Scheme 3.

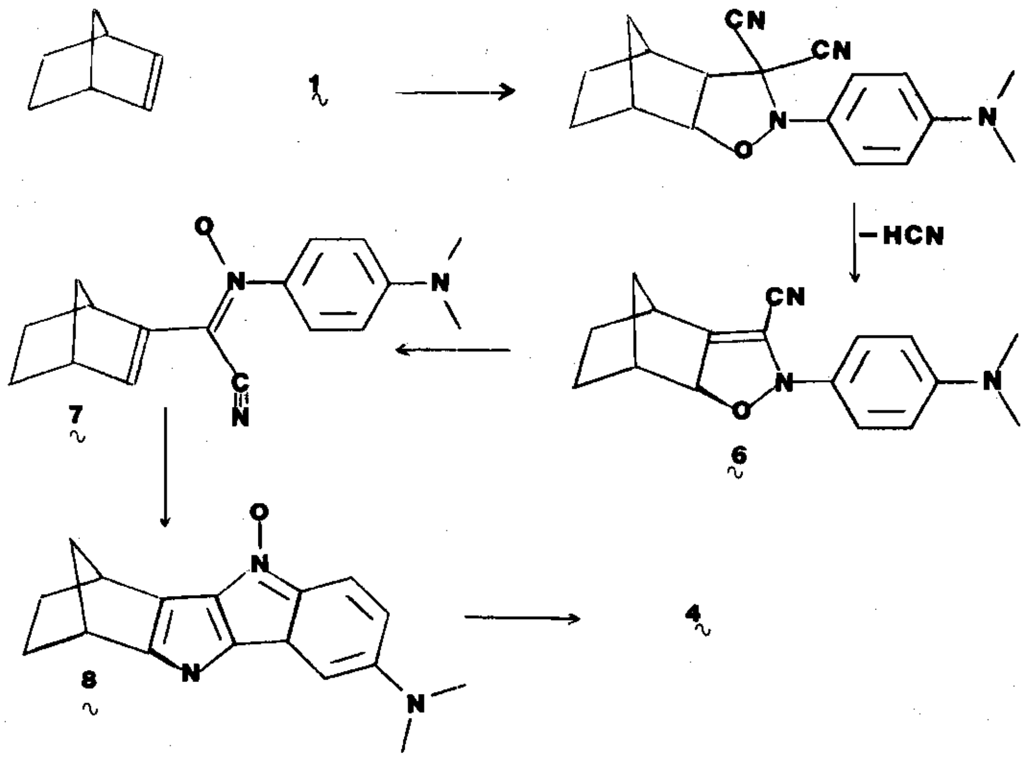


4

Table 6. Carbon 13 nmr Of 4

Proton	PPM
a	23.24 (t)
a_1	27.79 (t)
b	32.22 (t)
c	40.16 (q)
d	41.68 (d)
d_1	41.92 (d)
e	49.51 (d)
f	86.40 (d)
g	105.32 (d)
g_1	113.82 (d)
g_2	128.02 (d)
h_1	131.96 (s)
h_2	141.73 (s)
h_3	145.06 (s)
h_4	150.34 (s)
h_5	161.63 (s)

where two or more carbon cannot be assigned definitively subscripts are used.

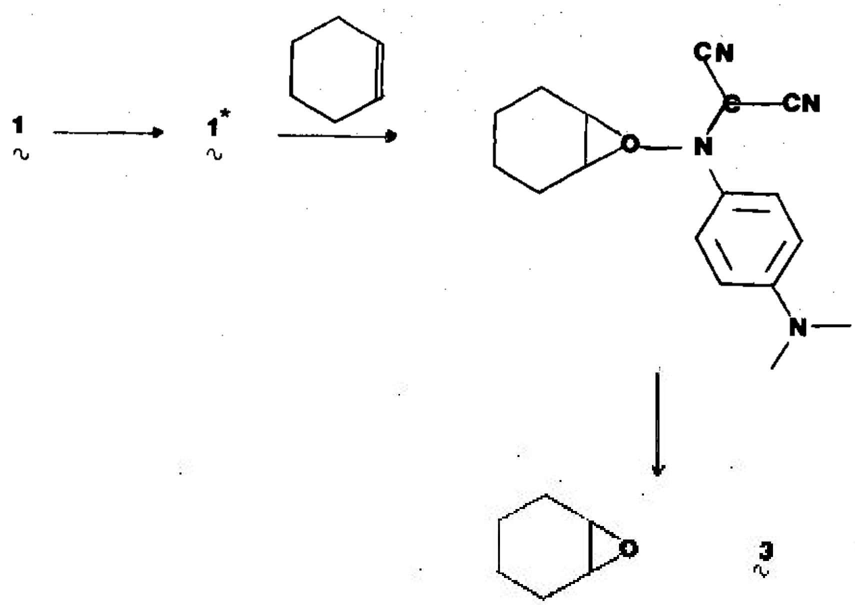


Scheme 3

Initial 1,3-dipolar addition to give intermediate 5 followed by loss of hydrogen cyanide yields intermediate 6. The loss of cyanide is promoted by the electron density on the adjacent nitrogen of the N,N-dimethylphenylenediamine system. An electrocyclic ring opening gives a new cyanovinylnitrone 7 whose cyclization to 8 followed by rearomatization affords the ultimate product 4.

The photolysis of nitrone 1 in THF lead via deoxygenation to imine 3. Photolysis in cyclohexene lead to a 10% yield of cyclohexene oxide, while photolysis in benzene lead inexplicably to no phenol.

The mechanism for the epoxidation is postulated to be photochemical 2 + 2 cyclo addition with subsequent elimination (eq. 3).



(3)

CONCLUSIONS

The thermal and photochemical deoxygenation reactions of nitrone **1** were investigated. Although **1** readily deoxygenated at its melting point, oxygen atom transfer to substrates was not observed. Photochemical deoxygenation of **1** in cyclohexene resulted in oxygen transfer to yield the corresponding epoxide in low yield.

An x-ray structure of **1** revealed a non-planar molecule with a shortened nitrogen-oxygen bond. Molecular orbital calculations were used to rationalize the structure and deoxygenation reactions of **1**.

The thermal reaction of **1** with norbornylene yielded a novel cycloadduct **4**, and a mechanism for the formation of **4** was postulated.

APPENDIX

Structure Factor Table for $\underline{\alpha}$,$\underline{\alpha}$-Dicyano $\underline{N}$-(p-dimethylaminophenyl)nitrone (1)

K	L	FO	FC
	H= -4		
0	0	6	9
0	2	14	16
0	4	9	12
0	14	6	2
1	0	12	13
1	7	8	7
1	9	6	3
1	14	6	2
2	0	9	10
2	4	5	2
2	12	7	7
2	14	5	5
3	0	7	7
3	8	11	9
3	10	5	3
3	12	6	6
4	2	5	3
4	6	5	1
4	8	6	7
4	9	5	0
4	10	7	8
4	11	5	1
5	9	8	6
6	4	6	1
6	6	8	7
6	9	6	7
	H= -3		
0	0	14	16
0	2	23	22
0	4	9	9
0	5	4	0
0	8	5	5
0	10	9	4
0	12	6	0
0	14	15	13
0	16	14	12
1	0	7	12
1	2	9	7
1	3	5	10
1	7	12	12
1	8	14	13
1	9	5	2
1	11	6	0
1	12	5	3
1	13	5	9
1	14	12	11
1	15	13	14
2	3	10	10
2	4	17	17
2	7	10	9
2	8	8	4
2	9	9	7
2	12	5	0
2	14	5	4
2	15	10	9
3	1	13	12
3	2	7	5
3	3	9	10
3	4	13	13
3	5	9	9
3	6	12	12
3	7	12	14
3	9	10	11
3	11	7	4
3	14	12	8
3	16	11	12
4	0	5	8
4	3	4	4
4	4	16	15
4	5	9	9
4	7	6	9
4	9	4	2
4	10	5	6
4	11	7	4
4	14	5	7
4	15	9	7
5	1	6	3
5	2	6	0
5	4	5	9
5	5	10	8
5	9	5	4
5	10	7	5
5	12	6	5
6	1	6	7
6	4	8	6
6	5	5	5
6	7	9	2
6	8	9	8
6	12	10	8
7	0	11	10
7	1	13	14
7	4	6	1
7	8	8	8
7	9	8	6
7	10	5	4
8	0	10	9
8	1	10	9
8	2	20	19
8	3	5	6
8	7	8	10
8	9	8	11
9	2	12	12
9	7	11	12
	H= -2		
0	0	24	26
0	2	47	49
0	3	4	0
0	4	16	14
0	6	10	2
0	6	34	33
0	10	54	55
0	12	7	4
0	14	5	9
0	15	5	0
0	16	7	18
1	0	7	4
1	2	5	7
1	3	19	23
1	4	13	12
1	5	11	13
1	6	7	4
1	8	17	16
1	9	15	11
1	10	30	30
1	11	19	16
1	12	8	7
1	13	4	0
1	14	6	8
1	15	6	7
2	1	28	32
2	2	9	10
2	3	7	12
2	4	26	28
2	5	10	7
2	6	14	13
2	7	11	4
2	8	5	3
2	9	37	38
2	10	27	26
2	11	8	7
2	12	26	30
2	13	10	1
3	0	9	7
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3	2	13	15
3	3	14	10
3	4	5	7
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3	6	11	14
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3	10	16	14
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3	15	8	4
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4	2	23	21
4	3	7	7
4	4	6	3
4	5	6	1
4	7	6	7
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4	11	20	20
4	12	12	10
4	13	9	16
4	15	9	8
4	17	5	10
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5	1	7	8
5	2	15	16
5	3	8	6
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6	7	14	13
6	9	8	12
6	11	9	8
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7	4	18	16
7	5	8	1
7	6	7	2
7	7	21	19
7	8	7	1
7	10	8	5
7	11	7	0
7	13	8	3
8	0	7	5
8	3	6	6
8	4	9	8
8	5	11	9
8	7	13	12
8	11	9	5
9	0	6	2
9	1	5	3
9	2	18	19
9	3	11	14
9	4	5	9
9	5	10	13
9	6	5	1
9	7	5	9
9	9	8	2
9	11	5	1
10	1	7	15
10	2	10	8
10	3	19	18
10	4	12	11

K	L	FO	FC
10	5	9	5
10	6	10	13

H= -1

K	L	FO	FC
0	0	49	56
0	4	16	14
0	6	70	65
0	8	10	9
0	10	21	23
0	12	5	7
0	14	10	9
0	16	5	12
1	0	4	0
1	1	9	16
1	2	8	14
1	3	46	55
1	4	107	114
1	5	143	149
1	7	46	41
1	8	32	31
1	11	10	14
1	12	7	2
1	13	12	12
1	14	7	11
1	17	5	15
1	18	7	7
2	0	35	34
2	2	22	23
2	3	18	19
2	4	53	56
2	5	6	0
2	6	33	32
2	7	4	0
2	8	17	16
2	10	9	13
2	11	15	11
2	14	7	5
2	15	5	2
2	16	6	4
3	0	7	3
3	1	7	5
3	2	32	38
3	3	7	10
3	4	9	10
3	5	15	10
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3	7	37	36
3	9	15	16
3	10	17	10
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4	5	10	13
4	7	29	30
4	8	20	21
4	9	6	8
4	10	9	4
4	12	8	10
4	14	11	12
5	1	5	2
5	2	15	14
5	3	7	12
5	4	9	13
5	5	19	20
5	6	15	16
5	9	23	27
5	10	12	3
5	11	5	3
5	12	5	10
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5	15	12	11
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6	9	10	13
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6	11	7	3
6	15	12	10
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7	4	21	22
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8	11	10	6
8	13	6	8
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9	9	9	12
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9	11	8	13
10	3	5	3
10	4	10	4
10	5	5	7
11	1	9	11
11	4	12	10

H= 0

K	L	FO	FC
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0	4	42	43
0	6	22	22
0	8	11	7
0	10	4	16
0	12	20	20
0	14	17	16
0	16	10	6
1	1	8	5
1	2	34	26
1	3	16	10
1	4	12	16
1	5	14	17
1	6	62	47
1	7	16	20
1	9	13	12
1	12	17	17
2	0	29	32
2	1	60	83
2	2	57	50
2	3	24	22
2	4	33	34
2	5	20	11
2	6	5	14
2	9	16	18
2	10	14	14
2	11	6	20
2	12	5	0
2	14	6	10
2	16	7	12
2	17	8	8
3	1	37	36
3	2	5	13
3	3	13	6
3	4	9	6
3	5	22	21
3	7	31	34
3	8	10	4
3	9	30	31
3	10	24	24
4	0	50	40
4	1	6	4
4	2	21	25
4	3	25	23
4	4	21	21
4	6	7	8
4	8	7	5
4	9	13	9
4	10	14	16
4	13	6	11
4	15	7	24
5	2	25	23
5	3	45	42
5	4	26	23
5	5	12	15
5	6	18	7
5	8	15	19
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8	11	11	13
9	3	9	1
9	4	6	8
9	5	13	9
9	6	24	24
9	7	7	6
9	8	21	19
9	9	11	6
9	10	7	2
10	0	10	8
10	1	6	9
10	2	6	3
10	3	6	0
10	5	6	1
10	7	9	11
10	8	7	10

K	L	FO	FC
11	2	8	6
11	5	8	11

H= 1

K	L	FO	FC
0	0	52	56
0	2	15	12
0	4	5	20
0	6	12	15
0	10	6	15
0	12	9	5
0	14	8	11
1	0	5	0
1	2	25	28
1	3	17	16
1	4	17	17
1	5	12	9
1	6	43	49
1	7	13	10
1	8	6	11
1	9	13	11
1	10	11	5
1	11	15	13
2	0	37	34
2	1	20	11
2	2	70	67
2	4	30	30
2	5	32	30
2	6	22	23
2	7	12	10
2	8	6	12
2	11	4	3
2	15	8	22
3	0	9	3
3	1	7	6
3	2	23	21
3	3	26	22
3	4	33	30
3	5	16	15
3	6	5	2
3	7	18	16
3	8	9	12
3	9	9	12
3	10	8	9
3	15	6	13
4	0	15	16
4	1	20	18
4	2	7	17
4	3	16	20
4	4	16	16
4	6	19	19
4	7	8	10
4	10	5	7
4	12	6	9
4	13	7	3
4	14	9	18
5	1	11	9
5	2	5	3
5	3	7	5
5	4	9	2
5	5	29	30
5	6	12	11
5	7	9	12
5	8	5	13
5	9	11	7
5	11	10	13
6	0	8	8
6	1	4	2
6	3	6	14
6	4	9	6
6	5	8	7
6	9	11	15
6	10	14	10
7	1	4	6
7	2	18	16
7	4	9	6
7	7	5	13
7	8	13	14
7	9	5	21
7	10	12	11
7	11	10	1
8	0	26	26
8	1	19	19
8	2	7	3
8	3	12	13
8	5	8	9
8	8	16	15
9	0	12	12
9	3	11	18
9	6	15	15
9	7	11	6
9	9	11	15
10	2	25	24
10	3	21	21
10	4	17	14
10	5	8	7
11	1	9	3
11	2	14	10

H= 2

K	L	FO	FC
0	0	26	26
0	2	15	20
0	3	4	0
0	4	11	12
0	5	7	0
0	6	18	19
0	10	5	0
0	12	6	10
1	0	7	4
1	1	33	29
1	2	17	18
1	3	6	10
1	5	11	10
1	6	9	1
1	8	13	11
1	9	9	13
1	10	9	11
1	11	16	19
1	12	6	8
2	1	17	17
2	2	45	35
2	3	7	18
2	4	20	19
2	7	7	8
2	8	9	8
2	10	6	12
2	11	9	6
3	0	9	7
3	1	6	2
3	2	6	16
3	3	5	0
3	7	7	10
3	8	16	13
3	9	10	10
3	10	10	22
3	12	11	19
4	0	31	30
4	1	14	15
4	2	5	7
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7	6	6	4
7	7	7	0
7	9	7	1
8	0	7	5
8	1	8	1
8	3	15	17
8	5	13	21
8	7	7	7
9	0	6	2
9	3	20	20
10	1	7	7
10	2	15	11

H= 3

K	L	FO	FC
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0	2	8	10
0	4	17	17
0	6	28	27
1	0	5	12
1	1	5	1
1	3	9	8
1	4	7	6
1	5	5	10
1	6	13	9
1	9	10	12
2	2	7	3
2	4	10	6
2	5	18	21
2	6	10	9
2	7	8	5
2	8	10	14
3	1	4	3
3	2	10	10
3	3	4	0
3	5	6	9
3	7	18	18
4	7	10	11
5	4	9	4
5	5	6	0
6	1	5	5
6	2	9	2
6	4	5	1
6	5	6	3
7	0	10	10
8	0	10	9
8	1	5	6

H= 4

K	L	FO	FC
0	4	9	3
1	0	14	13
1	1	18	18
1	2	6	5
2	0	10	10
2	2	17	19
3	0	7	7
3	2	11	7
3	3	6	5
4	1	6	10
4	3	8	9
5	0	6	4

H= -5

K	L	FO	FC
0	4	13	14
1	6	6	6
2	3	8	6
3	0	7	1

K	L	FO	FC
3	2	7	6
3	3	9	7
4	2	5	1
4	6	6	2
	H=	-4	
5	14	5	2
7	6	10	6
7	7	6	2
7	12	6	3
7	13	6	2
9	5	8	6
8	6	6	6
8	7	7	5
9	9	6	1
	H=	-3	
3	17	10	13
5	16	7	6
6	15	6	7
6	17	6	2
8	12	6	6
8	14	7	2
9	8	15	11
9	10	7	6
9	11	9	11
10	1	5	1
	H=	-2	
4	19	7	12
5	18	6	2
5	19	6	6
6	18	7	13
8	14	5	7
11	1	11	12
11	3	7	2
11	4	7	4
12	1	9	4
	H=	-1	
1	19	6	16
6	17	9	7
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7	16	8	2
8	14	8	3
9	12	7	2
10	10	12	12
10	11	7	4
10	12	8	12
10	13	11	7
11	9	7	0
11	10	6	1
12	0	7	5
12	1	10	11
12	3	6	16
	H=	0	
4	16	6	8
6	15	10	7
6	16	6	3
7	15	11	12
8	13	6	14
8	14	8	1
9	13	7	7
11	7	18	17
11	8	6	0
11	9	12	10
11	10	6	0
12	1	11	7
	H=	1	
0	16	6	9
2	16	13	15
2	17	7	1
7	13	6	10
8	11	6	1
8	13	6	1
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10	10	6	9
11	4	7	14
11	7	7	6
11	8	7	2
12	0	6	5
12	4	8	2
	H=	2	
0	14	8	24
3	13	15	9
5	12	6	3
5	13	8	10
6	13	6	2
7	11	6	8
10	3	6	10
	H=	3	
2	10	6	6
6	7	6	4
8	4	9	3
	H=	4	
6	2	6	3

K	L	FO	FC	K	L	FO	FC

REFERENCES AND NOTES

1. J. Hamer and A. Macaluso, Chem. Rev., 64, 473 (1964).

2. G. G. Spence, E. C. Taylor and O. Buchart, Chem. Rev., 70, 231 (1970).

3. W. Rundel, "Methoden zur Herstellung und Umwandlung von Nitronen," Methoden der Organischer Chemie, Eugen Muller, ed., (Georg ThiemVerlag, Stuttgart, 1968) vol. 10, 315.

4. D. R. Boyd, et. al., Tetrahedron Letts., 457 (1970).

5. M. Calvin and Alkaitis, Chem. Commun., 979 (1967).

6. L. Horner and E. Jurgens, Chem. Ber., 90, 2184 (1957).

7. W. D. Emmons, J. Amer. Chem. Soc., 79, 5739 (1956).

8. W. D. Emmons, J. Amer. Chem. Soc., 78, 6208 (1956).

9. D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, New York, 1966.

10. Sachs, Chem. Ber., 33, 963 (1899).

11. Gas-liquid chromatography comparison with authentic samples, under conditions which would allow detection of products in yields corresponding to five per cent conversion.

12. Identified by infrared spectral comparison with an authentic sample and mixed melting point where applicable.

13. Programs used were: R. Dewar and A. Stone's FAME; P. Main and M. Woolfson's MULTAN light atom program; Zalkin's FORDAP fourier summation program; Iber's NUCLS modification of K. O. Martin, W. R. Busing and H. A. Levy's least squares program; FINDH a locally written geometric prediction progrm which calculates atomic positions based on expected bond length, hybridization and position of other bonded atoms; and various other locally available programs.

14. M. J. S. Dewar, R. C. Bingham, and D. H. Lu, J. Amer. Chem. Soc., 97, 1285 (1975).

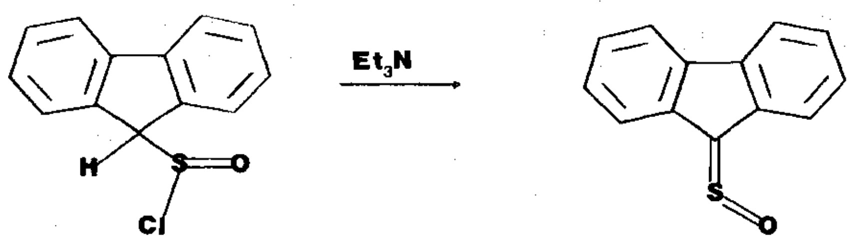
15. J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, New York, 1965, p. 99.

II. THE SYNTHESIS AND STABILITY OF CUMULENES DERIVED FROM DI-_t_-BUTYL THIOKETONE

CHAPTER I

INTRODUCTION

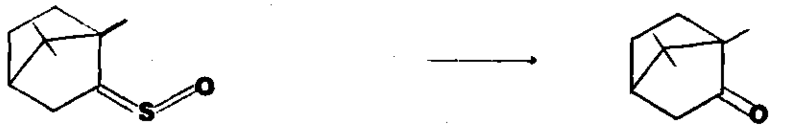
Sulfines, thione S-imides, and thione S-methylides are of great interest to both the experimental and theoretical chemist. Representative members of all three classes of compounds have been synthesized and studied.



(1)

(2)

Sulfines have been prepared by the dehydrohalogenation of sulfinyl chlorides (eq 1);[1,2] however, the peracid oxidation of monomeric thioketones is the most general synthesis of sulfines (eq 2).[3,4] Thermolysis of sulfines has been reported to yield predominantly the corresponding carbonyl compound and sulfur (eq 3);[5] however, products derived from a sulfine dimer have also been reported (eq 4 and 5).[6,7]



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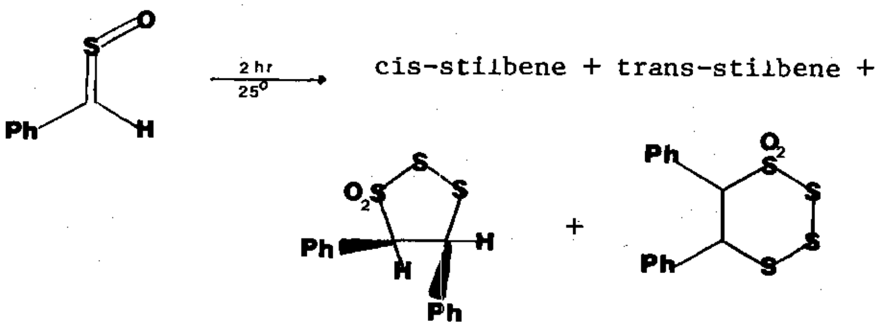

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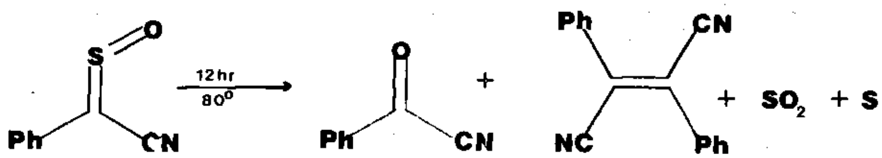
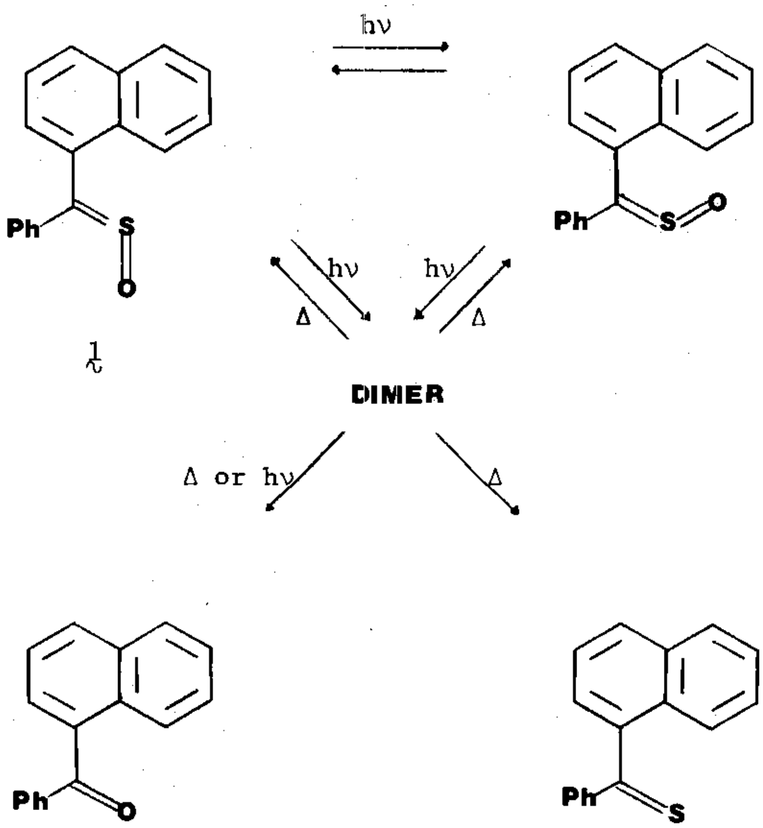


(5)

Oxathiiranes have been proposed as intermediates in the above desulfurization reactions, and Synder has reported that desulfurization of the intermediate oxathiirane is acid catalyzed. However, no mechanism has been presented for the formation of dimer-derived products.[8]

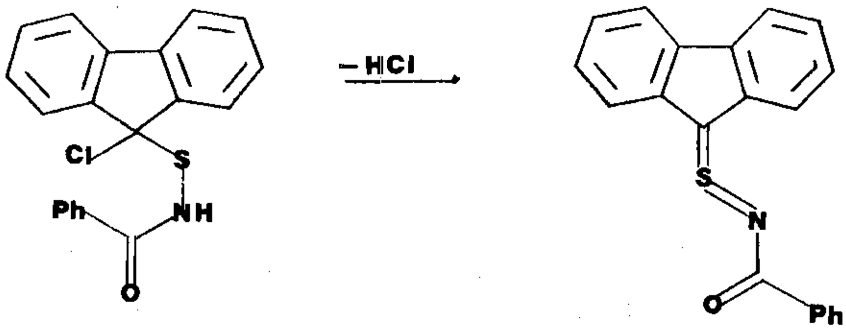
The course of photolysis of sulfines is analogous to the thermolysis reaction in both products produced and postulated intermediates.[9] Schessinger and Schutz[10] reported that the photolysis of sulfine 1 proceeded through a photodimer (Scheme 1); however, they concluded that at high dilution (1.4×10^{-3} M) photodesulfurization



Scheme 1

occurs by a unimolecular process via an oxathiirane.

Thione S-imides have been synthesized by the dehydrohalogenation of α-chloromethanesulfenamides (eq 6),[11] and by the condensation of chloramine-T with thioureas (eq 7),[12] 1,2-dithiole-3-thiones[13] or dithiobenzoates.[14] Thiaziridines have been proposed as intermediates in the desulfurization of thione S-imides upon heating to their melting points.[12,13] Zwanenburg reported that thione S-imide 2



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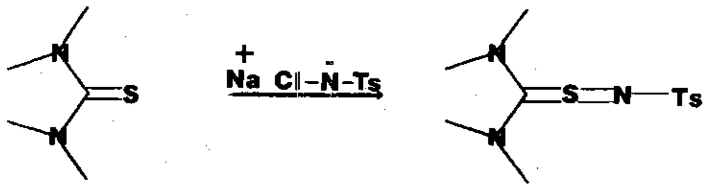

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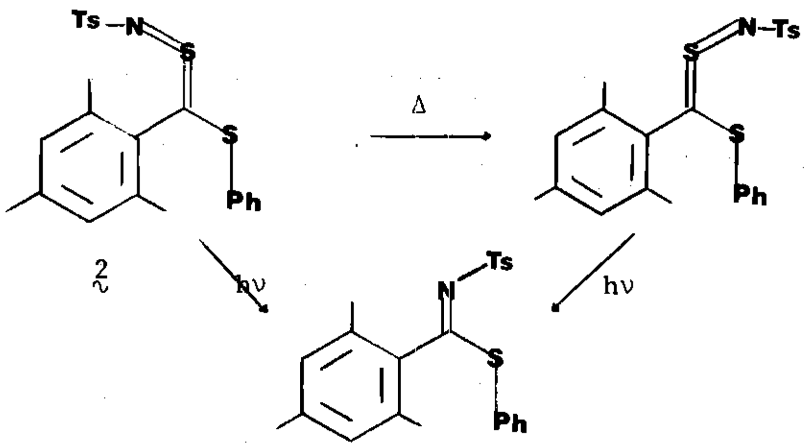
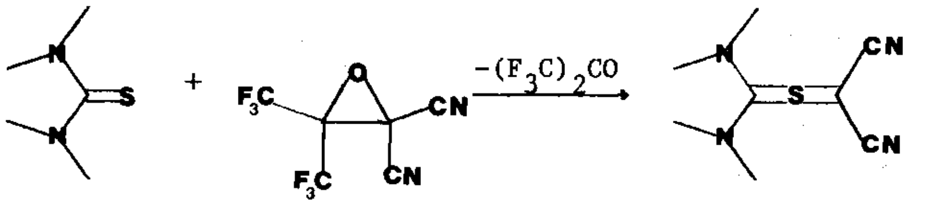


(8)

undergoes isomerization thermally but desulfurizes photochemically (eq 8).[14]

Thione S-methylides have been synthesized by a number of routes. Middleton synthesized ylide 4 by the reaction of α,α-bis(trifluoromethyl)-β,β-dicyanooxirane with tetramethylthiourea (eq 9).[15]



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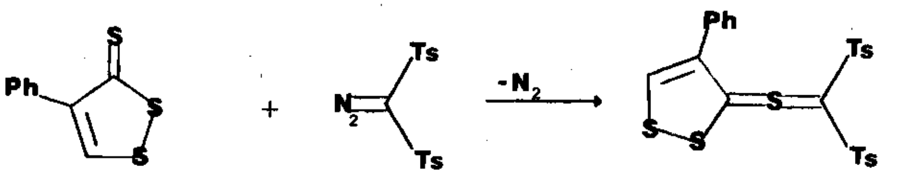
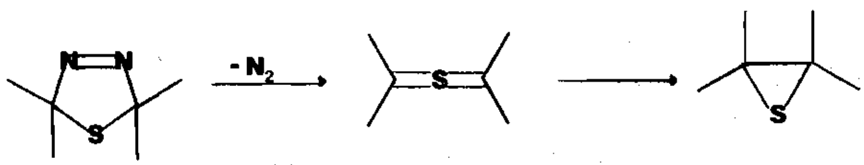


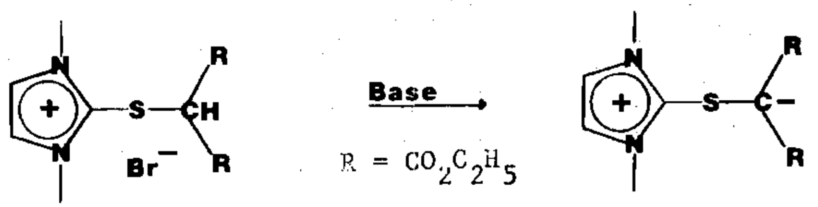
5 (10)

Oae synthesized ylide 5 by the reaction of ditosyl diazomethane with 4-phenyl-1,2-dithiole-3-thione (eq 10),[13] and Kellogg has reported a detailed study of substituted unperturbed thione S-methylides formed by the loss of nitrogen from dihydrothiadiazoles (eq 11).[16]



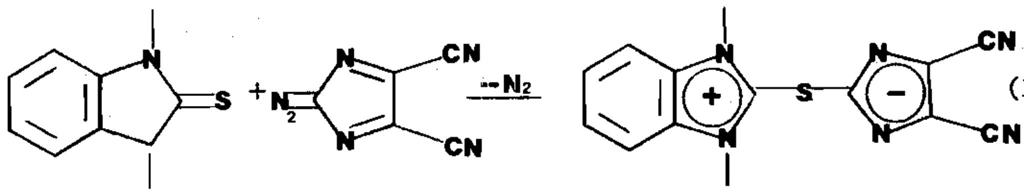
(11)

More recently, Burgess has reported the synthesis of highly perturbed ylides by the dehydrohalogenation of thiouronium salts (eq 12,)[17] and



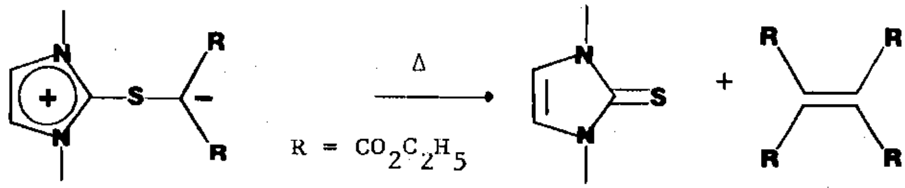
(12)

Hartke has reported the synthesis of highly stabilized ylides from 2-diazo-4,5-dicyano-2H-imidazole and thioureas (eq 13).[18]



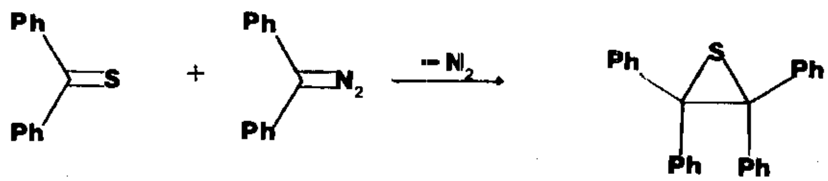
(13)

Unperturbed thione S-methylides electrocyclize by conrotatory closure to thiiranes (eq 11)[16] which can be desulfurized to yield olefins,[19,20] while highly perturbed ylides decompose to tetrasubstituted olefins and thioureas (eq 14).[17]



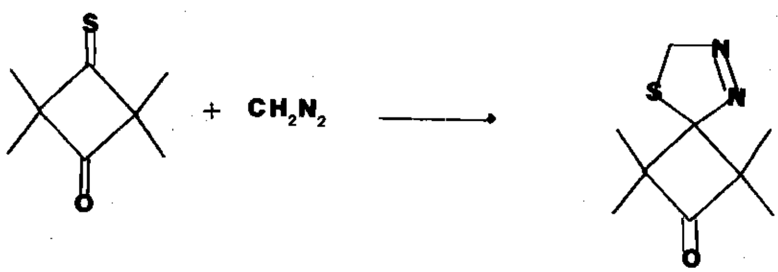
(14)

Previous work has shown that the usual products from the reaction of thiones with diazo compounds are thiadiazolidines, thione S-methylides, or thiiranes, while dithiolanes, lactones and olefins have been observed in a few cases. The diversity of products is dependent upon both the steric bulk of the thione substitutents and the electronic character of the diazo compound. Unhindered thiones react with diazo compounds to give thiiranes (eq 15),[21,22,23] while



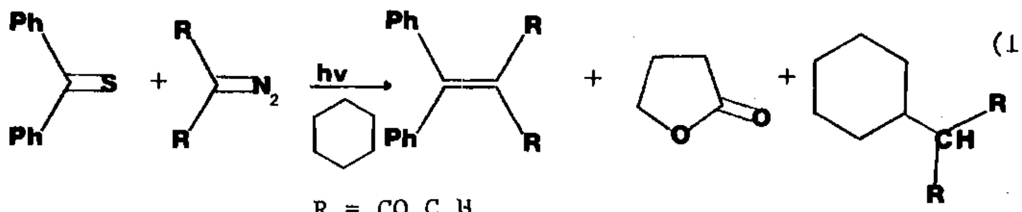
(15)

hindered thiones give thiadiazolidines (eq 16).[22,24]



(16)

Thioureas react with electrophilic diazo compounds to give thione S-methylides (eq 13)[18] and the photolysis of diethyl diazomalonate and thiobenzophenone in cyclohexane yields and olefin and δ-butyrolactone (eq 17)[25] via an unknown mechanism.



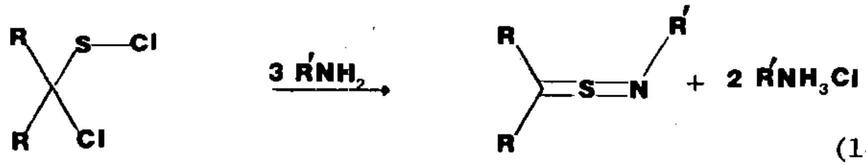
(17)

R = $CO_2C_2H_5$

Thione S-methylides have been reported to cyclize to stable thiiranes which can be subsequently desulfurized while sulfines and thione S-imides yield unstable oxathiiranes and thiaziridines respectively, which desulfurize spontaneously to ketones or imines. For example, 1,1-diphenyloxathiirane has been observed spectroscopically (λ max 390 nm (ε 200)) at -213° and decomposes thermally at -158° to give a quantitative yield of benzophenone.[9]

The use of bulky substituents to stabilize small rings is well documented[26] and this method could be used to stabilize oxathiiranes and thiaziridines. Consequently, di-t-butylthioketone whose synthesis and oxidation to the corresponding sulfine has been reported was chosen as a starting material.[19,27,28]

Prior to 1973 no general synthesis of thione S-imides had been developed;[12] therefore, one of the goals of this research was to develop a more generally applicable synthesis. The reaction of α-chlorosulfenyl chlorides with primary amines should yield thione S-imides via SN_2 displacement at sulfur followed by *in situ* dehydrohalogenation (eq 18). This process is analogous to the base promoted hydrolysis of α-chlorosulfenyl chlorides to sulfines (eq 19).[29] The desired α-chlorosulfenyl chloride should be obtained from the reaction of di-*t*-butylthione with chlorine (eq 20).



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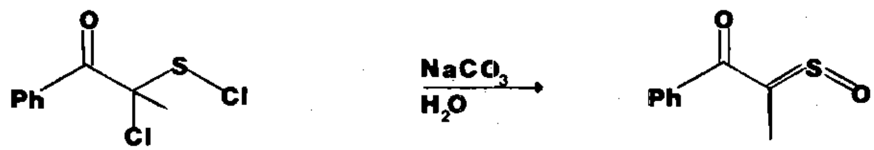
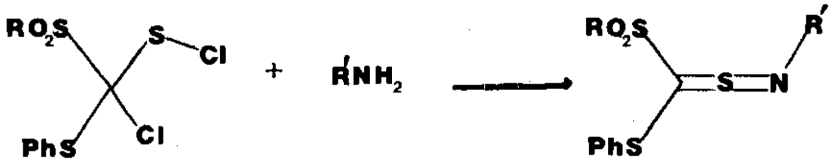


(19)

(20)

While the research described herein was in progress, there appeared two reports of the successful synthesis of thione S-imides using this scheme.[30,31] t-Butylamine was used in these two conversions and the α-chlorosulfenyl chloride carbon was substituted with electron withdrawing substituents (eq 21 and eq 22).



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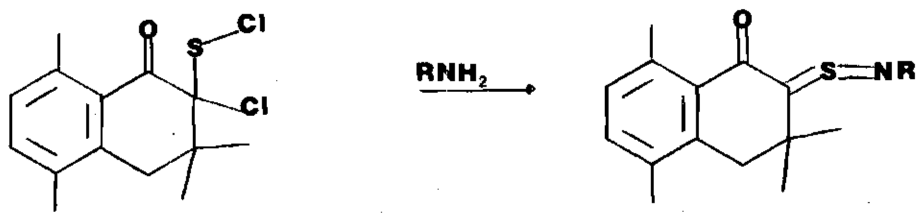
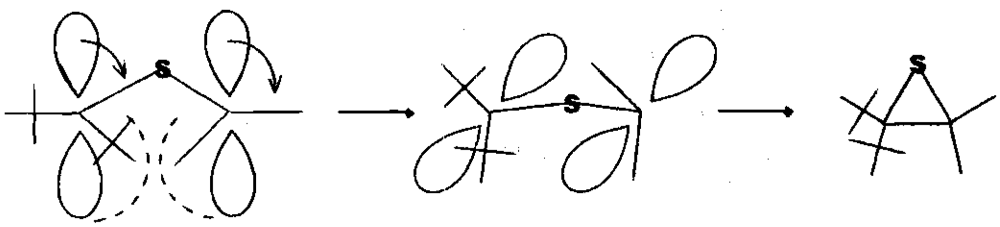


(22)

Ring closure of a thione S-imide should proceed most readily in the absences of such electronic perturbation as exemplified by the facile cyclization of unperturbed thione S-methylides to thiiranes.[16] Therefore, thione S-imides derived from di-t-butylthioketone should cyclize readily to thiaziridines.



Scheme 2

The reaction of di-t-butylthioketone with diazo compounds should yield thione S-methylides after the loss of nitrogen. Since the closure to a thiirane is predicted to be conrotatory, the closure would be sensitive to the developing steric interactions which would diminish the rate of ring closure (Scheme 2)[16] and result in a longer lifetime for the ylide.

The cyclization of an unperturbed sulfine has been calculated by Synder to be exothermic by 72 kcal/mole while the cyclization of an unperturbed thione S-methylide has been calculated to be exothermic by only 49 kcal/mole.[8] No calculations on the closure of a thione S-imide have been reported prior to this work; but, it can be expected that the ring closure will also be exothermic. Thus, it was the goal of this research to investigate the thermolysis and photolysis of di-t-butylsulfine, the synthesis of unperturbed thione S-imides, and the products derived from the reaction of di-t-butylthioketone with diazo compounds.

CHAPTER II

INSTRUMENTATION AND EQUIPMENT

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Hexane and pentane were washed with concentrated sulfuric acid, distilled and then redistilled from sodium metal. Methylene chloride was fractionally distilled and stored over 4Å molecular sieves. Anhydrous ether was purchased commercially in one pound cans and used without further purification. Acetonitrile, methanol and ehtanol were distilled from calcium hydride. Purification of all other organic reagents were achieved using established procedures.[43]

Anhydrous reaction conditions were established by drying the necessary glassware in an oven maintained at 150°. An inert atmosphere was provided by purified argon which had been dried by passing through a coiled glass the immersed in a dry ice-isopropanol bath.

Concentration or evaporation of solvents was performed under reduced pressure (ca. 20 mm Hg) using a Buchi rotary evaporator. Thin layer chromatography was performed using Eastman Chromagram sheets. Column chromatographies were performed using Silica gel (80-100 mesh) or Florosil (80-100 mesh) as indicated.

Whenever two solvents were indicated for a column chromatography, a general procedure was employed. The column was loaded with a 30:1 ratio of adsorbent to substrate using the adsorbent indicated in each case. The substrate was eluted with 2-5 column volumes of hexane followed by 5 column volumes of 90% hexane: 10% methylene chloride. Successive lots of 5 column volumes were eluted using 80/20, 60/40, 40/60, 20/80, and 100/0 ratios of hexane to methylene chloride. The elutant was analyzed by TLC and column volumes of equivalent composition were combined for further work-up. Proton nuclear magnetic resonance spectra (nmr) were recorded on a Varian Associates Model T-60A spectrometer in the solvent specified in each case. Variable temperature proton nmr spectra were recorded at the temperature indicated on a Varian Associates Model A-60 equipped with a variable temperature probe. Chemical shifts were reported versus an internal tetramethylsilane (TMS) standard and the abbreviations s, d, t, q and m refer to singlet, doublet, triplet, quartet, and multiplet, respectively. Carbon-13 nmr were obtained on a JOEL Model PFT-100 Fourier transform nmr spectrometer and the chemical shifts were reported versus a TMS standard in the same manner as proton nmr. Infrared spectra were obtained on a Perkin-Elmer Model 457 recording spectrophotometer using 0.1 mm sodium chloride cells in the solvent indicated in each case. Ultraviolet and visible spectra were recorded on a Cary-14 spectrophotometer using one centimeter balanced quartz cells. Gas-liquid chromatography separations were performed on a Hewlett-Packard Model 402 high efficiency gas chromatograph using either 6 ft 10% SE-30, 6 ft 5% Carbowax 20 M, 10 ft 10% QF1 or 30 ft 10% TCEP columns. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-7L high resolution mass spectrometer or a Varian Associates

Model M-66 medium resolution mass spectrometer. Osmotic molecular weights were determined on a Mechrolab vapor pressure osmometer Model 301A at 37° and in each the solvent is specified. Melting points were determined on a Thomas Hoover capillary melting point apparatus. Melting points are reported in degrees centigrade and are uncorrected.

Thermolyses were performed at the specified temperature using an oil bath, and the temperature was maintained (±2°) using an I^2R Thermo-Watch controller. The progress of each thermolysis reaction was monitored using proton nmr spectrometer and the percentage of each constitutent was determined by peak integration of the spectra.

Data for the x-ray structure was collected on a Syntex $P2_1$ four circle diffractometer. For the solution and refinement of the structure, computations were performed using standard programs[41] and were carried out with a CDC 6600-6800 computer.

Geometry-optimized molecular orbital calculations were performed using a MINDO/3 program,[42] and the computations were carried out on a CDC 6600-6800 computer.

Elemental analyses (C, H, N, S and Cl) were performed by Atlantic Microlab, Inc., Atlanta, Georgia.

CHAPTER III

EXPERIMENTAL

Di-t-Butylthioketone

A 1.09 M t-butyllithium solution (250 ml, 0.27 mol) in hexane was added dropwise over a 2 hr period to a solution of 23 g of pivalonitrile (0.28 mol) in 300 ml dry hexane maintained at -65° under an inert atmosphere. After the addition was complete the reaction was allowed to warm to room temperature and stirred overnight. The reaction mixture was cooled to -30° and 30.8 g (0.27 mol) of tetramethylethylenediamine were added rapidly. The reaction was stirred for 15 min and 76 g (1.0 mol) of carbon disulfide were added dropwise over a 1 hr period. After the addition was complete, the reaction was allowed to warm to room temperature and stirred overnight. The reaction was extracted with 6x100 ml water; the organic phase was dried and fractionally distilled to give 41 g (92%) di-t-butylthioketone: bp 67-70° (18 mm) (lit.[19] bp 61° at 14 mm); carbon-13 nmr ($CDCl_3$) δ 32.70, 53.15, 276.05.

Di-t-Butylsulfine (**8**)

Di-t-butylsulfine was prepared by the procedure of Barton:[19] mp 43-44, (lit. mp 42-45), carbon-13 nmr ($CDCl_3$) δ 29.18, 30.40, 39.92, 43.02, 214.41; UV max (hexane) 264 nm (ε 7390).

2,2,4,4-(Tetramethyl)Pentane-3-Chloro-3-Sulfenyl Chloride (10)

Chlorine gas was bubbled into a solution of 7.9 g di-t-butylthione (.05 mol) in 150 ml dry methylene chloride maintained at 0° under an inert atmosphere. The addition was stopped when all the thione was decolorized. After the addition was complete the reaction was allowed to warm to 25° while being purged with argon. The reaction was concentrated with a rotary evaporator under a reduced pressure to give 11.5 g (100%) of crude product which was sublimed at 40° (0.2 mm) to give 10.9 g (95%) of pure 10: mp 125-130°; proton nmr ($CDCl_3$) δ 1.40 (s); carbon-13 nmr ($CDCl_3$) δ 30.58, 46.96, 100.53; ir (CH_2Cl_2) 2965, 1480, 1395, 1375, 1200; UV max (hexane) 305 nm (ε 82), 220 (516); mass spectrum (70 ev) m/e (rel intensity) 158 (56), 101 (100), 67 (29), 57 (69).

Anal. Calculated for $C_9H_{18}SCl_2$: C, 47.16; H, 7.91; S, 13.99; Cl, 30.94. Found: C, 47.07; H, 7.90; S, 13.92; Cl, 30.86.

Kinetics of the Thermal Decomposition of Sulfine 8

The kinetics of the decomposition of sulfine 8 determined at 150° and 210° in diphenylmethane were monitored by proton nmr spectroscopy through the first half-life of the reaction. The results are shown in Appendix II and summarized in Table 5. The effect of several nucleophiles were also studied; these reaction were monitored for the first 25% of the reaction because of their extremely long half-lives.

The decomposition of sulfine 8 in the presence of tetramethlthiourea-S-p-toluenesulfonimide was accomplished as follows: 63 mg

(0.19 mmol) tetramethylthiourea-S-p-toluenesulfonimide and 34 mg (0.20 mmol) sulfine 8 were dissolved in .5 ml of diphenylmethane and thermolyzed at 210° to give a 3:1 ratio of thioketone to ketone. Tetramethylthiourea-S-p-toluenesulfonimdie decomposed at 210° with a half-life of <<5 sec. A control experiment also confirmed that N-[bis-(dimethylamino)]-methylene-p-toluenesulfonamide did not catalyze the decomposition of sulfine 8.

Thermolysis of Sulfine 8 at 125 and 180°

Two nmr tubes containing 35 mg (.2 mmol) sulfine 8 each in 0.5 ml of diphenylmethane were thermolyzed independently at 125° and 180° and the product ratio determined by proton nmr spectroscopy after the first half-life. The product ratios were: temperature (thioketone/ketone), 125° (8/99.2), 180° (38/62).

Attempt to React Sulfine 8 with TCNQ

TCNQ (1.0 g, 5 mmol) was added in one portion to a stirred solution of .9 g (5 mmol) sulfine 8 in 30 ml methylene chloride maintained at 25°. The reaction mixture was allowed to stand for two weeks. The reaction mixture was evaporated to dryness. Proton nmr analysis of the crude reaction showed that no reaction had occurred.

Photolytic Decomposition of Sulfine 8

A solution of 22 mg 8 (0.1 mmol) in deuterochloroform maintained at -78° was irradiated through pyrex with a high pressure Hg-discharge Hanovia lamp. After warming to room temperature, nmr and ir analysis indicated the presence of only di-t-butylketone. Control experiments confirmed that di-t-butylthioketone was stable under the reaction conditions.

Attempt to Generate Di-t-Butylsulfene

A solution of 20 mg m-chloroperbenzoic acid (0.11 mmol) in 1 ml chloroform was added to a solution of 17 mg of **8** (0.1 mmol) in 1 ml chloroform maintained at 25°. After 15 min. nmr analysis showed only the presence of di-t-butylketone.

Di-t-Butyl N-Tosylimine

Chlorosulfenyl chloride **10** (.75 g, 3.3 mmol) and 2.0 g sodium tosylamide (10.3 mmol) were combined with 30 ml of dry acetonitrile. The reaction was stirred at 27° for 12 hr under an inert atmosphere. The reaction was filtered and solvent removed by a rotary evaporator under reduced pressure. Repeated crystallization from ether yielded 0.35 g (39%) di-t-butyl N-tosylimine: mp 93-95°; proton nmr ($CDCl_3$) δ 1.37 (s, 18H), 2.41 (s, 3H), 7.50 (dd, 4H); ir (CCl_4) 1595, 1305, 1295, 1140, 1090 cm^{-1}, UV max (hexane) 304 nm (ε 619), 260 (1290), 230 (4140); mass spectrum (70 eV) m/e (rel intensity) 238 (15), 155 (100), 91 (68); carbon-13 nmr ($CDCl_3$) δ 21.36, 29.85, 45.20, 125.83, 128.44, 141.48, 197.61.

Anal. Calculated for $C_{16}H_{25}SNO_2$: C, 65.04; H, 8.53; S, 10.85; N, 4.74. Found: C, 65.10; H, 8.39; S, 10.97; N, 4.75.

Di-t-Butyl N-Cyanoimine

Cyanamide (0.21 g, 5 mmol) in 30 ml THF was added dropwise with stirring over a period of 3 hr to a suspension of the chlorosulfenyl chloride **10** (1.15 g, 5 mmol) and sodium hydride (0.5 g, 20 mmol) in 60 ml THF maintained at 0°. The reaction was allowed to warm to 25° after the addition was complete and stirred overnight. The reaction was filtered with suction and the solvent removed with a rotary evaporator. Crystallization from methylene chloride/hexane yielded 0.25 g (30%) di-t-butyl N-cyanoimine: mp 66-68°, proton nmr ($CDCl_3$) δ 1.39 (s, 18H); ir 2180, 1595, 1480, 1390, 1365, 1055, 990 cm^{-1}; UV max (EtOH) 260 nm (ϵ 1330); mass spectrum (70 eV) m/e (rel intensity) 166(1), 151(1), 124(3), 95(8), 69(22), 57(100); carbon-13 nmr ($CDCl_3$) 29.00, 45.08, 111.12, 211.55.

Anal. Calculated for $C_{10}H_{18}N_2$: C, 72.24; H, 10.91; N, 16.85. Found: C, 72.05; H, 10.86; N, 16.63.

Di-t-Butylthione-S-t-Butylimide (**15**)

A solution of 2.4 g t-butylamine (0.033 mol) in 50 ml dry THF was added rapidly to the chlorosulfenyl chloride **10** (2.3 g, 0.01 mole) in 50 ml dry THF maintained at 0° under an inert atmosphere. The reaction was stirred for 2 hr and filtered under an inert atmosphere. The solvent was removed under vacuum to yield 2.3 g (100%) crude thione-S-imide **15**. The crude material was sublimed at 20° (0.1 mm) to yield 2.0 g (87%) of pure **15**: mp 5°; proton nmr ($CDCl_3$) δ 1.25 (s, 9H), 1.28 (s, 9H), 1.51 (s, 9H); ir (CH_2Cl_2) 2960, 1480, 1390, 1360, 1188, 1110, 1039, 1020 cm^{-1}; UV max (hexane) 316 nm (ϵ 6200), (EtOH) 316 (18600); mass spectrum (70 eV) m/e (rel. intensity) 229 (1.5), 178 (2), 159 (4), 101 (11), 57 (100); carbon-13 nmr ($CDCl_3$) δ 28.03, 31.97, 32.40, 40.83, 42.53, 58.12, 163.33; osmotic molecular weight (chloroform) 212 (calc. 229).

Anal. Calculated for $C_{13}H_{27}SN$: C, 68.05; H, 11.86, S, 13.98; N, 6.11. Found: C, 67.75; H, 12.10; S, 13.95; N, 5.98.

Di-t-Butylthione-S-[1-(3,4-dichlorophenyl)-2-methyl-2-propyl]imide (24)

A solution of 7.0 g 1-(3,4 dichlorophenyl)-2-methylpropylamine (0.030 mole) in 30 ml THF was added rapidly to a solution of 1.15 g chlorosulfenyl chloride 10 (0.01 mole) in 70 ml THF maintained at 0° under an inert atmosphere. The reaction was stirred for 2 hr and filtered under an inert atmosphere. The solvent was removed under vacuum to yield 1.5 g (80%) of a yellow solid. This material was sublimed at 20° (.05 mm) to give pure 24: mp 43-45°; proton nmr (CCl_4) δ 1.28 (s, 6H), 1.20 (s, 9H), 1.55 (s, 9H), 2.73 (s, 2H), 6.85-7.32 (m, 3H); ir (CCl_4) 2960, 1470, 1385, 1305, 1130, 1030 cm^{-1}; UV max (EtOH) 319 nm.

Anal. Calculated for $C_{19}H_{29}SNCl_2$: C, 60.95; H, 7.81; S, 8.56 N, 3.74; Cl, 18.94. Found: C, 60.75; H, 7.74; S, 8.62; N, 3.52; Cl, 18.75.

Reaction of Di-t-Butylthione-S-t-Butylimide with TCNQ

TCNQ (1.0 g, 5 mmol) was added in one portion to a stirred solution of 1.15 g (5 mmol) thione-S-imide 15 in 30 ml methylene chloride maintained at 25°. The green reaction mixture was evaporated to dryness. The resultant solid was chromatographed on silica gel and eluted with methylene chloride/hexane to yield 1.75 g (81%) of

2,5,5-t-butyl-3-[7′-(7′, 8′, 8′-tricyanoquinodimethane)]Δ^3-1,2,4-thiadiazoline (25): mp 160°; proton nmr ($CDCl_3$) δ 1.21 (s, 18H), 1.36 (s, 9H), 7.42 (m, 4H); ir (CCl_4) 2960, 1670, 1465, 1385, 1360, 1095, 1030 cm^{-1}; UV max (hexane) 384 nm (ε 45100); mass spectrum (70 eV) m/e (rel intensity) 433 (.1), 402 (1.8), 401 (1.7), 321 (9), 320 (10.8), 288 (3.5), 84 (9.9), 57 (100); carbon-13 nmr ($CDCl_3$) δ 29.24 (q), 30.94 (q), 44.77 (s), 59.58 (s), 106.66 (s), 111.69 (s), 115.03 (s), 127.71 (d), 132.56 (d), 141.97 (s).

Anal. Calculated for $C_{25}H_{31}SN_5$: C, 69.25; H, 7.21; S, 7.40; N, 16.15. Found: C, 69.40; H, 7.26; S, 7.22; N, 16.03.

Di-t-Butylthione S-t-Octylimide (23)

A solution of 4.0 g t-octylamine (.031 mol) in 50 ml dry THF was added rapidly to chlorosulfenyl chloride 10 (2.3 g, .01 mol) in 50 ml dry THF maintained at 0° under an inert atmosphere. The reaction was stirred for 2 hr and filtered under an inert atmosphere and the solvent was removed under vacuum to yield 2.5 g (88%) crude thione S-imide. The oil was distilled at 35° (0.05 mm) for analysis: proton nmr ($CDCl_3$) δ .96 (s, 9H), 1.28 (s, 9H), 1.29 (s, 6H), 1.50 (s, 9H), 1.58 (s, 2H); ir (CH_2Cl_2) 2980, 1470, 1390, 1360, 1205, 1130, 1030, 1020.

Anal. Calculated for $C_{17}H_{35}SN$: C, 71.51; H, 12.36; S, 11.23; N, 4.91. Found: C, 71.50; H, 12.36; S, 12.25; N, 4.90.

Pyrolysis of Thione S-imide 15

Thione S-imide 15 (4.5 g, 0.02 mol) was heated to 150° under an inert atmosphere for 40 min with an evolution of a gas. The reaction mixture was dissolved in 25 ml pentane and fractional distillation yielded 2.8 g (90%) di-*t*-butylthioketone and a mixture of other products which could not be separated by fractional distillation. G.L.C. of this mixture showed 7 peaks, comparison with authentic samples ruled out the presence of any *t*-butylamine, 2,2,3,3,-tetramethylbutane, or azo-bis-(*t*-butane). Proton nmr of this mixture ruled out the presence of either *N*-methylacetone imine or 2,2,dimethylaziridine.

In a separate experiment the gas evolved was trapped in a liquid nitrogen trap and determined to be isobutylene by mass spectral comparison with an authentic sample.

Reaction of Di-*t*-Butylthioketone with Diphenyldiazomethane

Di-*t*-butylthioketone (0.8 g, 5 mmol) and diphenyldiazomethane (1.0 g, 5 mmol) were combined in 10 ml of methylene chloride and after 30 min all of the reagents color had been discharged. The methylene chloride was removed by a rotary evaporator and the resultant solid was washed with 2x5 ml pentane to give 1.0 g (55%) of 2,2-di-*t*-butyl-5,5-diphenyl-Δ^3-1,3,4-thiadiazoline: mp 115-116° (lit.[19] 118-20); proton nmr ($CDCl_3$) δ 1.04 (s, 18H), 7.10-7.75 (m, 10H), ir (CCl_4) 3050, 2960, 1590, 1490, 1445, 1390, 1365; carbon-13 nmr ($CDCl_3$) δ 30.52, 43.08, 125.35, 126.50, 127.59, 130.26, 139.53, 144.52.

Anal. Calculated for $C_{22}H_{28}N_2S$: C, 74.95; H, 8.00; N, 7.95; S, 9.10. Found: C, 74.67; H, 8.04; N, 7.89; S, 9.02.

Reaction of Di-t-Butylthioketone with Diazofluorene

Di-t-butylthioketone (0.8 g, 5 mmol) and diazofluorene (1.0 g, 5 mmol) were combined in 20 ml methylene chloride. After 2 hr bisfluorylidenesulfide, mp 161-162° (lit.[23] mp 162-163°), was removed by filtration. The mother liquor was evaporated to dryness and the resultant solid was chromatographed on silica gel using methylene chloride/hexane as the elutant . The first solid isolated, mp 184-188°, was identified as bisfluorenylidene (lit.[23] mp 184°) and the second product isolated was crystallized from pentane to give a yellow solid, mp 119-121° which was subsequently identified as 1,1-di-t-butyl-2-(9-fluorenyl)azine (27): proton nmr ($CDCl_3$) δ 1.37 (s, 18H), 7.2-7.95 (m, 8H); ir 3055, 2900, 1605, 1485, 1445, 1440, 1380, 1365; UV max (hexane) 318 nm (ε 10300), 253 (28700), 229 (25500), mass spectrum (70 eV) m/e (rel intensity) 261 (33), 235 (31), 205 (26), 179 (70), 178 (100), 151 (24), 57 (14); carbon-13 nmr ($CDCl_3$) δ 29.61, 35.80, 119.46, 121.46, 126.92, 127.29, 128.86, 129.59, 131.35, 136.63, 139.18, 141.18, 145.73, 165.87.

Anal. Calcualted for $C_{22}H_{26}N_2$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.92; H, 8.41; N, 8.67.

Reaction of Di-t-Butylthioketone with Ethyl Diazoacetate

Di-t-butylthioketone (0.8 g, 5 mmol) and ethyl diazoacetate (1.14 g, 10 mmol) were combined with cooling by a water bath. After 30 min all the color of the reagents was discharged and on cooling the solution to 0° colorless crystals of a product were deposited.

This reaction product was collected by filtration and washed with 10 ml pentane to give 1.0 g (73%) of 2,2-di-*t*-butyl-5-carboethoxy-Δ^3-1,3,4-thiadiazoline: mp 102-106°, proton nmr ($CDCl_3$) δ 1.19 (s, 18H), 1.37 (t, 3H), 2.65 (q, 2H), 6.71 (s, 1H); ir (CH_2Cl_2) 3425, 2965, 1725, 1709, 1550, 1140, 1085; UV max (EtOH) 221 nm (ϵ 8760); mass spectrum (70 eV) m/e (rel intensity) 244 (2.5), 215 (20), 199 (100), 171 (34), 142 (27), 127 (27), 113 (57), 57 (62).

Anal. Calculated for $C_{13}H_{24}SN_2O_2$: C, 57.32; H, 8.88, S, 11.77; N, 10.29. Found: C, 57.50; H, 8.93; S, 12.00; N, 10.33.

Reaction of Di-*t*-Butylthioketone with Diethyl diazomalonate

Di-*t*-butylthioketone (1.6 g, .01 mol) and diethyl diazomalonate (1.9 g, .01 mol) were combined under an inert atmosphere and heated to 85°. After 24 hr the reaction was cooled to room temperature, the solid which crystallized was collected by filtration to give 2.1 g (66%) of crude **38**. Chromotography of florisil using methylene chloride/hexane as the elutant gave pure 2,2-di-*t*-butyl-4-ethoxy-5-carboethoxy-Δ^4-1,3-oxathiole: mp 48-49°; proton nmr (CCl_4) δ 1.19 (s, 18H), 1.24 (t, 3H), 1.39 (t, 3H), 4.09 (q, 2H), 4.26 (q, 2H); ir (CCl_4) 2960, 1710, 1625; UV max (hexane) 316 nm (ϵ 5630); mass spectrum (70 eV) m/e (rel intensity) 316 (4), 259 (20), 231 (7), 185 (11), 159 (8), 147 (5.5), 111 (6), 85 (31), 57 (100); carbon-13 nmr ($CDCl_3$) δ 7.04 (q), 7.99 (q), 22.23 (q), 40.95 (s), 57.63 (t), 65.36 (t), 113.11 (s), 169.05 (s), 172.11 (s).

Anal. Calculated for $C_{16}H_{28}SO_4$: C, 60.72; H, 8.92; S, 10.13. Found: C, 60.83; H, 8.95; S, 10.12.

Reaction of Di-t-Butylthioketone with Di-t-Butyl diazomalonate

Di-t-butylthioketone (1.6 g, .01 mol) and di-t-butyl diazomalonate (2.4 g, .01 mol) were combined under an inert atmosphere and heated to 80°. After 24 hr the reaction mixture was cooled to room temperature, the solid which separated was crystallized from pentane to give 1.7 g (60%) of 2,2-di-t-butyl-4-oxo-5-carbo-t-butoxy-Δ^4-1,3-oxathiole: mp 43-45°; proton nmr ($CDCl_3$) δ 1.19 (s, 9H), 1.23 (s, 9H), 1.45 (s, 9H), 4.48 (s, 1H); ir 2970, 1770, 1740, 1140; UV max (EtOH) 314 nm (ε 1503); carbon-13 nmr ($CDCl_3$) δ 27.61 (q), 28.27 (q), 29.12 (q), 43.62 (s), 45.50 (s), 52.30 (d), 83.06 (s), 105.50 (s), 164.17 (s), 168.54 (s).

Anal. Calculated for $C_{16}H_{28}SO_4$: C, 60.72; H, 8.92; S, 10.13. Found: C, 60.75; H, 8.93; S, 10.01.

CHAPTER IV

X-RAY STRUCTURE

X-Ray Structure of 2,5,5-Tri-t-butyl-3-[7′-(7′, 8′,8′-tricyanoquinodimethane)]Δ^3-1,2,4-thiadiazoline (25)

A green crystal with approximate dimensions 0.05x0.05x1.5 mm was mounted on a glass fiber using epoxy cement such that the longest crystal dimension was approximately parallel to the fiber axis.

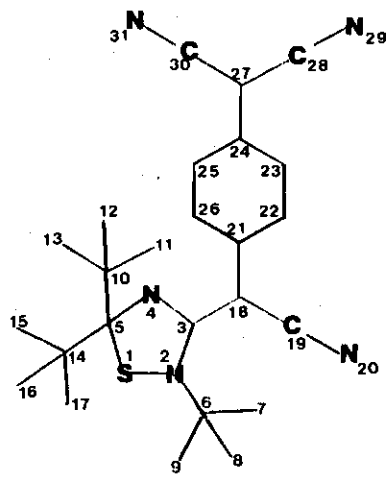
Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four circle diffractometer equipped with a graphite monochromator (Bragg 2θ angle = 12.2°) using MOKα radiation at a takeoff angle of 6.5°. Thirteen reflections of various 2θ value were machine-centered and used in least-squares refinement of the lattice parameters and orientation matrix. Unit cell parameters obtained were a = 12.44 (1) A°, b = 8.09 (1) A°, c = 12.96 (1) A°, α = 93.336 (1)°, β = 94.040 (1)°, γ = 104.051 (1)°, and V = 1259.26 A°.[39,40] Omega scans of three low 2θ angle reflections gave peak widths at half-height of less than 0.3° indicating a satisfactory mosaic spread for the crystal.

Intensity data were collected using θ-2θ scans with x-ray and monochromator settings identical to those used for determination of the unit cell parameters. A variable scan rate of from 2.0° to 29.3°/minute was used. No significant fluctuations were observed in the intensities of three standard reflections (003; 400; 020) monitored every 97 reflections. A total of 3812 reflections were collected in a complete hemisphere of data out to $2\theta = 45°$; 1643 reflections were accepted as statistically above background on the basis that I was greater than 3 sigma.

The space group was determined to be centric ($P\bar{1}$) on the basis of a Wilson plot performed by FAME.[41] The phases of 242 E's with $|E|>1.5$ were set using MULTAN.[41] One solution contained 20 of the 31 anticipated atoms in a chemically reasonable arrangement. The coordinates and isotropic temperature factors of these 20 atoms were refined by full matrix least-squares.[41] An electron-density map phased by these atoms revealed the missing atoms. Further isotropic least-squares refinement on all 31 atoms reduced the value of the reliability index to R = 0.12.

The coordinates of a majority of the hydrogens were easily located from a difference electron-density map. The remaining hydrogen atom position were predicted by FINDH.[41] All 31 hydrogens were then included in the atom list and assigned temperature factors of 5.0 and were not refined further. The sulfur, nitrogens and selected carbons were refined anisotropically until convergence was reached at R = 0.085 with the weighed $R_w = 0.067$. The highest peak in the final E map was 0.38 e. Structure factor tables are listed in the appendix.

Using the numbering system indicated below, the atomic fractional coordinates are listed in Table 1.



25

Table 1. Atomic Fractional Cell Coordinates Of 25

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S_1	-.3797	.1428	.4067	.005701	.025719	.005731	-.001516	.001069	.000429
N_2	-.3254	.2127	.2902	4.880806					
C_3	-.2190	.3214	.3160	3.863439					
N_4	-.1780	.3473	.4093	4.453507					
C_5	-.2512	.2686	.4877	4.036126					
C_6	-.4058	.2056	.1999	.005651	.043789	.006062	.003188	.000383	.002483
C_7	-.3524	.2380	.1004	.010415	.048824	.007138	-.001208	-.001381	.000221
C_8	-.4924	.0432	.1895	.012933	.066714	.008734	-.012322	-.001122	.005620
C_9	-.4662	.3462	.2178	.019540	.085690	.010990	.029107	-.003914	.000842
C_{10}	-.1958	.1380	.5429	4.802912					
C_{11}	-.1607	.0230	.4602	.013062	.031509	.0079117	.010709	.002356	.002203
C_{12}	-.2757	.0169	.6078	.013089	.022415	.009111	.002032	.003361	.005649
C_{13}	-.0894	.2219	.6122	.008382	.032681	.008313	.005813	-.000899	.001933
C_{14}	-.2791	.4179	.5548	.014763	.021525	.005062	.006984	.001133	-.001076
C_{15}	-.3352	.5264	.4814	.014699	.022921	.019370	.008533	.000676	-.000204
C_{16}	-.1708	.5481	.6083	.022184	.024187	.011903	.006057	-.006013	-.010178
C_{17}	.3633	.3579	.6332	.026385	.038788	.008526	.019585	.007035	.003510

Table 1. (continued)

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C_{18}	-.1470	.4048	.2370	4.082796					
	.1490	.5821	.2281	4.684221					
N_{20}	-.1480	.7187	.2196	.012262	.019456	.011541	.001624	-.000976	.002189
C_{21}	-.0725	.3341	.1925	4.001048					
C_{22}	.0130	.4371	.1348	4.211510					
C_{23}	.0901	.3682	.0952	4.401656					
C_{24}	.0942	.1922	.1065	4.698934					
C_{25}	.0054	.0866	.1617	4.577720					
C_{26}	-.0729	.1565	.2012	4.568439					
C_{27}	.1761	.1248	.0703	4.631813					
C_{28}	.1773	-.0457	.0829	5.295002					
N_{29}	.1774	-.1861	.0911	.010099	.027505	.012415	.003939	.004751	.002636
C_{30}	.2645	.2237	.0200	.006488	.032872	.007513	.001130	.001107	.004333
N_{31}	.3381	.2989	-.0190	.008728	.048702	.01262	.002477	.001908	.010949
H11A	-.10	.08	.40						
H11B	.12	.08	.50						
H11C	.229	.042	.594						
H12A	.280	-.210	.32						
H12B	.360	.06	.46						

Table 1. (continued)

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
H12C	.24	.10	.34						
H13A	+.10	-.30	.32						
H13B	.04	-.06	.40						
H13C	.06	-.26	.46						
H15A	.34	-.65	.48						
H15B	.42	-.46	.54						
H16A	.22	-.68	.36						
H16B	.16	-.46	.30						
H16C	.10	-.54	.50						
H17A	.36	-.42	.28						
H17B	.44	-.28	.42						
H17C	.34	-.26	.32						
H7A	-.26	.32	.10						
H7B	-.42	.18	.02						
H7C	-.28	.18	.099						
H8A	-.42	-.06	.18						
H8B	-.54	-.02	.26						
H8C	-.54	.02	.10						

Table 1. (continued)

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
H9A	-.42	.50	.22						
H9B	-.54	.36	.16						
H9C	-.497	.353	.296						
H22	.16	.44	.04						
H23	.02	-.42	.12						
H25	-.14	.10	.26						
H26	.00	-.08	.16						

Table 2. Selected Bond Length and Angles of Adduct 25

	Bond Length Å	Angle Degrees
S_1N_2	1.764(2)	
N_2C_3	1.406(9)	
$S_1N_2C_3$		129.7°
C_3N_4	1.264(8)	
$N_2C_3N_4$		100.0°
N_4C_5	1.481(9)	
$C_3N_4C_5$		116.37(61)
C_5S_1	1.881(8)	
$C_5S_1N_2$		92.46(34)
$N_4C_5S_1$		103.10(49)
N_2C_6	1.47(1)	
C_6C_7	1.50(1)	
C_6C_8	1.48(1)	
C_6C_9	1.52(1)	
C_5C_{10}	1.57(1)	
C_5C_{14}	1.57(1)	
$C_{10}C_5C_{14}$		119.26(66)
$C_{10}C_{11}$	1.53(1)	
$C_{10}C_{12}$	1.55(1)	
$C_{10}C_{13}$	1.53(1)	
$C_{14}C_{15}$	1.57(1)	
$C_{14}C_{16}$	1.58(1)	

Table 2 continued

	Bond Length Å	Angle Degrees
$C_{14}C_{17}$	1.53(1)	
C_3C_{18}	1.49(1)	
$N_4C_3C_{18}$		116.63(64)
$N_2C_3C_{18}$		123.06(65)

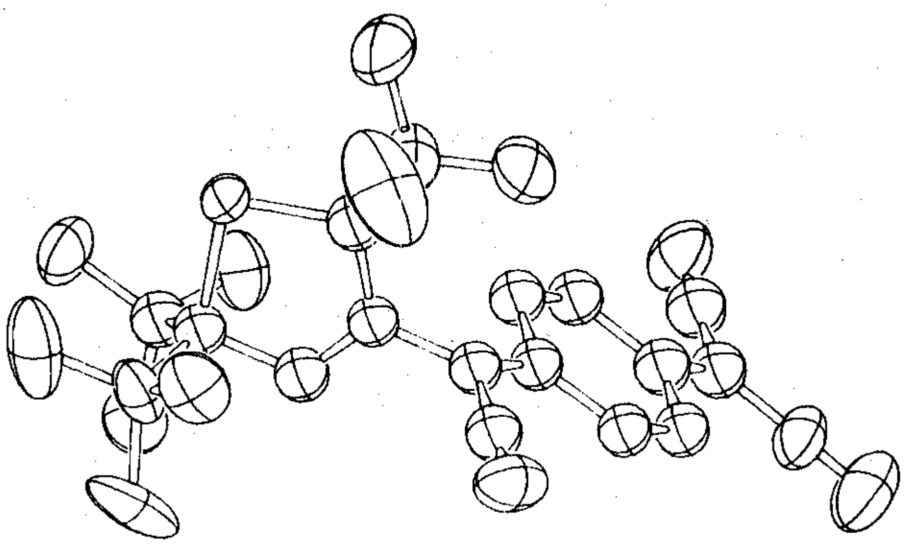
Table 3. Dihedral angles in Adduct 25

$(C_{21}C_{18}C_{19})(N_2C_3N_4)$	93.85(39)
$(N_4C_5S_1)(C_{10}C_5C_{14})$	88.84(32)
$(S_1N_2C_3)(S_1N_2C_6)$	22.12(91)

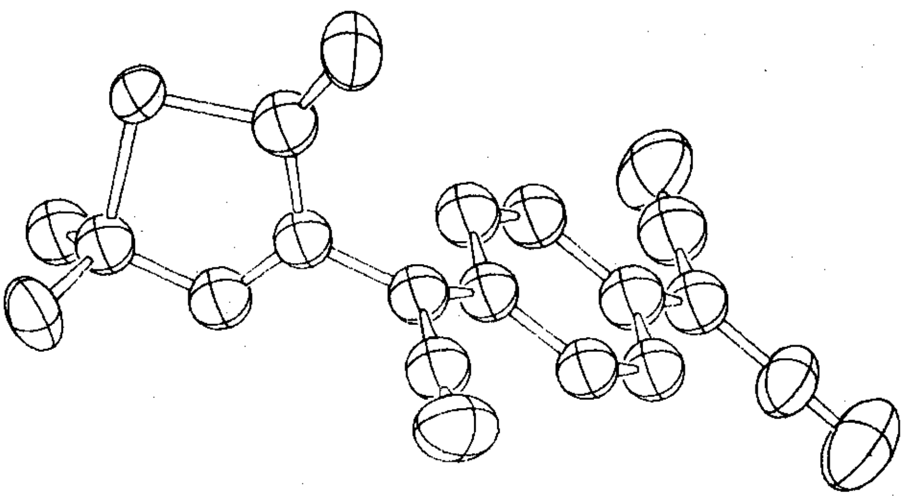
Table 4. Deviation From Planarity in Adduct 25

Plane defined by atoms S_1, N_2, C_3, N_4 and C_5.

	Deviation Å
S_1	-.0076
N_2	-.0023
C_3	.0162
N_4	-.0236
C_5	.0170



ORTEP Drawing of 25 Showing all non-hydrogen atoms



ORTEP Drawing of 25 with methyl carbons omitted for clarity

CHAPTER V

DISCUSSION OF RESULTS

The purpose of the research described herein was to investigate the possible synthesis and thermal fate of sulfur heterocumulenes derived from di-t-butylthioketone. The synthesis of di-t-butylsulfine has been previously reported,[19,28] and its thermal and photochemical stability will be described. A general synthesis for thione S-imides derived from di-t-butylthioketone was developed and their chemistry was investigated. The generation of thione S-methylides derived from di-t-butylthioketone was attempted by the reaction of the thione with a series of diazo compounds and was found to yield cycloadducts. The results of these investigations were correlated using the MINDO/3 generated surface potential energy for the ring closure of the cumulene to the corresponding heterocycle.

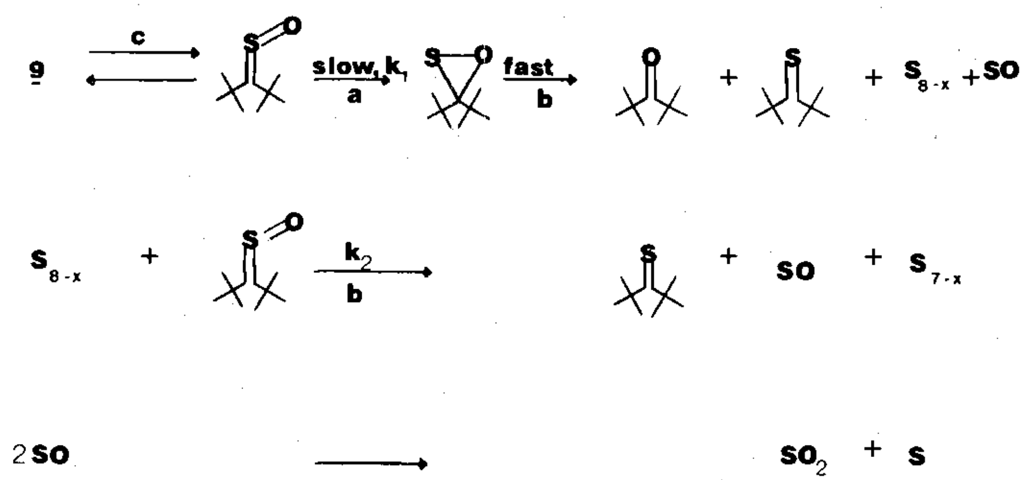
The thermolysis of di-t-butylsulfine (8) in diphenylmethane yielded di-t-butylthioketone and di-t-butylketone in a ratio which changed during the course of the reaction and which was temperature dependent. The kinetics of the thermolysis were determined at 150° and 210° in diphenylmethane in an effort to delineate the mechanism (plots are shown in Appendix II and summarized in Table 5). At 150° low concentrations of 8 decomposed via a first order process to a 1:9 mixture of thioketone and ketone. However, at 210° 8 decomposed through the first quarter-life via a first order process to a 1:3

Table 5. Kinetics Of Sulfine **8** Thermolysis In Diphenylmethane

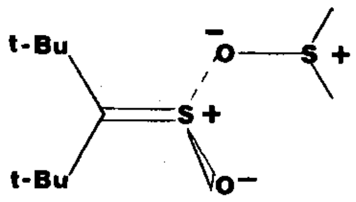
Conc (M)	Temp (C)	Conc. of added nucleophiles (M)	Product Ratio (Thione/Ketone)	k (min^{-1})
.4	125		.8/99.2	
.053	150			0.002
.08	150			0.003
.094	150			0.003
.19	150			0.004
.26	150	.17 Benzoylperoxide	9/91	0.002
.27	150			0.004
.30	150	.6 Dimethisulfoxide	9/91	0.0003
.31	150	1. Diphenylsulfide		0.0002
.36	150	.6 Triphenylphosphine		0.0002
.61	150	.6 Chloroacetic acid	6/94	0.0005
1.04	150			0.002 ($k_{int.}$)
.4	180		38/62	
.11	210		25/75(int.); 43/57(final)	0.002 ($k_{int.}$)
.39	210	.38 Thione-S-imide	75/25	0.023
.54	210		25/75(int.); 52/48(final)	0.002 ($k_{int.}$)

mixture of thioketone and ketone; after the first quarter-life the reaction accelerated rapidly to give a final product ratio of thioketone/ketone of 1:1. These observations can be accommodated by an autocatalytic mechanism in which the inital stage of the reaction proceeds via a slow first order process to give predominately ketone (Scheme 1, path a) but as the reaction proceeds sufficient catalysis is produced to allow a faster second order process to take over which yields thioketone (Scheme 1, path b). At low concentrations of **8** this faster second order process is not operative and first order kinetics are observed. Although there is no evidence for the intermediacy of sulfur monoxide, the proposed mechanism was substantiated by the observation that the addition of tetramethylthiourea S-p-toluenesulfonimide which thermally extrudes sulfur at temperatures greater than 70° accelerated the decomposition of **8** at 210°. The addition of cyclooctasulfur (S_8) did not accelerate the decomposition of **8** at 150°; therefore only some highly reactive form of sulfur (S_{8-x}) was capable of accelerating the decomposition of sulfine **8**. The sulfur accelerated reaction followed first order kinetics through three half-lives and gave a 3:1 mixture of thioketone and ketone which did not change during the reaction. The observed rate constant ($k_{obs.}$) in the sulfur accelerated reaction is a summation of k_1 and Kk_2 (where K equals the concentration of S_{8-x}); since k_1 is equal to the initial rate constant ($k_{int.}$) in an uncatalyzed reaction, then Kk_2 equals $k_{obs.}$ $-k_{int.}$ (0.021 min^{-1}).

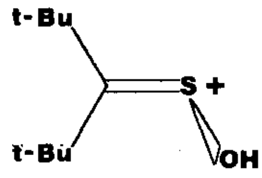
At low concentrations of **8**, first order kinetics are consistent with the slow step being either closure to the oxathiirane or attack of a nucleophile on the intermediate oxathiirane; therefore, the effect of several external nucleophiles was investigated. It was found that triphenylphosphine, dimethylsulfoxide-d_6, and diphenylsulfide retarded the rate of reaction (Table 5); therefore it is proposed that these added nucleophiles stabilize the ground state and prevent the cyclization as shown in Scheme 1, path b. This mechanism is supported by the observation that the addition of 2.1 equivalents of DMSO-d_6 to a solution of the sulfine in diphenylmethane reduces the observed t-butyl group separation (H^1 nmr) from 28 Hz to 25 Hz. The solvent effect is even more dramatic when the spectra is run in pure DMSO-d_6; the separation in the t-butyl groups is reduced to 9 Hz indicating a complex such as **9a** which places the t-butyl groups in nearly equivalent chemical



Scheme 1



9a



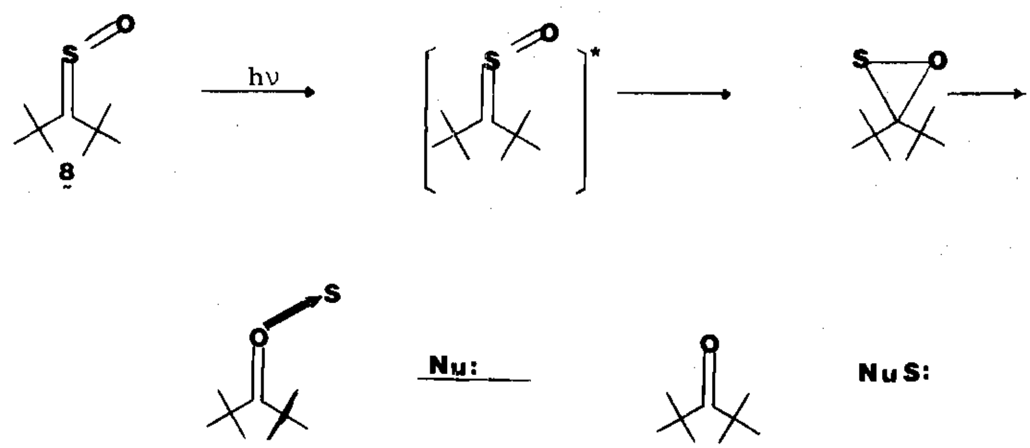
9b

environments and thus reduces the observed proton nmr separation. Further aggregation of 9a with dimethylsulfoxide increases the electron density at the sulfine carbon diminishing the propensity of the sulfine to cyclize. This mechanism is further substantiated by the high temperature proton nmr in diphenylmetahane. The spectra shows no coalescence even at 200° and no new peaks which could be assigned to di-t-butyloxathiirane. Only starting material and product peaks are observed at temperatures in the range from 100° to 200°. This is mechanistically consistent with oxathiirane formation being the rate limiting step followed by rapid ring fission to the observed products. The effect of acid on the thermolysis was studied and was found to reduce the reaction rate (Table 5). This result is rationalized by a mechanism involving protonation on oxygen (9b) which necessarily reduces the electron density at oxygen and thus the propensity to cyclize; this mechanism is supported by the theroretical work of Synder[8] and the work of Zwanenburg with diarylsulfines.[37]

A radical mechanism for the decomposition is discounted upon the observation that the addition of benzoylperoxide did not accelerate the decomposition of the sulfine (Table 5).

The nucleophile which serves to desulfurize the intermediate oxathiirane is undoubtedly a growing oligomeric chain of sulfur (S_{8-n}), since sulfur (S_8) is the ultimate product from the desulfurization; however, deoxygenation does not produce detectable oxygen containing compounds. The possibility of oxygen insertion into the solvent was investigated. Thermolysis in diphenylmethane does not produce benzophenone and thermolysis in naphthalene does not afford $\underline{\alpha}$ or $\underline{\beta}$-naphthol.

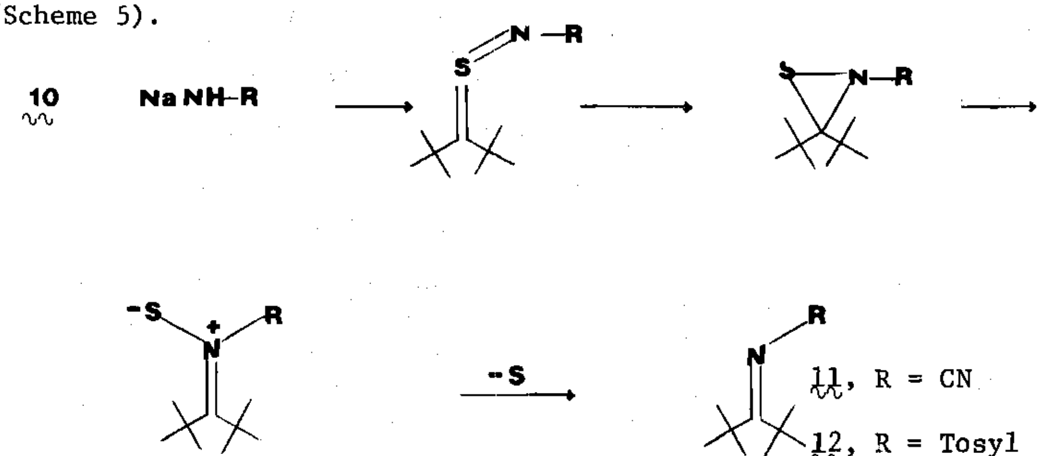
The photolysis of di-t-butylsulfine in chloroform yielded only di-t-butylketone, and control experiments confirmed that di-t-butylthioketone is stable under the reaction conditions. These results are consistent with the mechanism in Scheme 3. The photochemical desulfurization is postulated to be the result of selective nucleophilic attack on the oxathiirane at 27°. The product ratio in the sulfine thermolysis showed increased selectivity as the temperature was lowered. Extrapolation to temperatures below 125° indicates that desulfurization of the intermediate oxathiirane is the only reaction which would be observed; and as expected, when the intermediate oxathiirane was generated photochemically at 27°, only the desulfurization reaction was observed.



Scheme 3

The synthesis of di-*t*-butyl thione *S*-imides was accomplished by the reaction of primary amines or amine salts with the *α*-chlorosulfenylchloride **10** which was synthesized by the reaction of di-*t*-butylthioketone with one equivalent of chlorine and characterized by its osmotic molecular weight and consistent elemental analysis.

The reaction of two equivalents of sodium cyanamide with **10** yielded the desulfurized *N*-cyanoimine **11**, (Scheme 5). Proton nmr taken of the crude reaction showed the only other products were cyanamide and a small amount of di-*t*-butylthioketone. The analogous reaction with two equivalents of sodium tosylamide yielded the *N*-tosylimine **12**, (Scheme 5).



11, R = CN

12, R = Tosyl

Scheme 5

The insolubility of these amines and their salts precluded reaction temperatures below 25°. These reactions undoubtedly proceed via intermediate formation of the thione *S*-imide followed by cyclization and desulfurization, a well documented process.[12,13,14] MINDO/3 calculations defining the cyclization reaction coordinate of two model compounds (**13** and **14**) showed that cyclization and ring opening to the

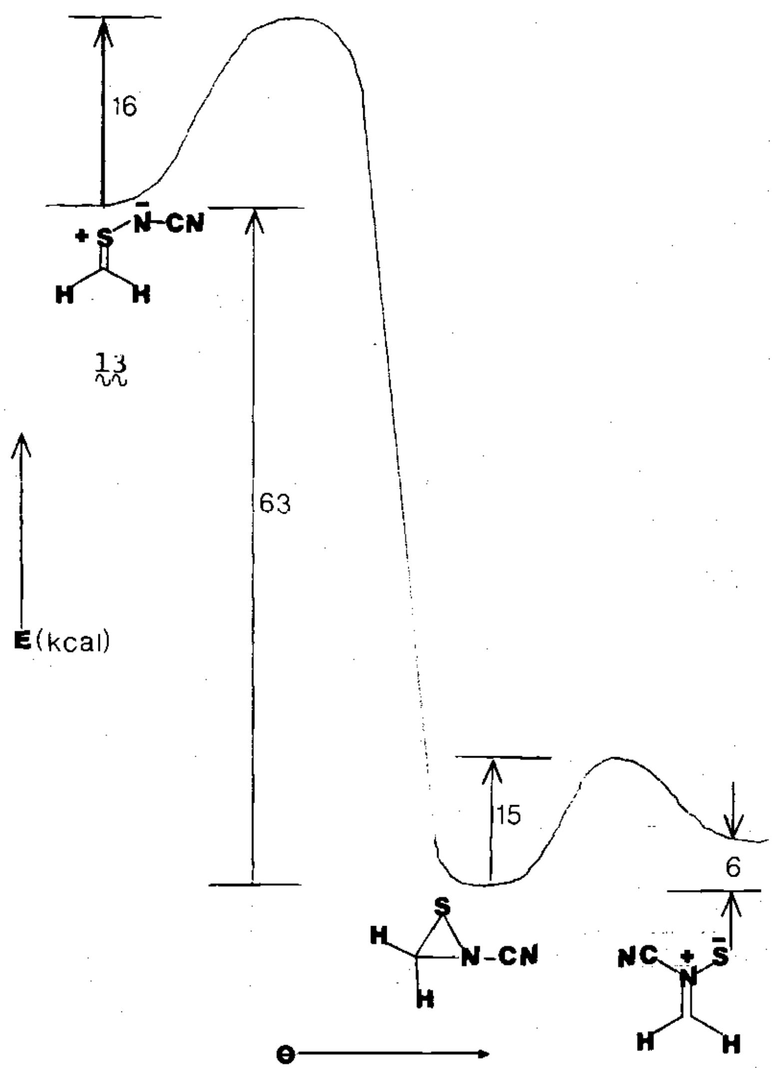


Figure 1. Potential Surface for the Closure of 13

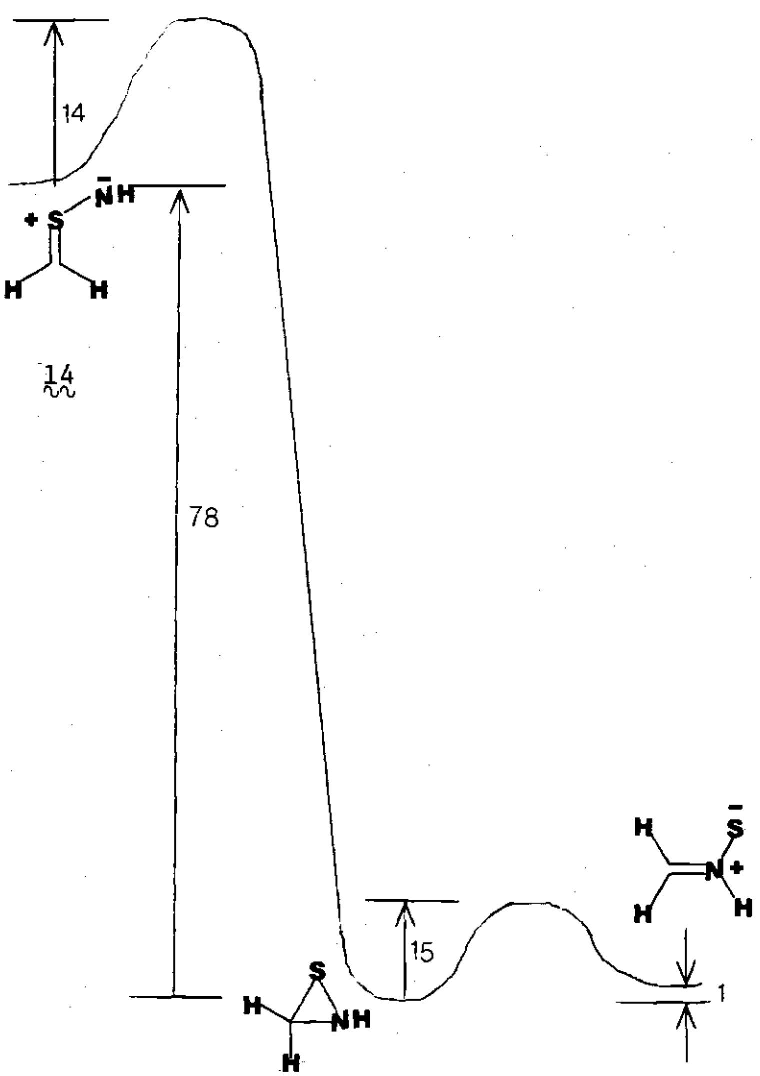
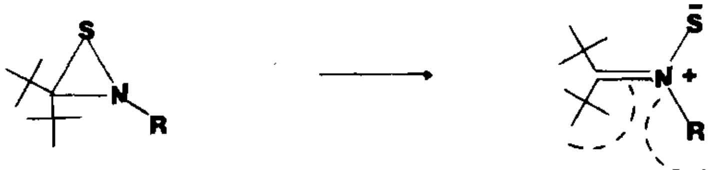


Figure 2. Potential Surface for the Closure of 14

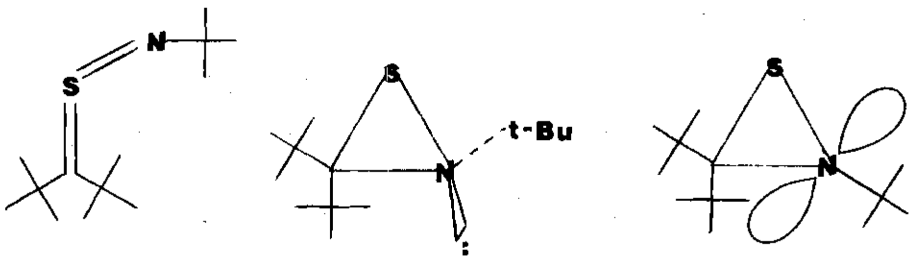
corresponding thionitrones were exothermic in both cases (Figures 1 and 2).

Desulfurization of the proposed thionitrone to the imine is analogous to the desulfurization of the carbonylsulfide in Scheme 1. Previously synthesized thione S-imides derived their stability from stronger electronic perturbation[11,12,30,31] which lowered the ground state of the thione S-imide and consequently raised the activation energy for the cyclization. A bulky substitutent on nitrogen should theoretically slow the ring closure but should not prevent it, and the desulfurization reaction of such a hindered thiaziridine should suffer strong steric repulsion between the vicinal groups (eq 1).



(1)

The reaction of 10 with three equivalents of t-butylamine gave t-butylamine hydrochloride and a yellow oil. The elemental analysis and mass spectrum of the oil were consistent with either 15a or 15b.



15a 15b 16

The proton nmr showed three singlets at δ 1.25 (N-C(CH_3)$_3$), 1.28, and 1.51 while di-t-butylsulfine showed two singlets at δ 1.37 and

1.53. The proton nmr precluded structure **16** which would have been less hindered but should have shown only two singlets. Low temperature (-95°) proton nmr showed slight peak broadening (peak width at 1/2 height 2.5 Hz) due to viscosity changes and partial precipitation of **15**, but no peak coalescence was observed. The high temperature (95°) proton nmr also showed no peak coalescence; therefore, the variable temperature proton nmr ruled out any equilibrium between **15a** and **15b**. The carbon-13 nmr showed one downfield singlet at δ 163 ppm assigned to the carbon bonded to sulfur. This differed significantly from the corresponding carbon of sulfine **8** which appears at δ 214 ppm. Although a sulfine is isoelectronic with a thione S-imide it is not obvious that the two carbons should have similar carbon-13 shifts; therefore, the carbon-13 shifts of **17** and **18** (θ = 68°-160°) were calculated. The calculated values shown in Table 6 and Appendix III were based upon the following assump-

17 **18**

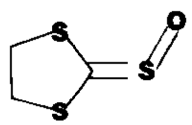
tions: (1) the dominant contribution to the differences in chemical shift were nearest neighbor dependent and derived from variation in the second-order paramagnetic shielding tensor ($\sigma^{(2)}_{xyz}$) for the 2p orbitals of carbon, (2) the mean excitation energy (ΔE) was localized at the carbon-sulfur bond and could be approximated by the calculated n_s -

Table 6. Observed C^{13} shifts (Relative to TMS) And Calculated Parameters

Compound	δ(obs.)	$\sigma^{(2)}$	θ(degrees)
8	-214.4		
17		-211.5	118.3
15	-163.3		
18		-125.	68.7
18		-261.7	118.3
18		-163	77

π^* or $n_s - \sigma^*$ transition.[33] The second-order paramagnetic shielding tensors were calculated using the Karplus-Pople relationship, $\sigma^{(2)} \approx [-e^2h^2/48m^2c^2a_o^3]\ [3.25 - .35(P_{ii} - 1)]^3\ (P_{ii} + \Sigma_j\ P_{ij})/\Delta E$. The diagonal ($P_{ii}$) and off-diagonal ($P_{ij}$) density matrix elements as well as ΔE were calculated using MINDO/3. These parameters were obtained for a fully geometry-optimized structure 17, and the parameters for 18 were calculated at various CSN angles (θ); C-S and S-N bond distances were optimized at each angle. At small values of θ (68°-95°) 18 has no distinct π system, therefore the carbon-13 shift was taken as the sum of σ_x, σ_y, σ_z. The agreement between the observed valve for 8 and 17 suggest that the assumptions were reasonable. Since the observed shift for 15 is intermediate between the two calculated values of 18, a plot of the carbon-13 shift versus θ was made (Appendix III). These calculations indicate the CSN angle to be 77° which corresponds to a C-N distance of >2 Å.

The results of these calculated carbon-13 shifts suggest that the valence angle at sulfur is smaller than those observed for other sulfur cumulenes. Sulfine 19 has an angle of 109.4°[35] and thione S-methylides 20 and 21 have angles of 104.3°[17] and 102.24°[36], respectively. This



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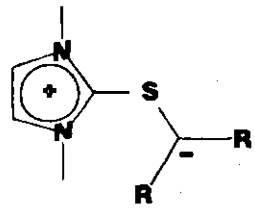
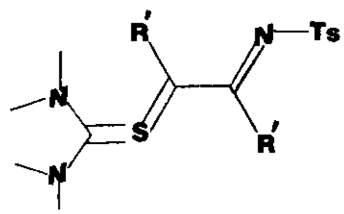
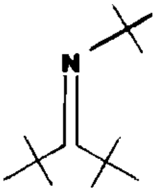


20 R = $CO_2C_2H_5$



21 R' = CO_2CH_3

small valence angle results in a decrease in the charge separation in 18 as shown by the atomic charges calculated for 18 (Table 7). Presumably, the complete cyclization of 15a to 15b is precluded for steric reasons. Therefore the decomposition of 15 should not yield the normal desulfurization product (22). This conclusion is supported



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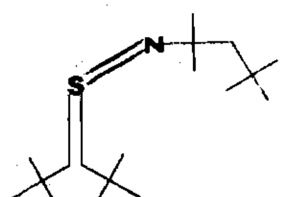

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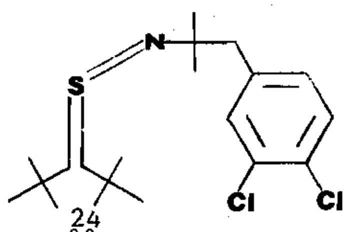


24

by experimental evidence. Thermolysis of **15**, at 150° does not yield sulfur, but results in cleavage of the sulfur-nitrogen bond to give di-*t*-butylthioketone (90%) and isobutylene.

Table 7.

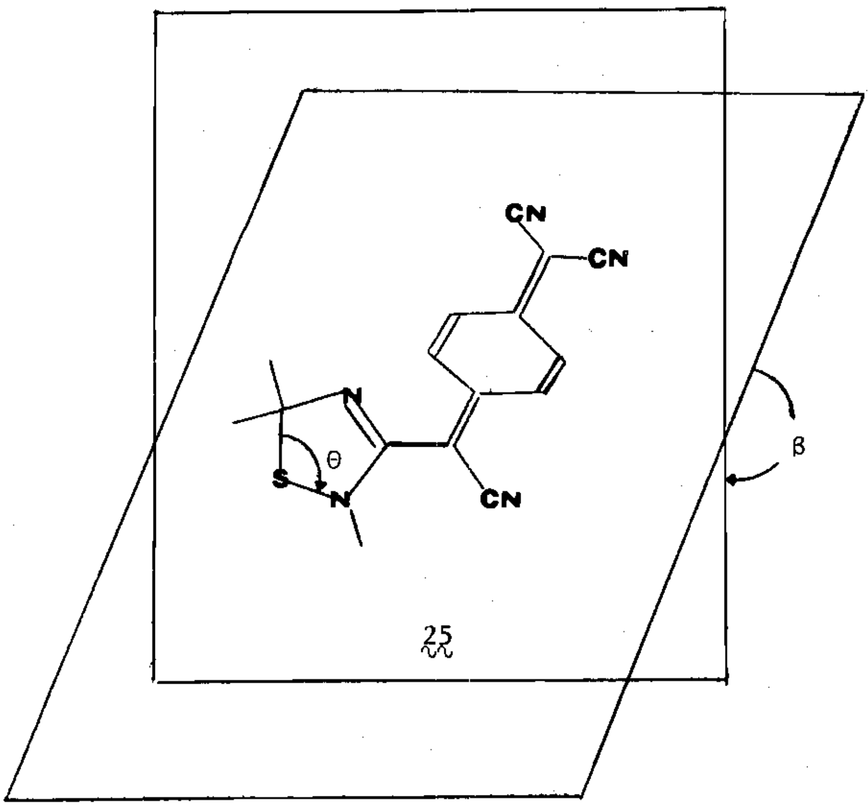
Atomic charge as a function of angle (θ) for **18**

θ(Degrees)	68.72	80.0	90.0	118.34	130.0
P_c	.13	.16	.18	.11	.11
P_s	-.04	-.01	.06	.16	.165
P_n	-.08	-.12	-.17	-.275	-.25
C-S (A°)	1.612	1.613	1.621	1.593	1.605
S-N (A°)	1.662	1.685	1.705	1.737	1.682

Attempts to prepare a solid derivative of di-*t*-butylthione *S*-imide lead to the synthesis of di-*t*-butyl *S*-*t*-octylimide (**23**) and Di-*t*-butylthione *S*-[1-(3,4-dichlorophenyl)-2-methyl-2-propyl] (**24**). Although **24** is a solid (mp 43-45°) all attempts to obtain x-ray quality single crystals failed. Assignment of the proton nmr spectra of these two derivatives confirmed the assignment of di-*t*-butylthione *S*-*t*-butylimide. **23** showed three singlets at δ .96 (9H), 1.58 (2H), and 1.29 (6H) assigned to the amine fragment and the thione fragment showed two singlets at δ 1.28 and 1.50. **24** showed signals at δ 1.28 (s, 6H), 2.73 (s, 2H), and 7.08 (m, 3H) assigned to the amine fragment and the thione fragment showed two singlets at δ 1.30 (9H) and 1.55 (9H).

The unusual reactivity of **15** was demonstrated by its reaction with 7,7,8,8-tetracyanoquinodimethane (TCNQ). TCNQ and **15** reacted immediately at 25° to yield a cycloadduct; however, sulfine **8** failed to react upon standing at 25° for several weeks. The 1:1 TCNQ adduct was characterized by its mass spectrum fragmentation pattern of M^+ at 433 m/e, and M^+ -S at 431, infrared absorption at (C=N, 1670 cm^{-1}) and elemental analysis. The proton nmr showed two singlets at δ 1.21 (18H), (9H), and a multiplet at 7.42 (4H). The structure of this novel adduct was determined to be structure **25** using x-ray crystallography. The new ring had resulted from a 1,3-dipolar addition of the electron rich thione _S_-imide to the electron deficient nitrile. The resulting thiadiazole has long sulfur bonds (S-C, 1.881; S-N, 1.764) and a valence angle at sulfur of only 92.46°. The thiadiazole ring which adopts a planar conformation lies perpendicular to the plane of the quinone ring due to the steric requirements of the three _t_-butyl groups (Figure 3).

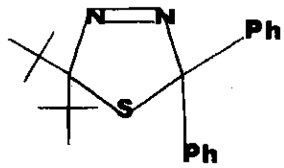
The reaction of di-_t_-butylthioketone with five diazo compounds was studied as a possible route to stable thione _S_-methylides. The reaction of di-_t_-butylthioketone with diphenyl diazomethane afforded the crystalline adduct **26**, whose synthesis and chemistry has been subsequently reported by Barton.[19] The reaction of di-_t_-butylthioketone



$\Theta = 92.5^{\circ}$

$\beta = 93.9^{\circ}$

Figure 3. 3-d Representation Of Adduct 25



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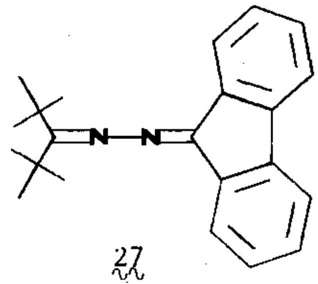
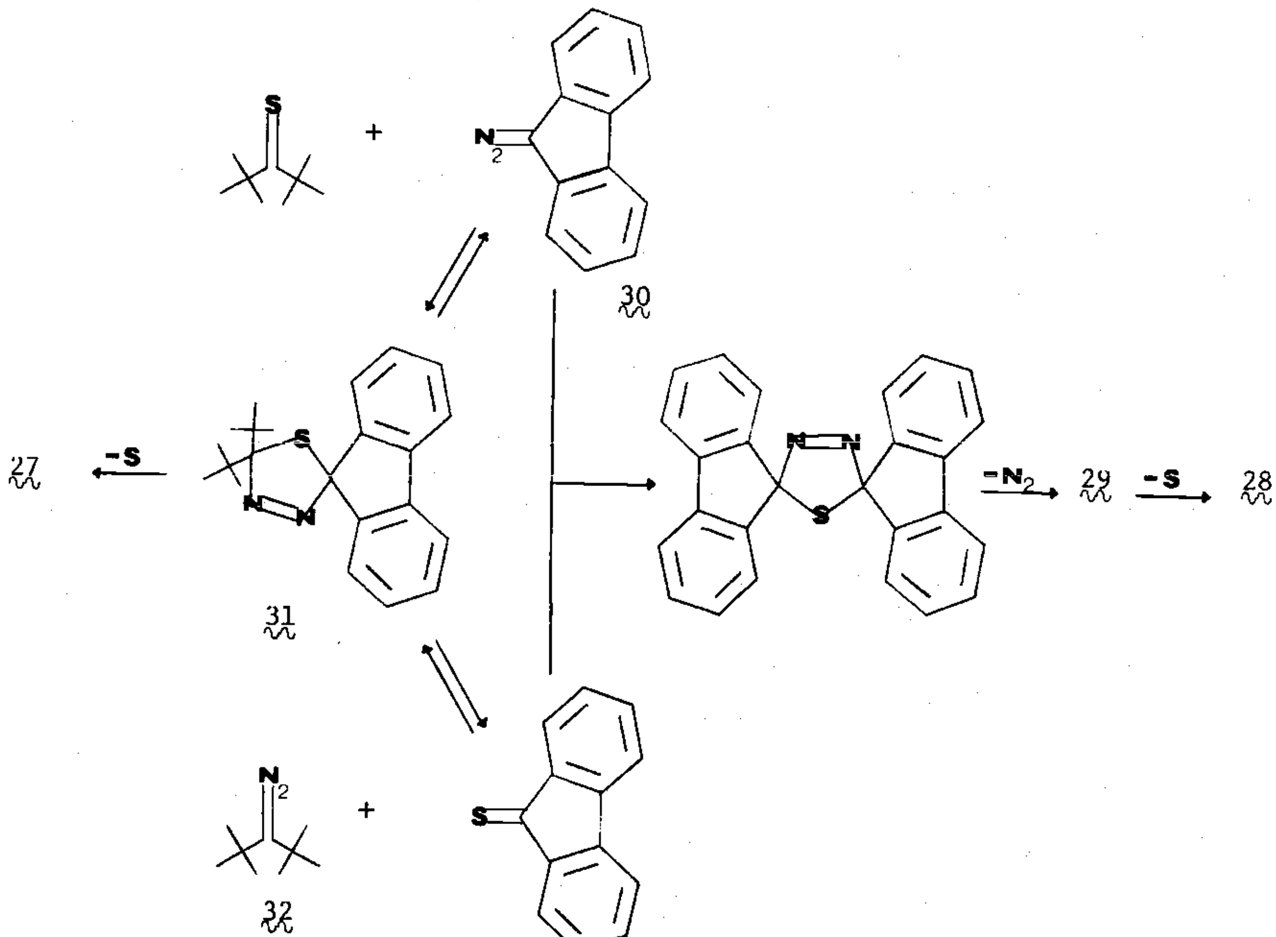


27

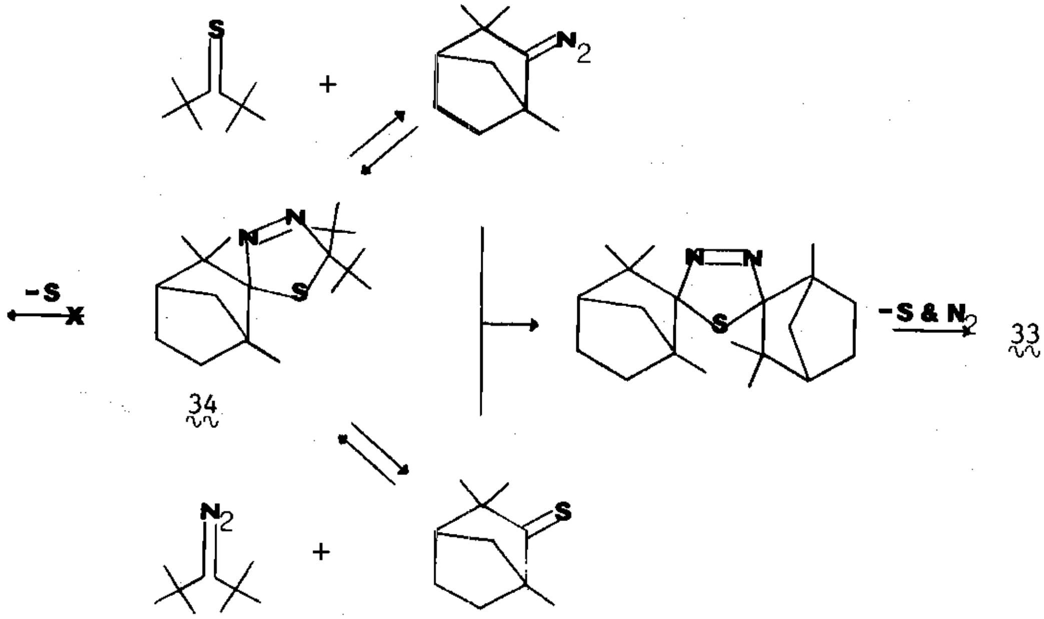
with diazofluorene yielded azine 27, bisfluorenylidene (28) and bis-fluorylidenesulfide (29) and a postualted mechanism (Scheme 6) parallels the mechanism proposed by Barton for the formation of hexamentyl-2,2´-binorbornylidene (33) from the reaction of di-t-butylthione with 2-diazo-1,3,3-trimethylnorborane (Scheme 7). The abscence of azine 35 or 36 supports the proposal that 27 arises from desulfurization of 31 and not from mixed decomposition of 30 and 32.

The reaction of di-t-butylthioketone with ethyl diazoacetate afforded a crystalline compound whose proton nmr showed signals at δ 1.19 (s, 18H), 1.37 (t, 3H), 2.65 (q, 2H), and 6.71 (s, 1H). The ir in solution showed N-H (3425 cm^{-1}), N=N (1550 cm^{-1}) and two carbonyls absorptions (1725, 1709 cm^{-1}). Thin layer chromotography and nmr indicate a single compound while the solution ir spectrum is consistent with a mixture of isomers. Therefore an equilibrium must exist between 37a and 37b in solution.

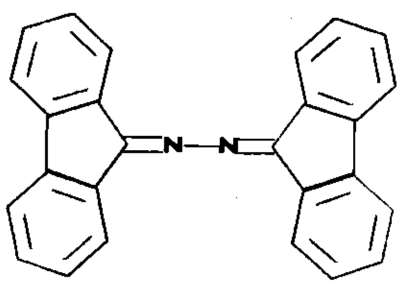
Although diphenyl diazomethane, diazofluorene and ethyl diazoacetate reacted with di-t-butylthioketone at 25°, derivatives of diazomalonic acid reacted only upon heating to 80°. The increased temperature resulted in a product which had extruded nitrogen. Diethyl diazomalonate yielded 38 which showed a single t-butyl group in the proton nmr at δ 1.19 (18H)



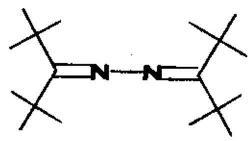
Scheme 6



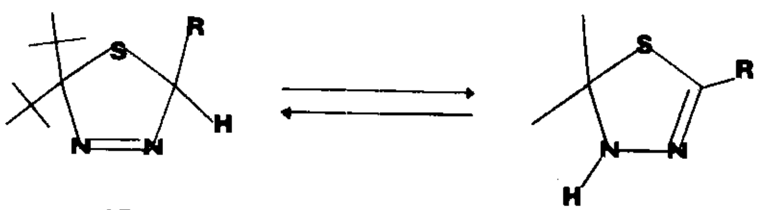
Scheme 7



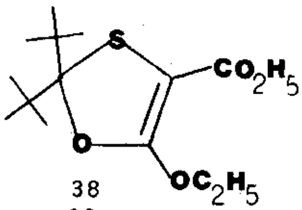
35



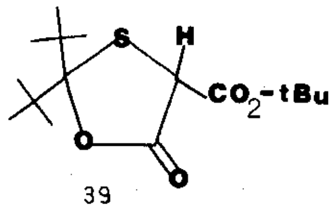
36



37a $R = CO_2C_2H_5$ 37b

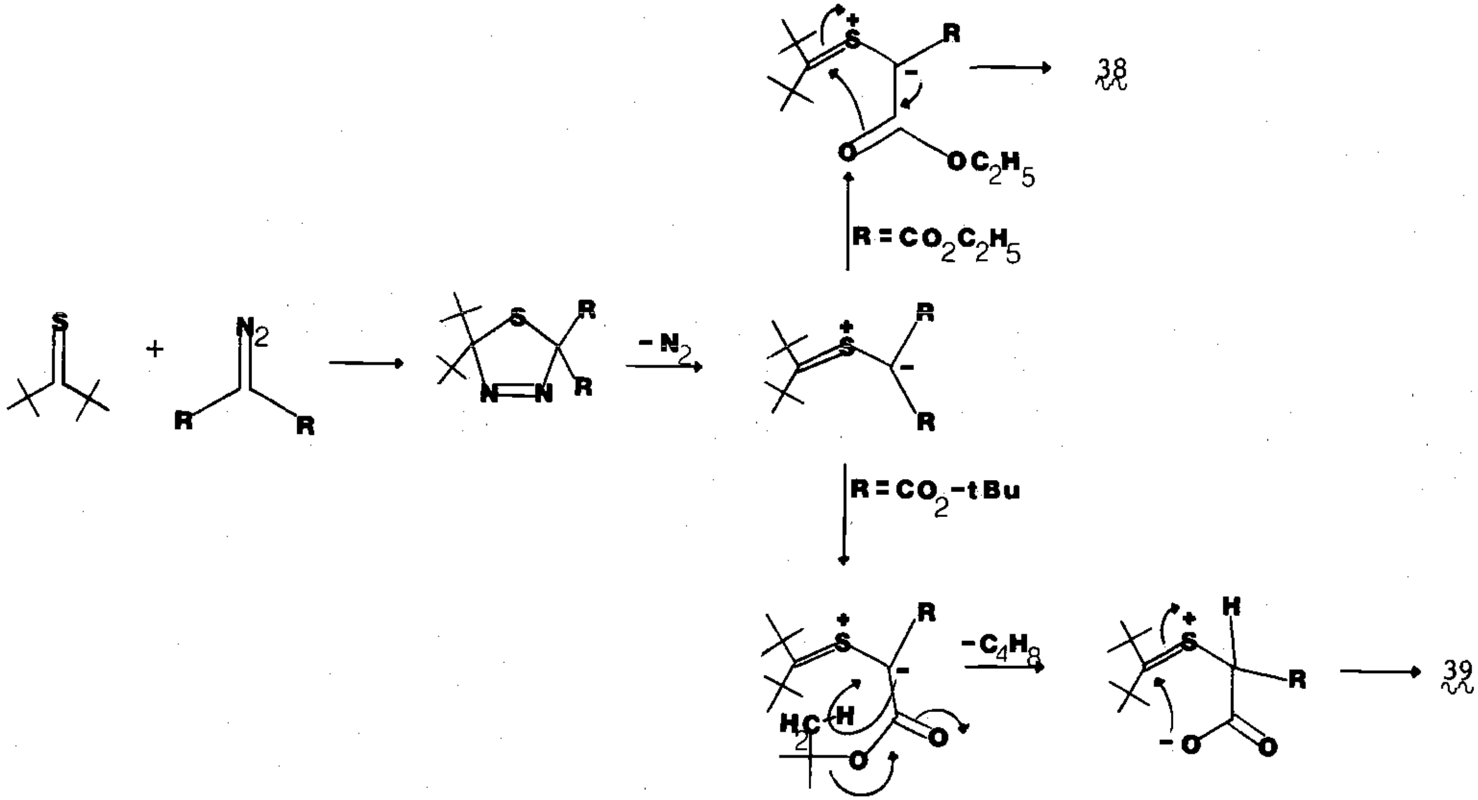


38

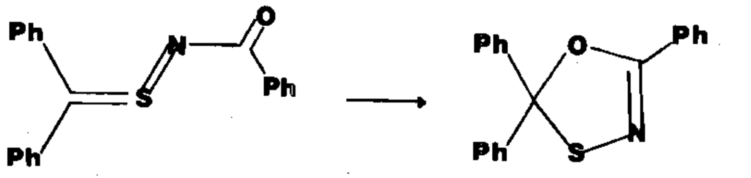


39

and two separate ethyl patterns at 1.24 (t, 3H), 4.90 (q, 2H), and 1.39 (t, 3H), 4.26 (q, 2H). The ir of 38 showed only one carbonyl (1710 cm^{-1}) consistent with an α-β-unsaturated ester. Di-*t*-butyl diazomalonate yielded 39 which showed four singlets in the proton nmr at δ 1.19 (9H), 1.23 (9H), 1.45 (9H), and 4.48 (1H). The ir of 39 showed two carbonyls (1770, 1740 cm^{-1}) consistent with the five membered ring lactone of 39 and the saturated *t*-butylester. The proposed mechanism (Scheme 8) for the formation of 38 and 39 finds precedent in the cyclization of thione *S*-imides with adjacent carbonyls (eq 2).[11] However, the only previously reported reaction of a thione with a diazomalonate yielded an olefin (40) and not a cyclized product (41). The synthetic utility of the cyclization of thiones with diazomalonates to generate oxathiole derivatives has not previously been investigated.



Scheme 8



(2)

40 R = $CO_2C_2H_5$ 41

CHAPTER VI

CONCLUSIONS

While the thermolysis of di-t-butylsulfine (8) proceeded via a first order reaction to yield di-t-butylthioketone and di-t-butylketone, the photolysis of 8 yielded only di-t-butylketone. Both reactions are postulated to proceed via the intermediate 1,1-di-t-butyloxathiirane, the thermal reaction representing the first observed deoxygenation of a sulfine.

A general synthesis of thione S-imides has been developed which required initial chlorination of a thioketone and subsequent reaction with a primary amine. Recent developments in the synthesis of thiones and the availability of primary amines makes this an attractive method for the synthesis of thione S-imides. Di-t-butyl thione S-t-butylimide (15) was synthesized and did not desulfurize thermally to the expected imine. 15 underwent a facile cycloaddition reaction with TCNQ to form a thiadiazole ring.

The reaction of di-t-butylthioketone with a series of diazo compounds was explored. The reaction with diethyl diazomalonate and di-t-butyl diazomalonate yielded cyclized products derived from the intermediate thione S-methylide.

APPENDIX

Structure Factor Table for Cycloadduct 25

K	L	FO	FC
	H= 7		
-6	6	7	6
-5	0	10	10
-5	4	6	5
-5	8	6	6
-4	0	6	5
-4	2	6	5
-4	3	17	16
-3	0	7	5
-3	2	6	6
-3	3	8	8
-3	4	17	16
-3	5	7	7
-3	6	10	9
-2	0	27	28
-2	1	14	14
-2	3	6	4
-2	4	28	29
-2	5	17	17
	H=-14		
1	3	8	7
	H=-13		
-2	1	7	7
2	2	9	9
2	3	7	6
3	3	12	12
3	4	10	7
	H=-12		
-2	3	6	7
0	1	22	21
1	2	13	13
1	3	8	9
1	6	10	8
2	3	10	8
2	4	8	7
2	5	7	5
2	7	9	6
3	3	8	8
3	6	6	3
4	1	10	9
	H=-11		
-4	1	7	5
-4	2	7	6
-2	1	8	6
-1	2	8	9
-1	3	11	9
-1	5	8	7

K	L	FO	FC
-1	6	7	8
0	2	20	21
0	3	10	8
0	4	15	15
0	6	11	11
0	7	9	8
1	2	6	6
1	3	14	15
1	5	6	8
2	2	7	6
2	5	6	6
3	2	8	8
3	5	6	7
4	3	7	6
5	4	8	6
	H=-10		
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-3	2	6	5
-2	1	12	11
-2	3	6	5
-2	4	11	9
-2	5	7	6
-2	6	8	9
-2	8	7	4
-1	1	10	12
-1	2	9	11
-1	5	10	7
-1	6	9	8
0	4	34	33
0	5	6	3
1	1	12	12
1	2	8	9
1	3	9	7
1	4	9	9
1	5	21	22
1	6	10	10
2	2	6	6
2	6	7	7
2	7	7	6
2	12	8	5
3	3	6	3
3	7	9	10
3	8	8	8
4	6	6	5
4	8	7	6
5	5	10	12
	H= -9		
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-3	5	8	7
-2	1	7	6
-2	2	8	8
-2	5	6	5

K	L	FO	FC
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-1	3	19	18
-1	4	12	12
-1	5	12	12
-1	6	11	10
-1	10	6	6
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0	5	29	28
0	6	19	19
0	7	15	15
0	8	11	10
1	2	17	18
1	3	6	6
1	5	14	15
1	6	24	24
1	12	7	5
2	1	8	9
2	2	7	6
2	7	11	12
3	2	9	8
3	3	11	10
3	7	8	6
4	1	7	4
4	5	10	12
4	6	14	15
5	6	10	9
5	7	8	7
6	3	7	4
6	5	6	3
	H= -8		
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-5	2	7	6
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-3	1	9	8
-3	2	7	8
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-2	2	24	25
-2	3	16	17
-2	4	26	25
-2	6	8	7
-2	7	9	10
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-1	2	9	10
-1	3	8	8
-1	4	9	9
-1	5	18	18
0	1	10	12
0	4	7	7
0	5	9	8

K	L	FO	FC
0	7	17	17
0	8	17	15
0	9	6	5
0	11	9	9
1	1	8	10
1	3	15	15
1	4	6	5
1	5	11	11
1	6	17	17
1	9	11	10
1	11	6	7
2	2	8	7
2	3	11	11
2	4	6	6
2	5	5	6
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3	1	8	7
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3	3	6	4
3	4	9	8
3	5	11	9
3	6	17	16
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3	11	9	6
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4	2	9	5
4	4	6	5
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4	6	7	6
4	7	16	17
5	2	10	11
5	3	6	4
5	8	10	11
6	2	6	5
6	3	7	5
6	4	6	4
7	2	6	6
7	7	6	2
	H= -7		
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-4	1	15	18
-4	2	7	7
-4	5	12	12
-4	6	7	10
-4	8	8	8
-4	10	6	4
-3	1	16	17
-3	2	16	16
-3	3	23	23
-3	4	14	12
-3	6	17	17
-3	9	9	8
-2	1	9	9
-2	2	7	6

K	L	FO	FC
-2	4	12	15
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-2	7	8	7
-2	9	8	9
-1	1	8	9
-1	3	20	20
-1	5	12	14
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0	11	8	5
0	13	7	6
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1	3	15	16
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1	5	19	18
1	6	19	19
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2	4	5	7
2	5	13	11
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3	6	15	15
3	7	15	15
4	2	9	8
4	3	8	6
4	4	6	4
4	5	7	9
5	1	18	20
5	2	6	3
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5	4	11	9
5	6	7	3
5	9	8	9
6	3	6	7
7	1	7	6
7	2	6	6
7	8	8	5
8	3	7	4

H= -6

K	L	FO	FC
-6	5	7	5
-5	1	13	13

K	L	FO	FC
-5	2	8	5
-5	4	6	6
-5	5	15	15
-4	1	6	7
-4	2	12	12
-4	3	6	7
-4	4	10	10
-4	5	8	8
-4	6	6	6
-3	2	8	6
-3	3	9	8
-3	4	16	15
-3	5	21	20
-3	8	7	7
-3	10	8	8
-2	2	22	21
-2	3	25	23
-2	5	7	9
-2	7	8	8
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-1	3	8	10
-1	5	5	7
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-1	8	9	10
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0	4	11	12
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0	6	15	13
0	7	10	10
0	8	16	16
0	9	12	14
0	10	17	15
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1	2	30	29
1	3	5	6
1	4	15	16
1	5	17	18
1	6	6	5
1	7	19	19
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2	5	6	5
2	6	20	19
2	7	20	19
2	12	6	2
3	1	4	4
3	2	17	17
3	5	15	14
3	6	8	7

K	L	FO	FC
3	7	12	11
4	1	5	4
4	2	10	10
4	6	5	4
4	8	7	6
4	10	6	7
5	1	23	24
5	5	6	6
6	1	24	26
6	2	21	23
6	3	6	11
6	4	10	13
6	8	6	4
7	1	6	8
7	2	10	11
7	3	6	4

H= -5

K	L	FO	FC
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-1	7	16	15
-1	8	12	13
-1	12	7	6
0	1	8	9
0	3	5	9
0	4	37	35
0	5	22	23

K	L	FO	FC
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0	8	7	7
0	10	8	9
0	13	9	7
1	2	30	29
1	4	8	8
1	5	17	16
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2	3	8	8
2	4	4	1
2	6	21	20
2	7	22	23
2	8	17	18
2	9	12	11
3	1	20	20
3	3	4	3
3	4	7	6
3	6	14	16
3	8	7	6
4	1	10	9
4	3	8	7
4	6	9	9
4	7	6	4
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4	11	8	9
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5	2	18	18
5	4	14	14
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5	12	7	6
6	1	8	10
6	3	19	21
6	4	7	12
6	6	8	10
6	7	6	7
7	2	10	11
7	4	7	7

H= -4

K	L	FO	FC
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-7	3	7	6
-6	1	7	9
-6	2	18	17
-6	3	16	14
-6	4	9	8
-6	8	9	9

K	L	FO	FC
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-5	3	20	20
-5	4	17	18
-5	5	12	12
-4	1	6	6
-4	2	7	6
-4	4	14	16
-4	5	10	12
-4	9	6	8
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-1	11	10	11
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1	3	21	20
1	4	17	14
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1	10	5	2
1	11	6	5
1	12	6	5
1	13	7	7
1	14	10	9
2	1	35	41
2	2	23	25
2	3	10	13
2	4	38	38
2	5	19	18

K	L	FO	FC
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2	8	5	2
2	11	13	12
2	12	8	7
3	2	45	44
3	3	15	17
3	4	14	12
3	5	26	24
3	6	13	12
3	9	10	11
3	10	12	11
4	1	30	32
4	2	15	15
4	3	14	16
4	4	7	8
4	5	13	12
4	6	8	10
4	7	9	9
5	1	4	2
5	5	6	5
5	8	11	10
6	1	11	11
6	2	8	7
6	4	9	8
6	6	14	16
6	7	6	9
7	2	5	8
7	5	12	13
	H =	-3	
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-7	3	8	7
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-6	1	7	6
-6	4	32	31
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-5	3	11	10
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-5	5	17	18
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-4	5	11	11
-4	10	9	8
-3	1	5	7
-3	3	19	19
-3	4	5	4
-3	5	12	11
-3	7	5	5
-3	8	12	14
-2	4	33	31

K	L	FC	FC
-2	5	20	21
-2	8	11	11
-2	9	10	9
-2	10	10	10
-2	11	11	10
-2	12	8	7
-1	1	11	14
-1	2	17	18
-1	4	17	17
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-1	7	6	4
-1	8	5	6
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-1	11	11	13
-1	12	8	6
0	1	37	40
0	2	18	21
0	3	24	22
0	4	29	29
0	5	20	20
0	7	23	21
1	1	43	42
1	2	36	34
1	3	17	19
1	4	5	6
1	5	17	15
1	7	19	20
1	9	14	15
1	11	15	16
1	12	10	9
1	15	10	9
2	1	36	34
2	2	42	44
2	3	66	67
2	4	4	5
2	5	20	19
2	6	26	24
2	7	7	5
2	9	5	4
2	10	9	8
2	13	6	5
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3	5	14	15
3	6	7	7
3	10	10	9
3	11	14	14
4	1	18	16
4	2	14	14
4	3	13	13
4	7	5	4
4	9	8	7

K	L	FO	FC
4	10	7	8
5	1	16	17
5	2	11	11
5	3	9	9
5	4	11	8
5	5	8	8
6	2	6	6
6	4	8	6
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7	7	12	9
	H=	-2	
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-6	5	13	13
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-3	11	7	7
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-2	12	10	9
-1	1	35	33
-1	2	39	38
-1	3	5	4
-1	4	4	1
-1	5	29	26

K	L	FO	FC
-1	6	48	49
-1	7	8	9
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H= 7

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-1	1	32	31
-1	2	5	6
-1	3	6	8
-1	6	9	6
0	0	7	8
0	1	5	4
0	2	6	8
0	3	19	20
0	4	17	17
0	10	8	7
1	0	12	11
1	1	18	19
1	5	25	26
1	11	12	10
2	0	6	9
2	2	8	7
2	4	8	8
2	5	13	12
2	6	9	9
3	2	6	7
3	3	8	7
3	4	10	8
3	5	7	6
3	6	8	5
3	7	9	7
3	8	8	7

K	L	FO	FC
3	9	7	6
4	0	6	8
4	4	7	7
4	5	10	11
5	5	7	7
6	2	10	10
	H=	8	
-6	0	11	15
-6	1	10	12
-6	2	9	9
-6	3	14	17
-5	1	10	14
-5	2	12	12
-4	3	19	21
-4	4	7	7
-4	5	9	6
-4	6	6	5
-4	8	8	9
-3	0	10	10
-3	1	12	13
-3	5	8	6
-3	7	7	7
-2	1	12	12
-2	2	10	8
-2	3	7	7
-1	0	6	6
-1	1	16	14
-1	2	18	17
-1	3	22	22
-1	4	11	10
-1	5	13	13
-1	10	6	6
0	3	5	5
0	4	13	13
0	5	11	11
1	1	10	12
1	2	8	10
1	3	10	11
1	4	6	7
1	5	10	9
1	6	7	6
1	7	10	11
2	1	7	9
2	3	18	18
2	4	13	12
2	7	8	8
2	8	9	8
2	9	7	6
3	1	7	6
3	4	12	12
6	3	8	8

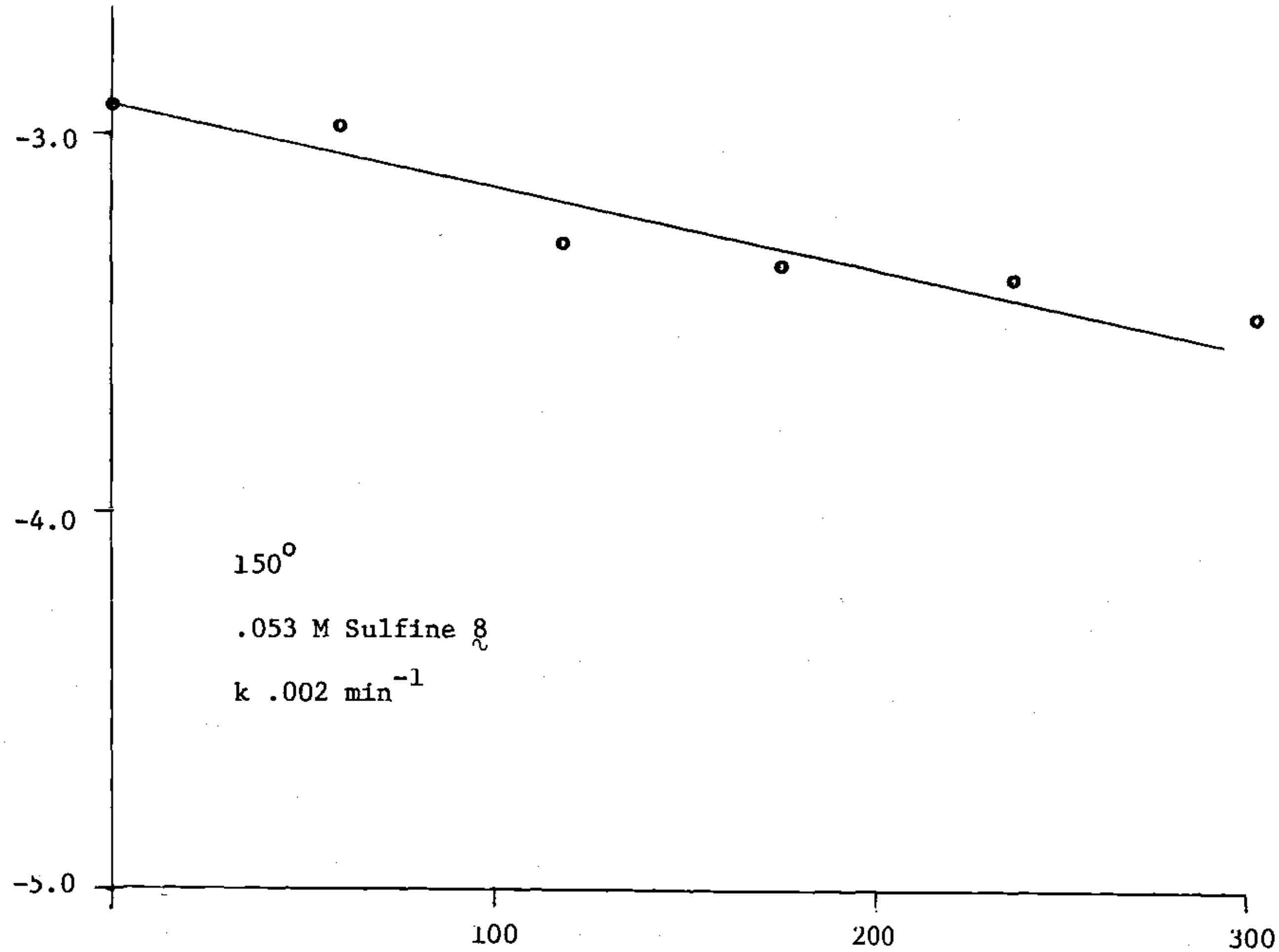
K	L	FO	FC
	H=	9	
-7	0	6	2
-7	1	8	6
-6	3	13	13
-6	4	7	9
-5	1	11	13
-5	3	8	10
-5	4	11	11
-5	7	8	7
-5	9	8	4
-4	4	6	6
-3	2	17	18
-3	3	10	10
-3	9	6	5
-2	3	20	21
-2	4	9	9
-1	0	5	5
-1	2	9	9
-1	4	17	16
-1	6	8	6
-1	7	6	2
0	0	14	14
0	1	14	12
0	3	11	12
0	5	11	9
0	6	11	11
1	0	13	14
1	2	7	9
1	3	14	15
1	4	10	11
1	8	12	12
2	3	6	3
2	4	8	8
2	5	12	10
2	9	7	6
3	5	9	9
4	1	7	6
5	1	6	4
5	3	7	6
	H=	10	
-6	6	9	9
-5	1	6	9
-5	5	9	10
-5	7	6	2
-4	0	6	4
-4	1	12	11
-4	2	16	17
-4	5	8	6
-4	8	8	7
-3	3	10	10
-3	5	8	8
-2	4	14	13
-2	6	7	5

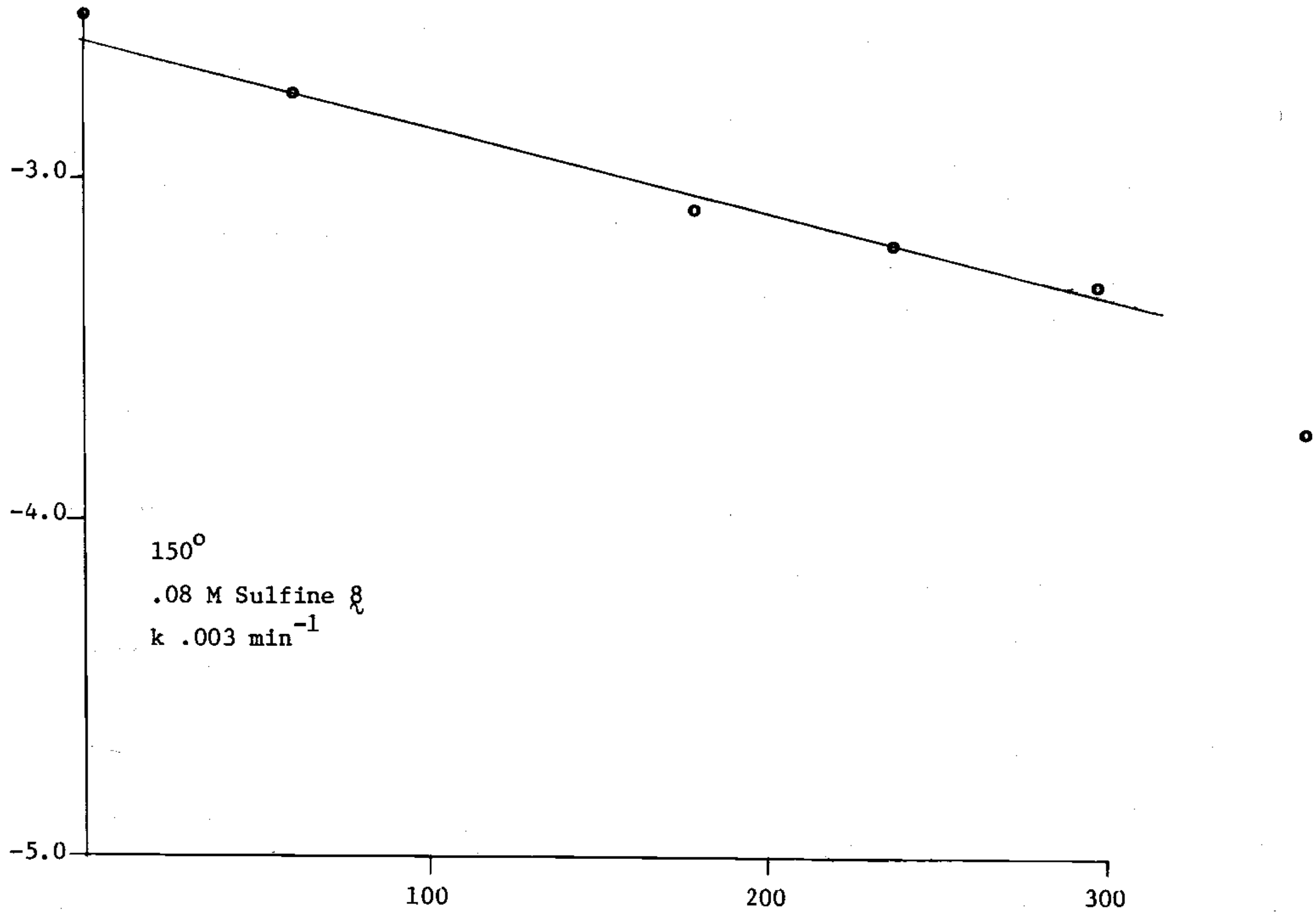
K	L	FO	FC
-1	0	16	17
-1	2	10	10
-1	3	10	9
-1	5	13	13
-1	6	6	3
0	7	8	7
0	8	10	8
1	4	15	13
2	1	6	6
3	0	11	10
4	2	8	8
	H=	11	
-6	0	8	6
-6	6	8	8
-5	1	7	8
-5	2	10	9
-5	7	7	7
-4	2	7	6
-3	1	8	8
-2	0	6	5
-2	4	7	8
-2	5	7	5
-1	1	7	7
-1	3	6	4
-1	6	6	4
-1	7	11	10
0	0	11	12
0	4	7	8
1	0	9	8
3	1	9	8
	H=	12	
-4	1	8	6
-2	3	10	9
-2	7	7	8
-1	1	9	9
0	0	8	8
1	0	9	7
1	2	7	5
	H=	13	
-1	4	7	7
0	0	8	6
0	2	9	7
1	1	9	8
1	3	7	5
	H=	14	
0	2	11	11

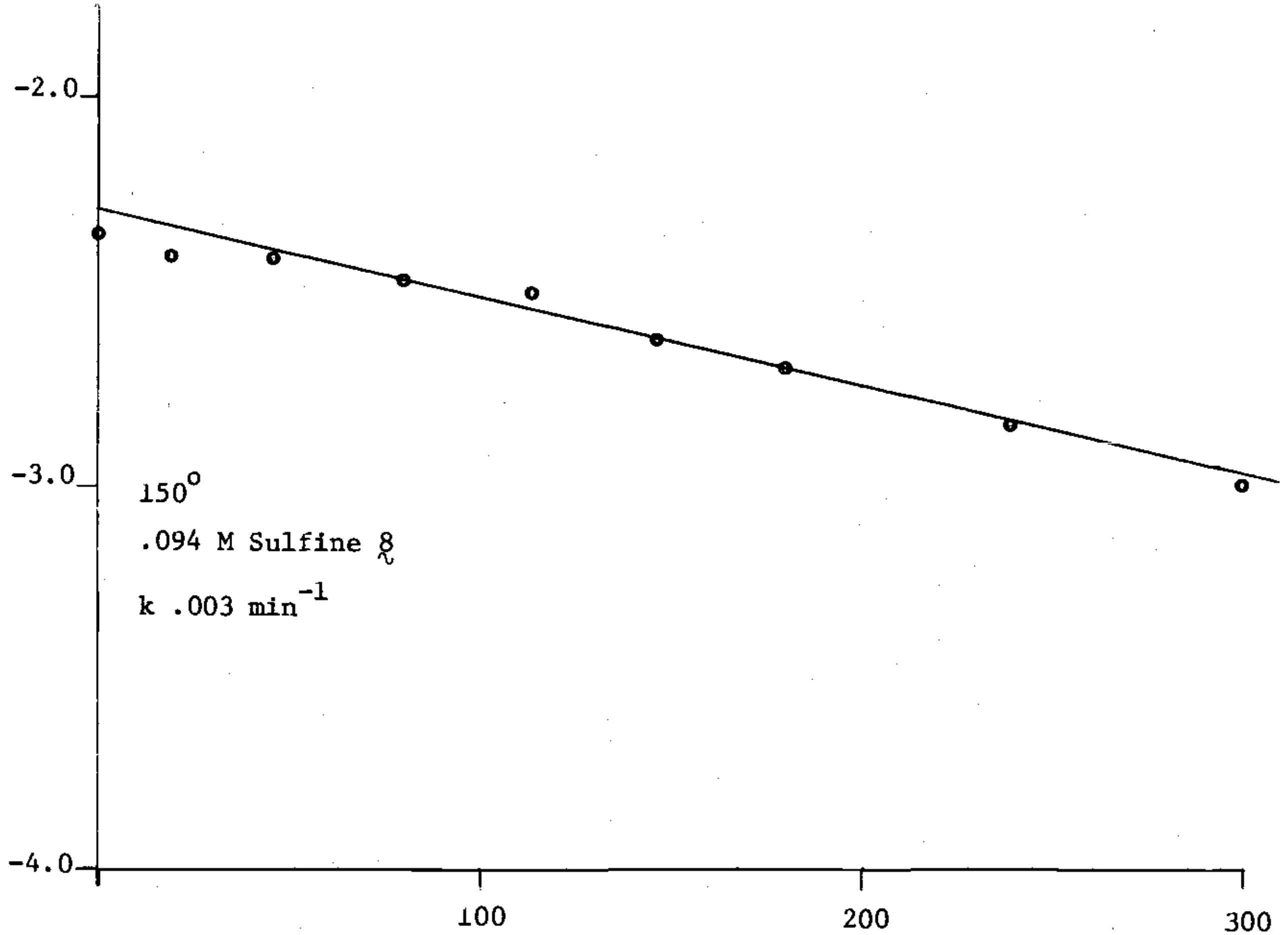
K	L	FO	FC

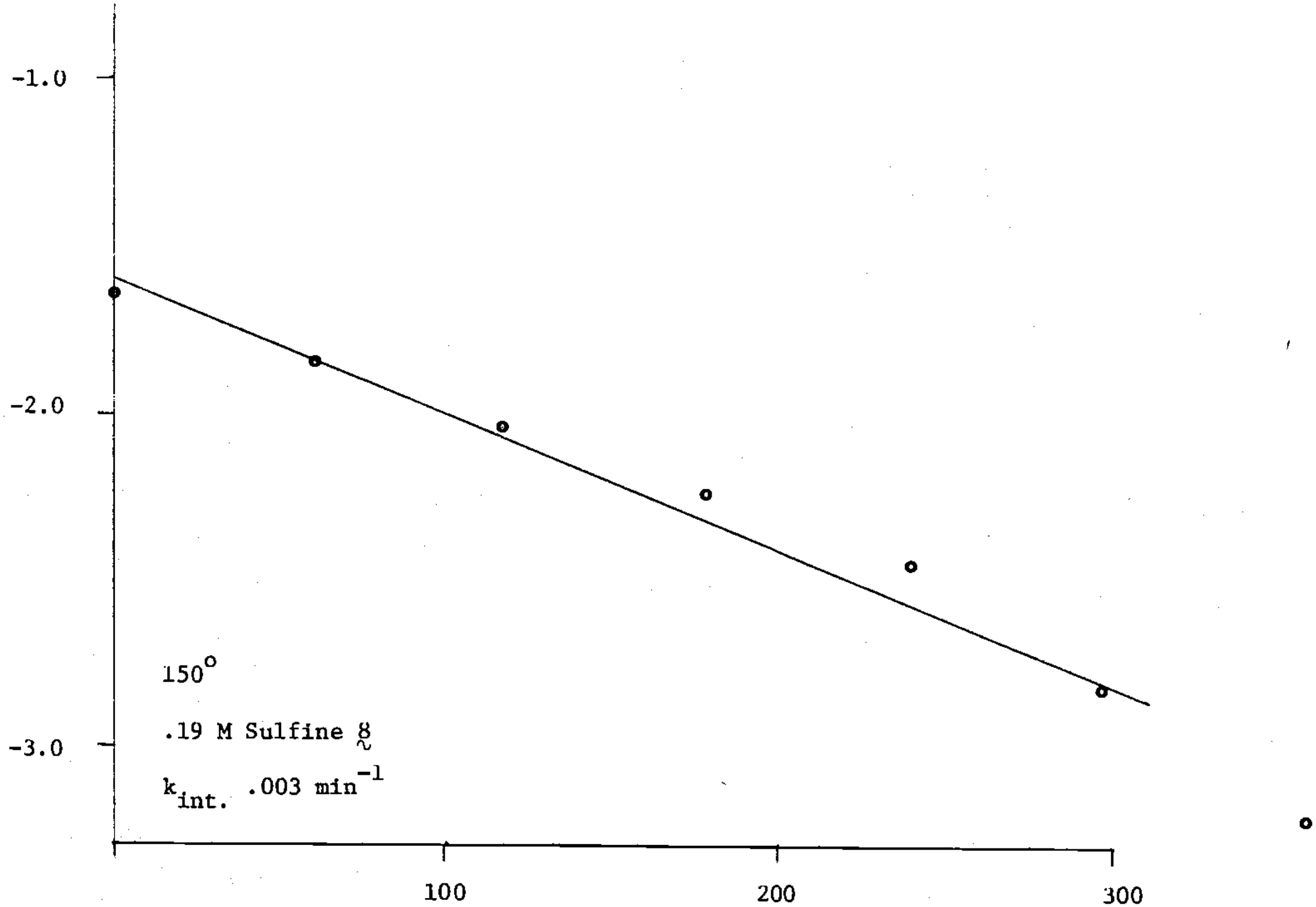
APPENDIX II

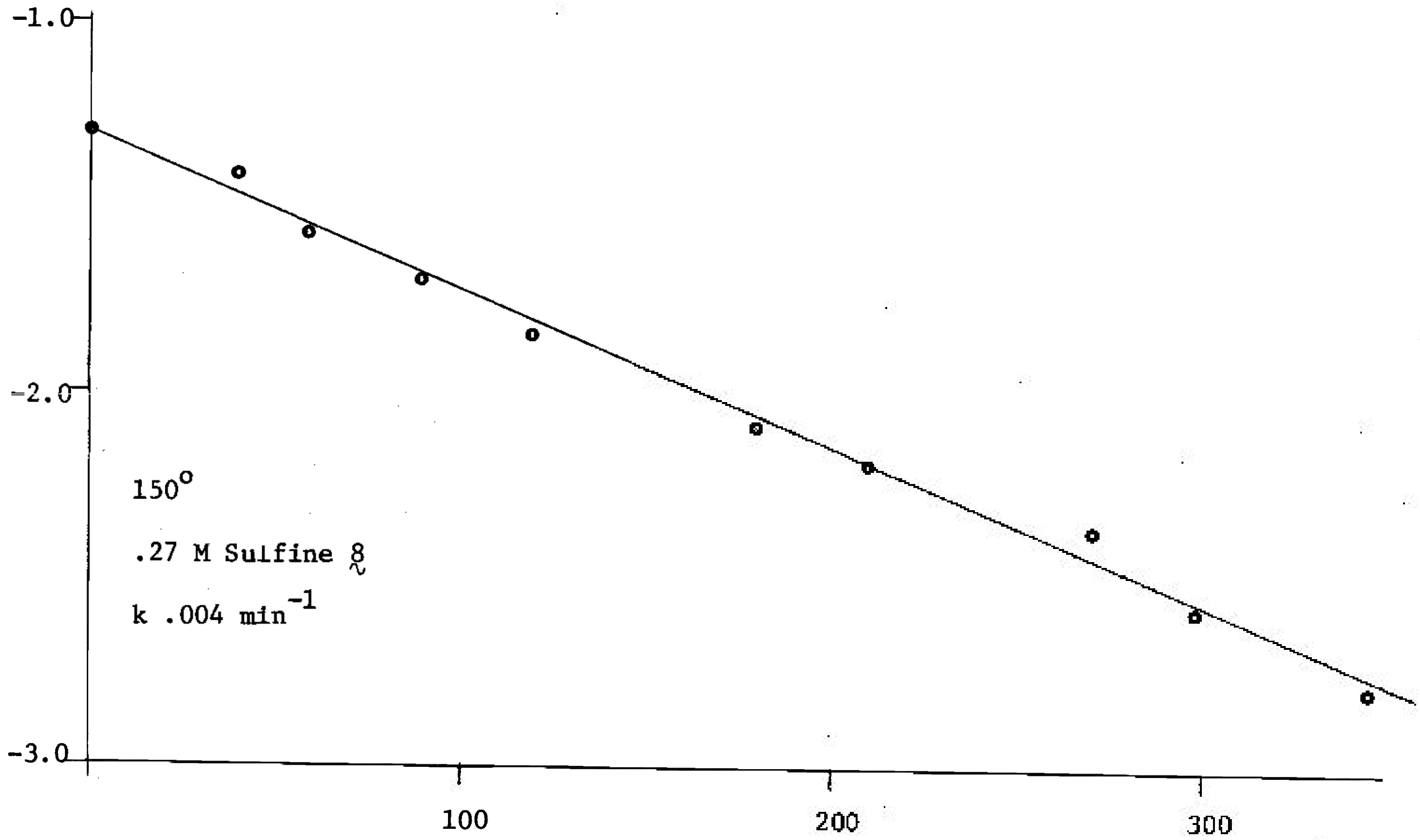
Plot of ln C versus t for the Thermolysis of 8

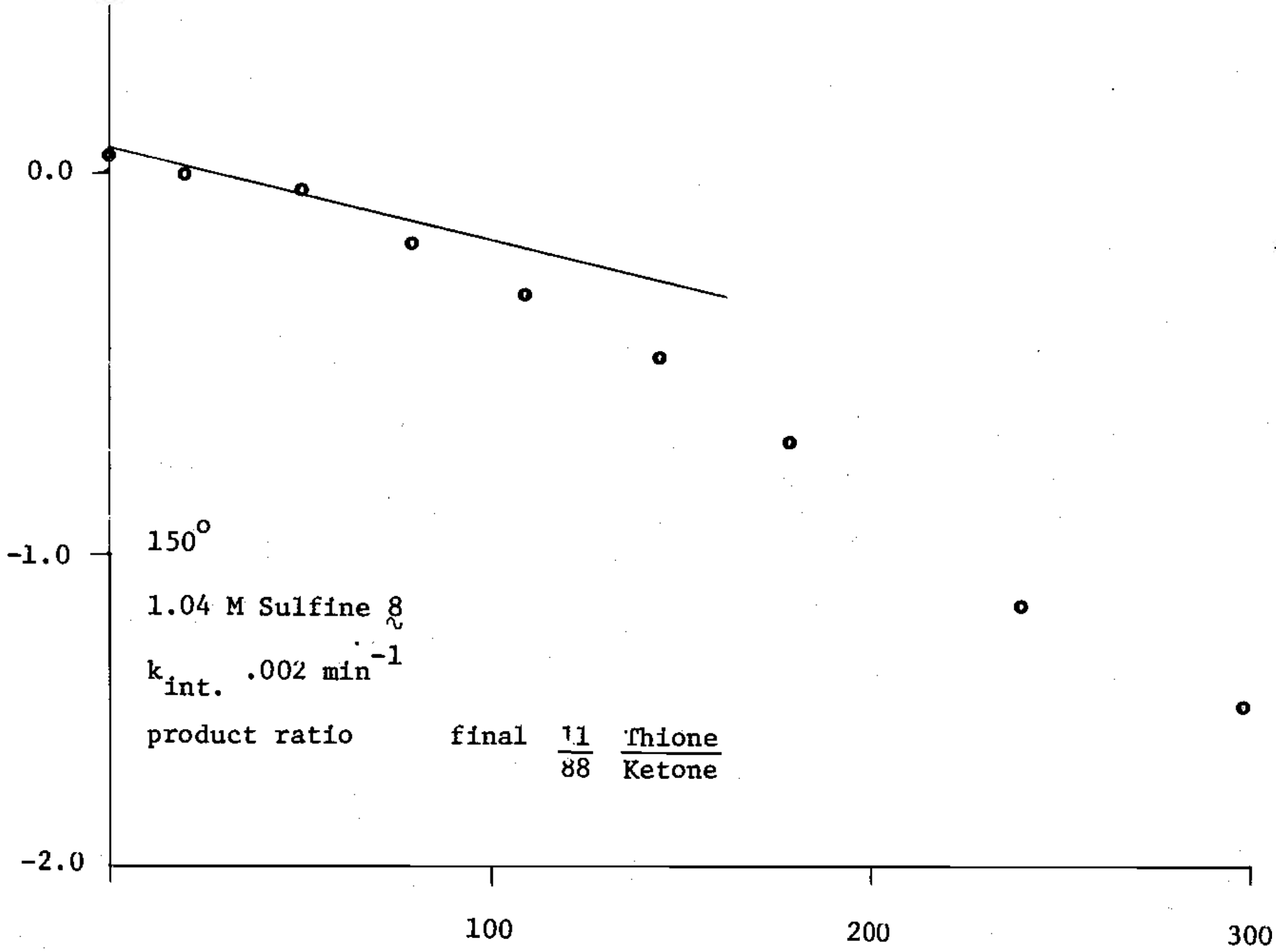

-3.0
-4.0
-5.0
100
200
300
150°
.053 M Sulfine 8
k .002 min⁻¹

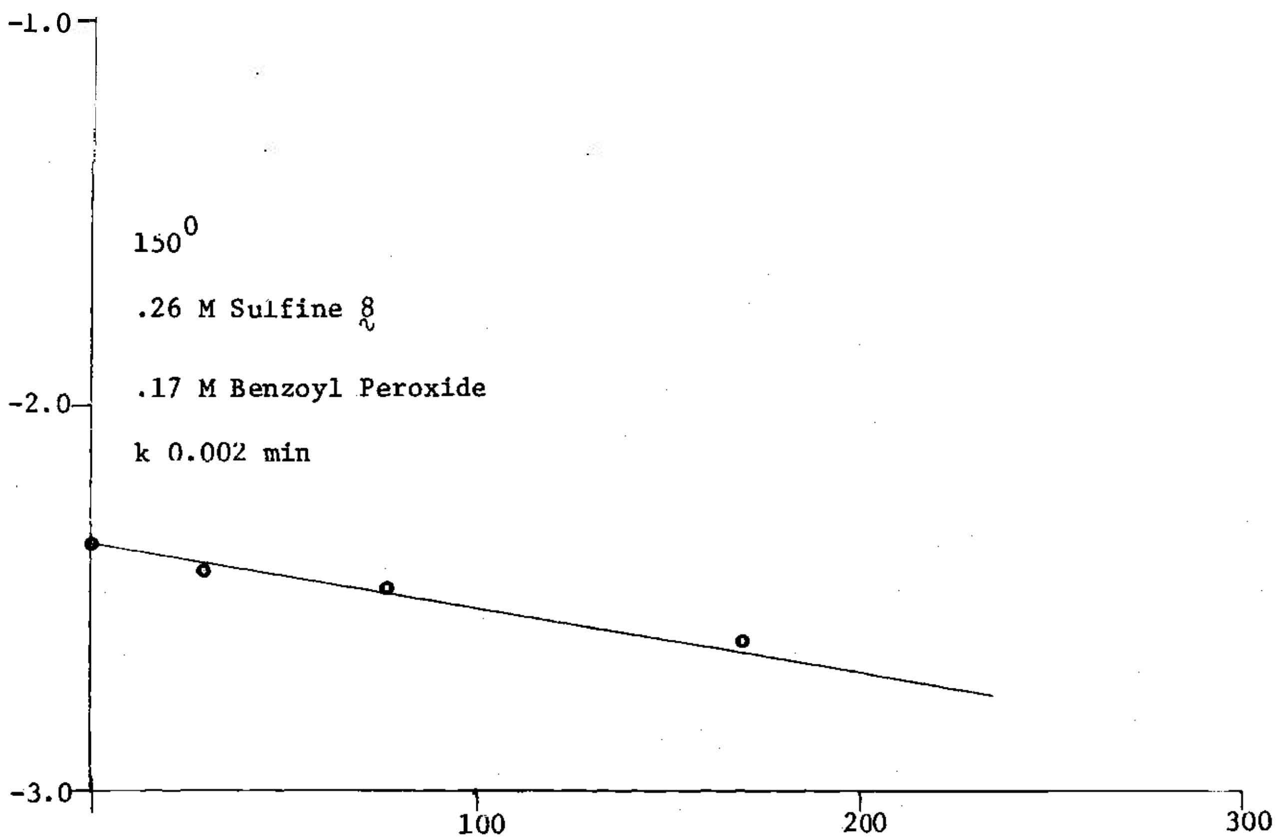

-3.0
-4.0
-5.0
100
200
300
150°
.08 M Sulfine 8
k .003 min-1

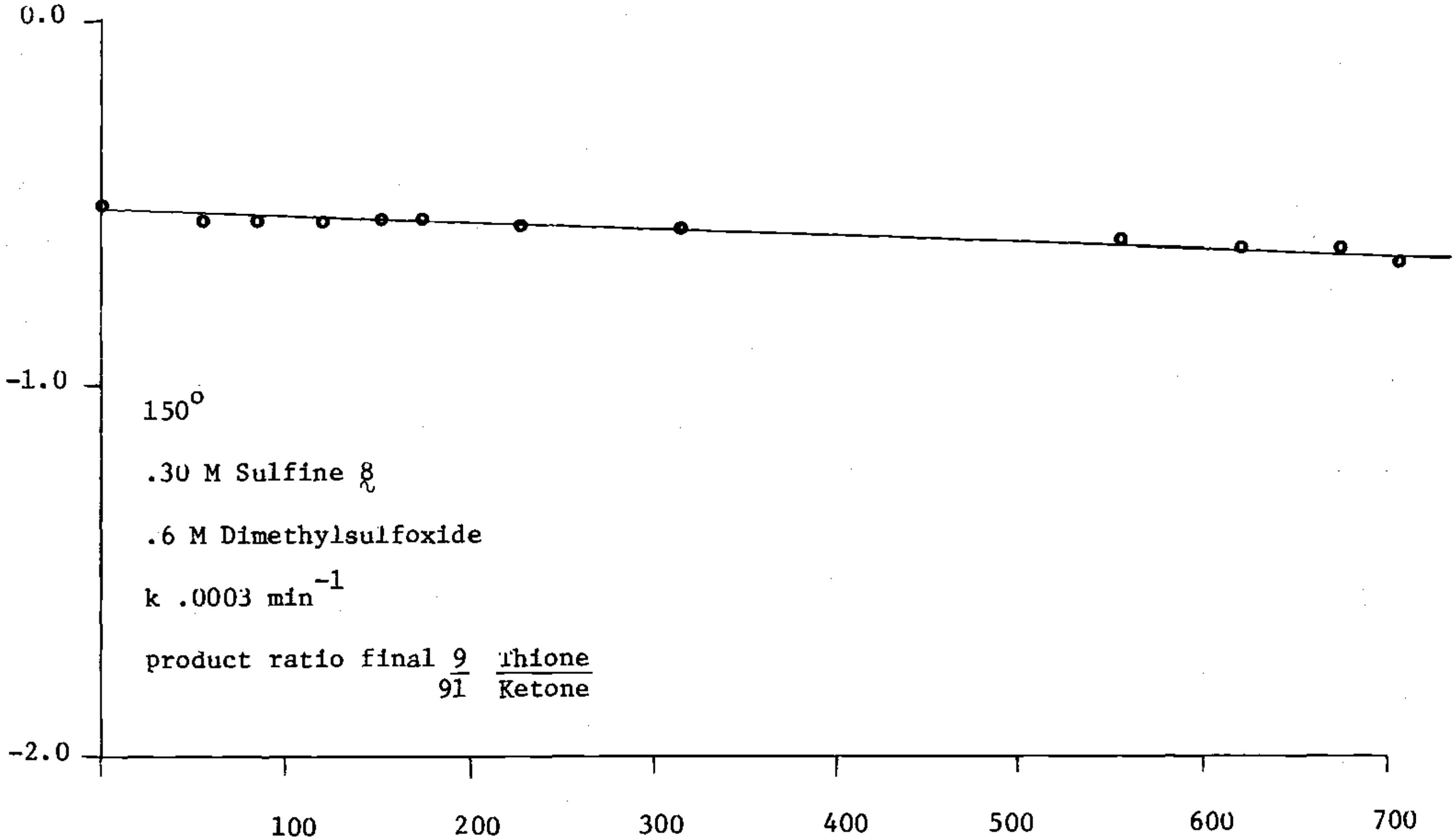

-2.0
-3.0
-4.0
100
200
300
150°
.094 M Sulfine 8
k .003 min-1

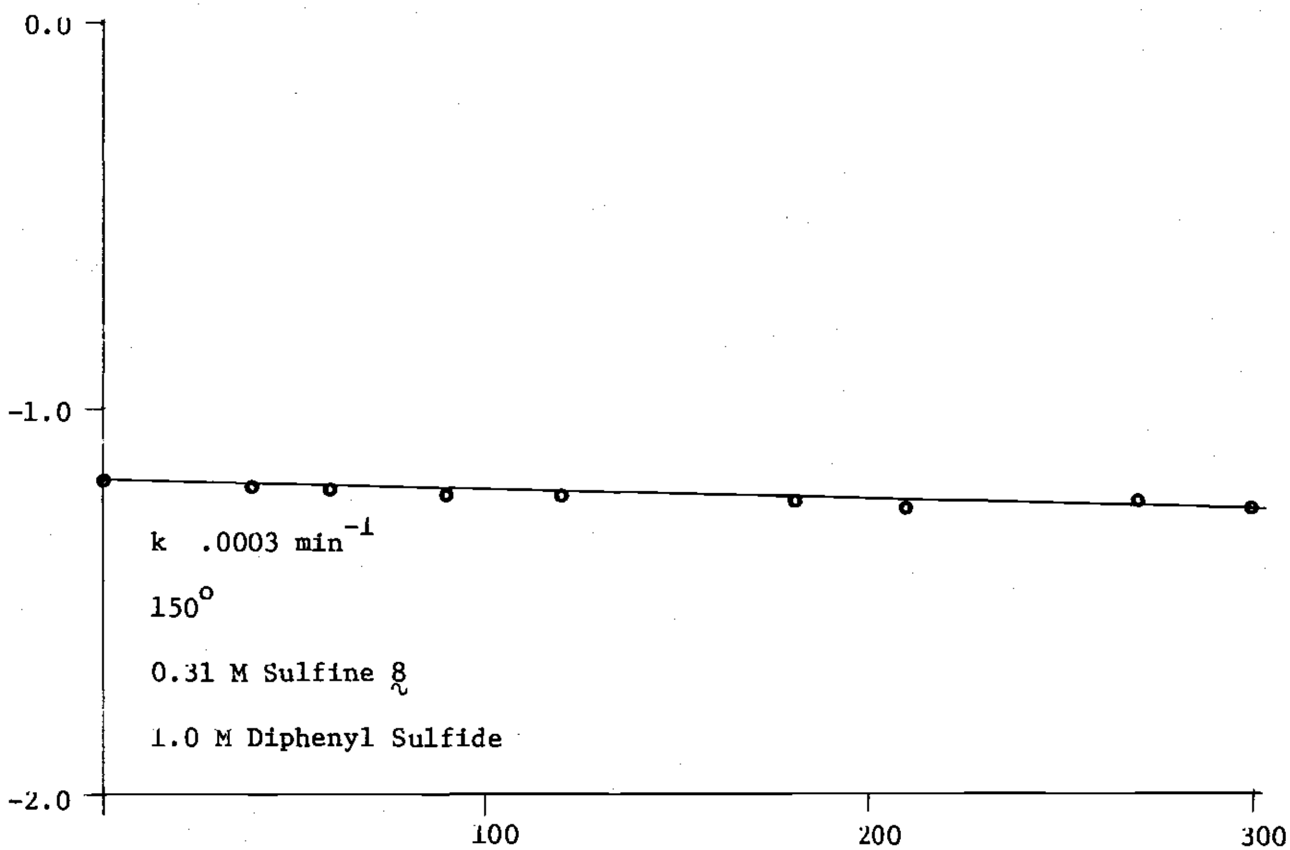

-1.0
-2.0
-3.0
100
200
300
150°
.19 M Sulfine 8
k int. .003 min-1

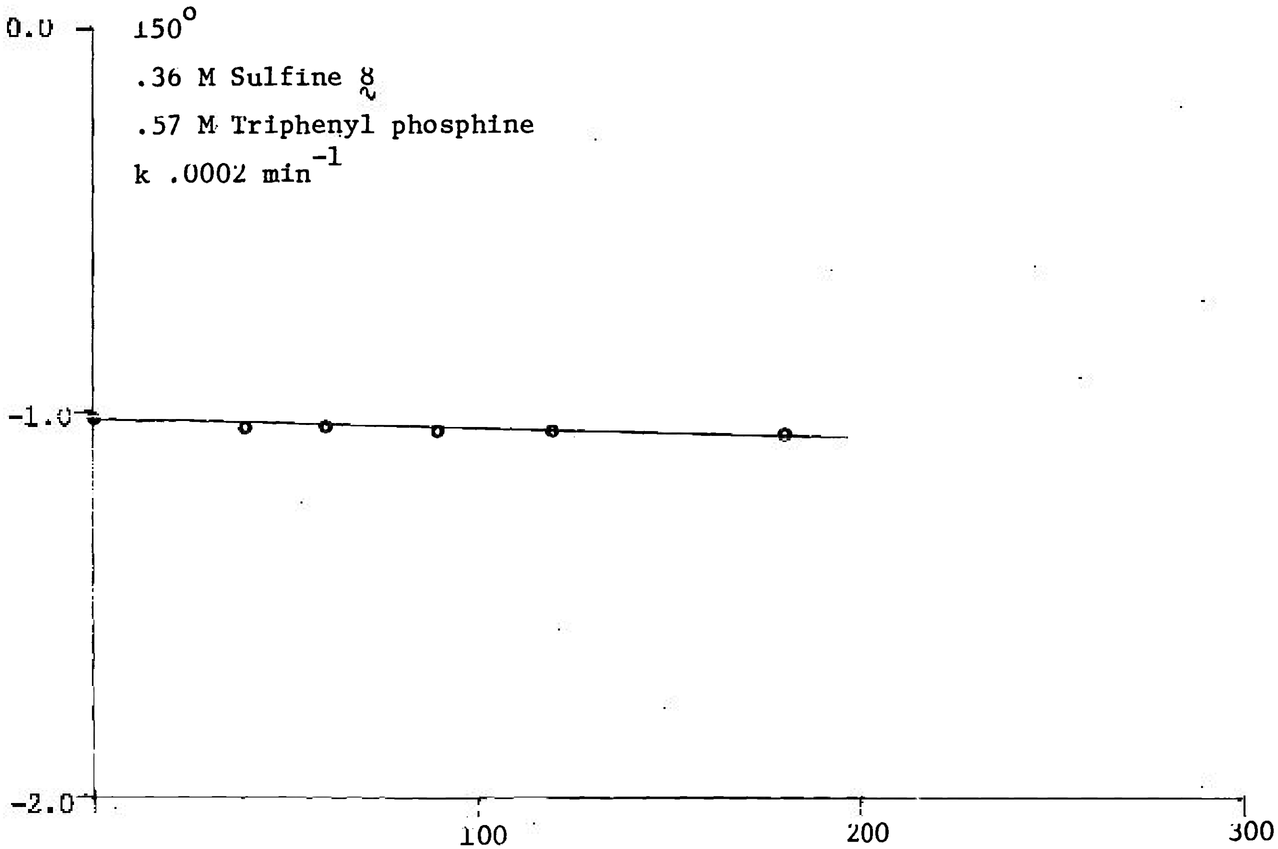

-1.0
-2.0
-3.0
100
200
300
150°
.27 M Sulfine 8
k .004 min-1

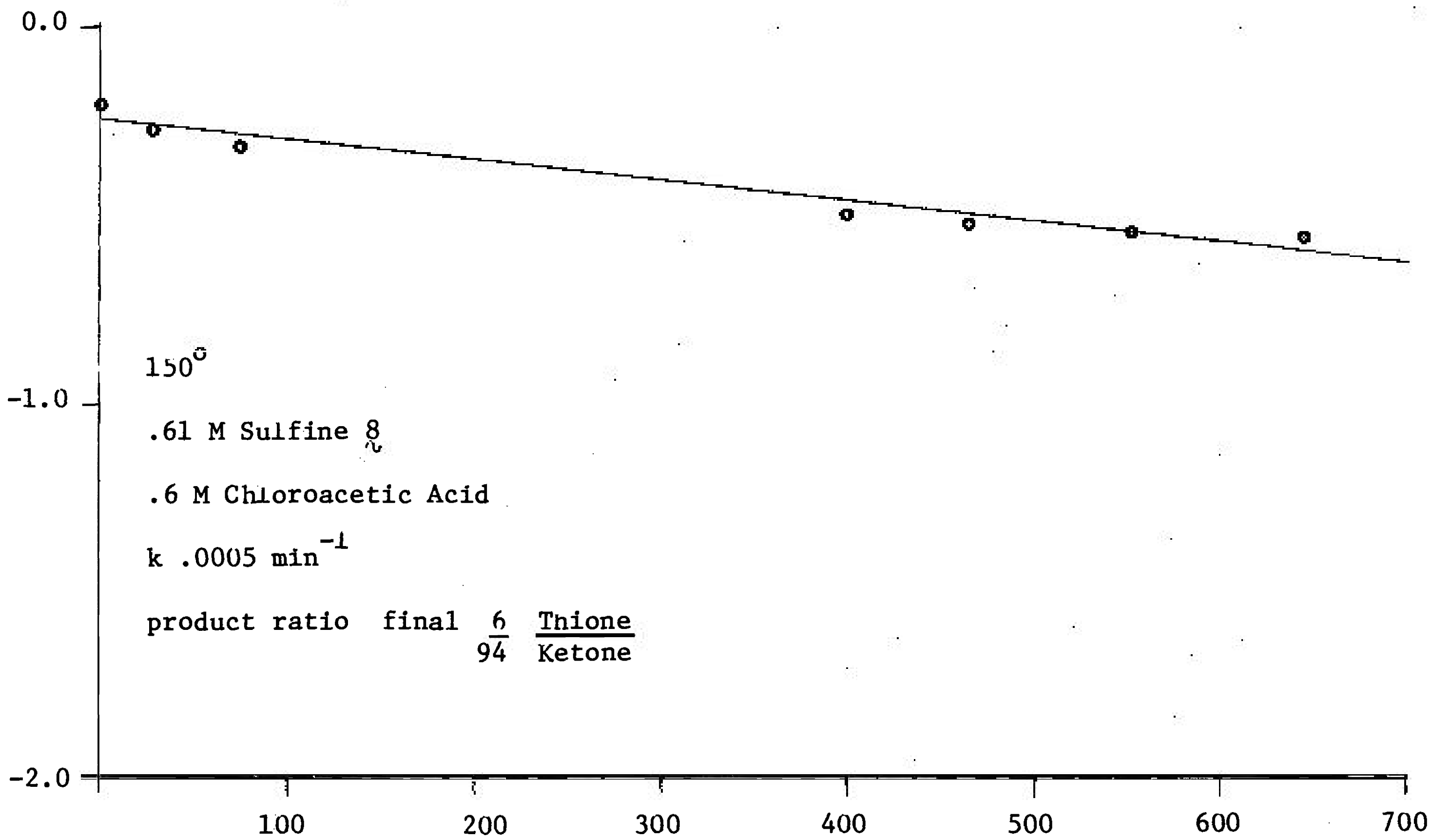

0.0
-1.0
-2.0
100
200
300
150°
1.04 M Sulfine 8
k int. .002 min-1
product ratio final 11/88 Thione/Ketone

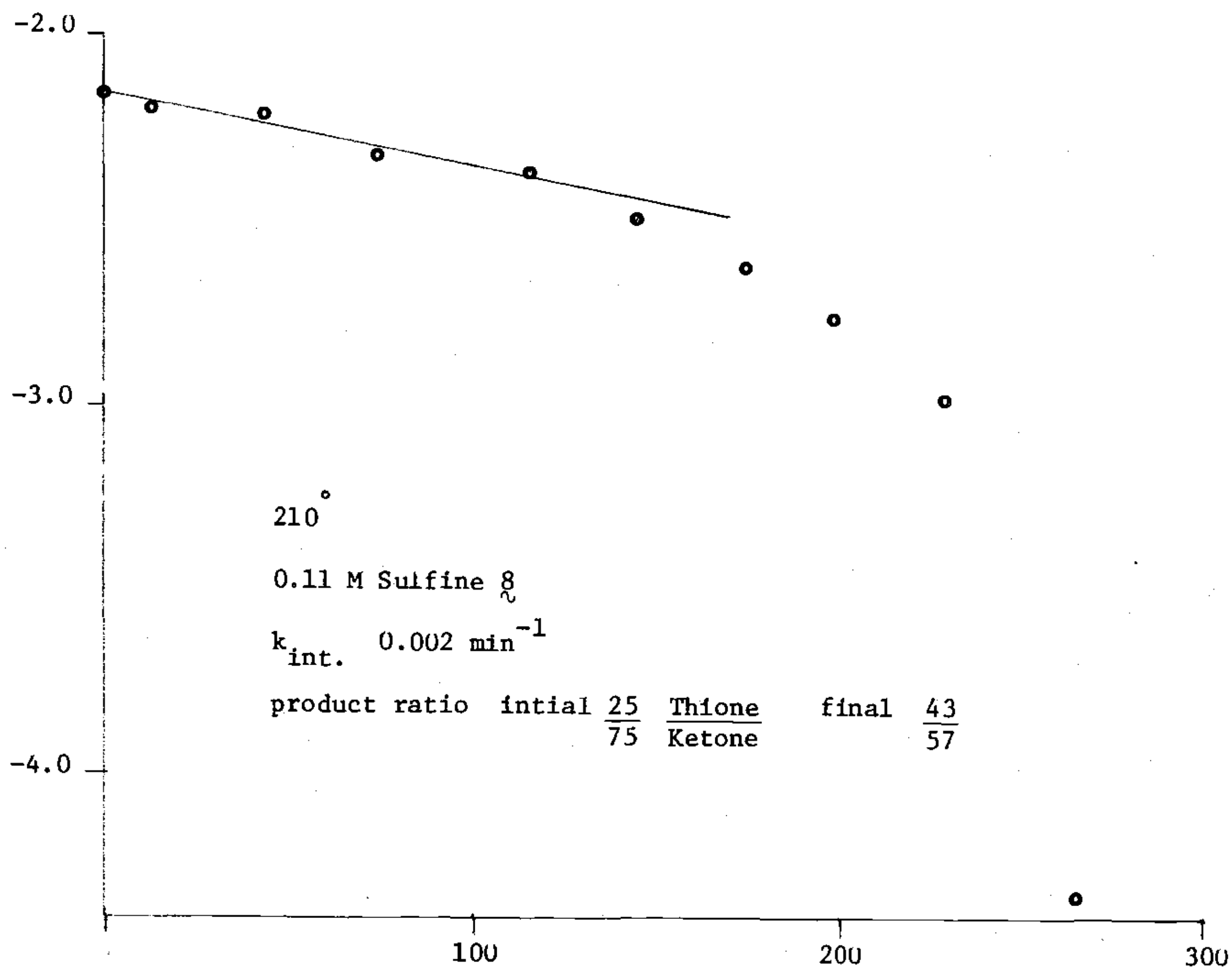

-1.0
-2.0
-3.0
100
200
300
150^0
.26 M Sulfine 8
.17 M Benzoyl Peroxide
k 0.002 min


0.0
-1.0
-2.0
100
200
300
400
500
600
700
150°
.30 M Sulfine 8
.6 M Dimethylsulfoxide
k .0003 min⁻¹
product ratio final 9/91 Thione/Ketone

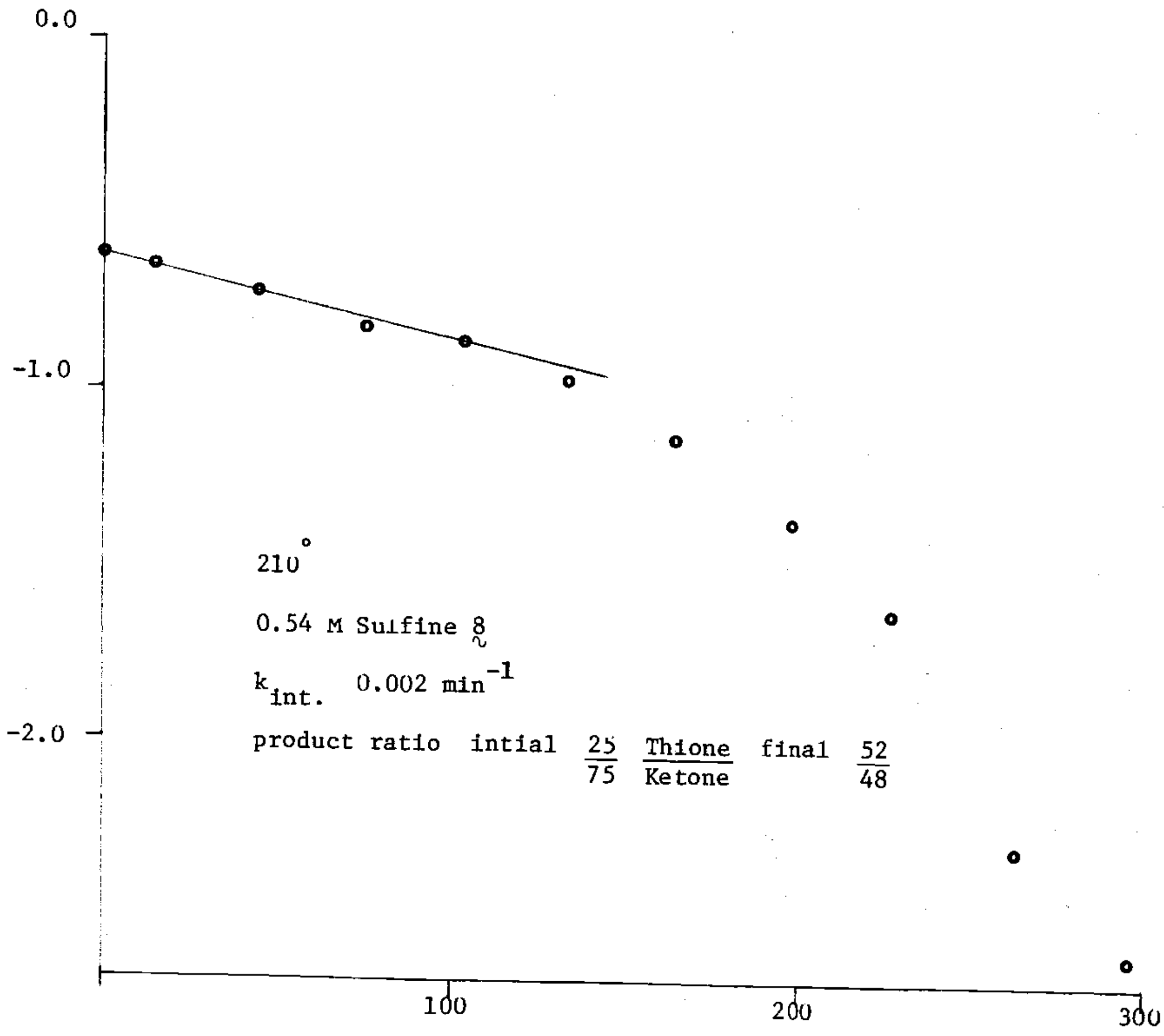

0.0
-1.0
-2.0
100
200
300
k .0003 min^{-1}
150^{o}
0.31 M Sulfine 8
1.0 M Diphenyl Sulfide

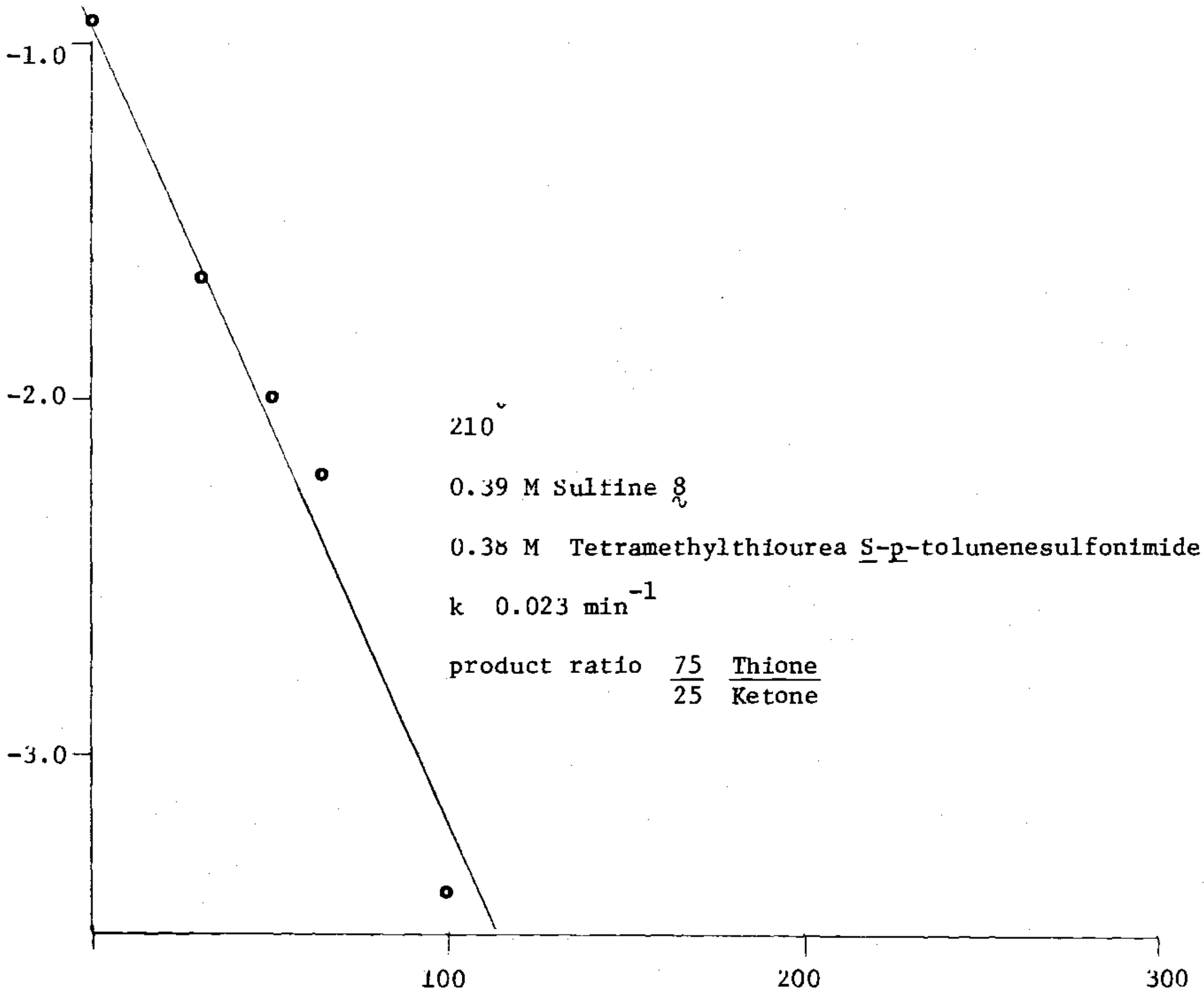

0.0
150°
.36 M Sulfine 8
.57 M Triphenyl phosphine
k .0002 min⁻¹
-1.0
-2.0
100
200
300


0.0
-1.0
-2.0
100
200
300
400
500
600
700
150°
.61 M Sulfine 8
.6 M Chloroacetic Acid
k .0005 min⁻¹
product ratio final 6/94 Thione/Ketone



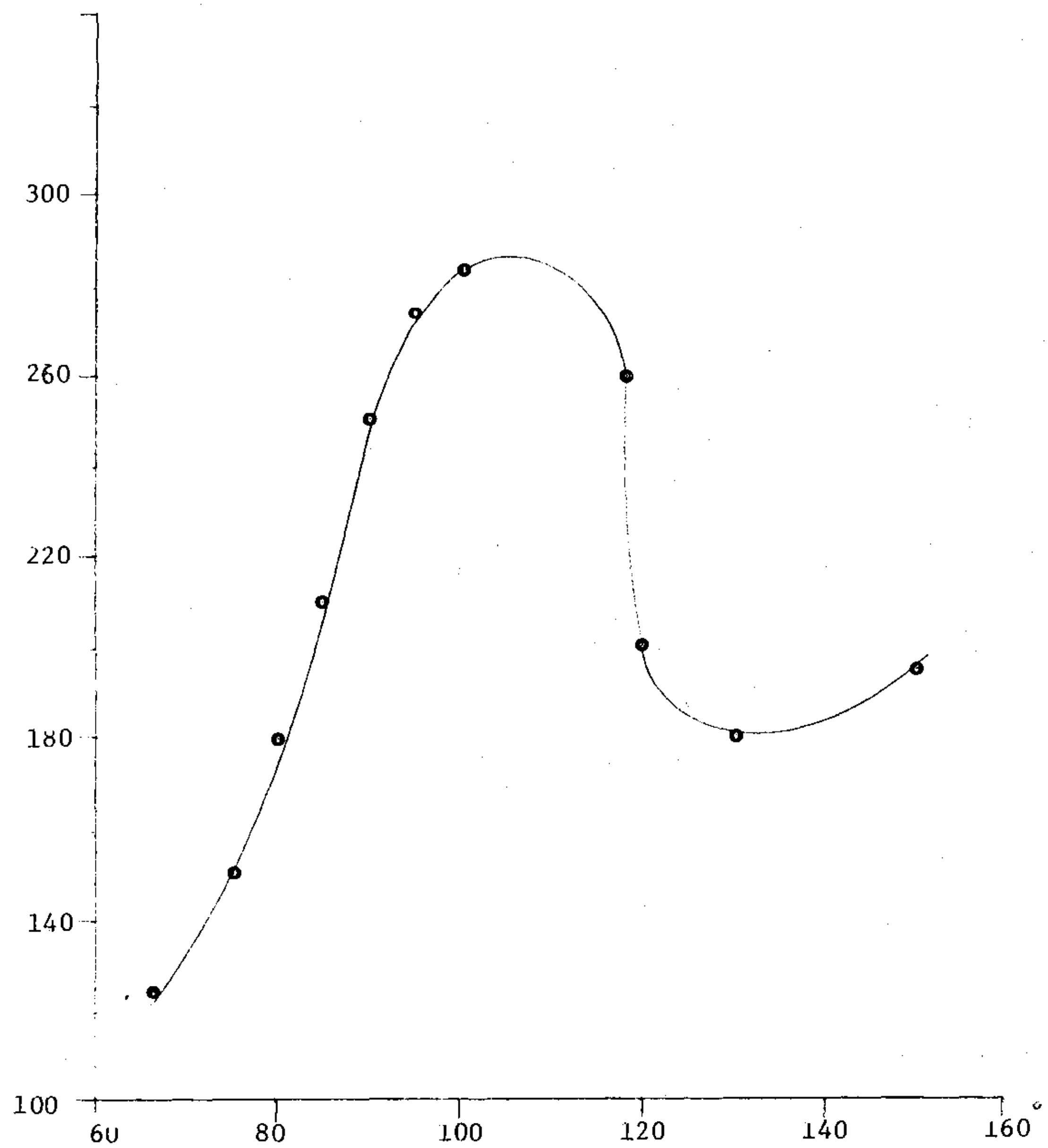
-2.0
-3.0
-4.0
100
200
300
210°
0.11 M Sulfine 8
k int. 0.002 min-1
product ratio intial 25/75 Thione/Ketone final 43/57


0.0
-1.0
-2.0
100
200
300
210°
0.54 M Sulfine 8
k int. 0.002 min-1
product ratio intial 25/75 Thione/Ketone final 52/48


-1.0
-2.0
-3.0
100
200
300
210°
0.39 M Sulfine 8
0.38 M Tetramethylthiourea S-p-tolunenesulfonimide
k 0.023 min^{-1}
product ratio 75/25 Thione/Ketone

APPENDIX III

Plot Of σ Versus θ For Thione S-Imide 18



300
260
220
180
140
100
60
80
100
120
140
160

REFERENCES AND NOTES

1. W. A. Sheppard and J. Diekmann, J. Amer. Chem. Soc., 86, 1891 (1964).

2. B. Zwanenburg, L. Thijs, and J. Strating, Rec. Trav. Chim. Pays-Bas, 86, 577 (1967).

3. B. Zwanenburg, L. Thijs, and J. Strating, Tetrahedron Letts., 4461 (1969).

4. B. Zwanenburg, L. Thijs, and J. Strating, Tetrahedron Letts., 65 (1966).

5. J. B. Bredenberg, E. Honkanen, and A. I. Virtanem, Acta Chem. Scand., 16, 513 (1962).

6. A. M. Hamid and S. Trippett, J. Chem. Soc. (C), 1612 (1968).

7. M. Ohoka, et. al., J. Org. Chem., 40, 3540 (1975).

8. J. P. Synder, J. Amer. Chem. Soc., 96, 5005 (1974).

9. L. Carlsen, N. Harrit, and A. Holm, J. Chem. Soc. Perkin I, 1404 (1976).

10. R. H. Schlessinger and A. G. Schultz, Tetrahedron Letts., 4513 (1969).

11. E. M. Burgess and H. R. Penton, Jr., J. Amer. Chem. Soc., 95, 279 (1973).

12. H. R. Penton, Jr., "The Chemistry of Thione S-Imides," Thesis, Georgia Institute of Technology, 1973.

13. S. Tangerman and S. Oae, Tetrahedron Letts., 1159 (1972).

14. A. Tangerman and B. Zwanenburg, Tetrahedron Letts., 259 (1972).

15. W. J. Middleton, J. Org. Chem., 31, 3731 (1966).

16. R. W. Kellogg, S. Wassenaar, and J. Butler, J. Org. Chem., 37, 3045 (1972).

17. A. J. Arduengo and E. M. Burgess, J. Amer. Chem. Soc., 98, 5020 (1976); 98, 5021 (1976).

18. P. Gronski and K. Hartke, Tetrahedron Letts., 4139 (1976).

19. D. H. Barton, F. S. Guzier, and I. Shahak, J. Chem. Soc. Perkin I, 1794 (1974).

20. D. H. Barton, T. G. Bock, M. R. Britten-Kelly, and Frank S. Guzier, J. Chem. Soc. Perkin I, 2076 (1976).

21. S. Holm and A. Senning, Tetrahedron Letts., 2389 (1973).

22. D. Paqwer, Int. J. Sulfur Chem. B, 7, 269 (1972).

23. N. Latif and I. Fathy, J. Org. Chem., 27, 1633 (1962).

24. A. P. Krapcho, D. R. Rao, M. P. Silvon, and B. Abegaz, J. Org. Chem., 36, 3885 (1971).

25. J. A. Kaufmann and S. J. Weininger, Chem. Comm., 594 (1964).

26. F. D. Greene, J. C. Stonewell, and W. R. Bergmark, J. Org. Chem., 34, 2254 (1969).

27. A. Ohno, K: Nakamura, Y. Nakazima, and S. Oka, Bull. Chem. Soc. Japan, 48, 2403 (1975).

28. A. Ohno, K. Nakamura, M. Yohamo, and S. Oka, Chem. Letts., 983 (1975).

29. W. G. Phillips and K. W. Ratts, J. Org. Chem., 37, 3819 (1972).

30. I. Crossland, private communication, 1976.

31. A. Senning, et. al, Chem. Ber., 109, 1069 (1976).

32. A. J. Arduengo and E. M. Burgess, J. Amer. Chem. Soc., 99, 2378 (1977).

33. H. O. Kalinowski and H. Kessler, Angew. Chem. Int. Ed. Engl., 13, 90 (1974).

34. J. A. Pople, Mol. Phys., 7, 301 (1963); M. Karplus and J. A. Pople, J. Chem. Phys., 38, 2803 (1963).

35. R. B. Bates and G. A. Wolfe, J. Amer. Chem. Soc., 90, (1968).

36. E. M. Burgess, H. R. Penton, Jr., and M. C. Pulcrano, unpublished work.

37. B. Zwanenburg and J. Strating, Quart. Rep. Sulfur Chem., 5, 79 (1970).

38. B. Zwanenburg, A. Wagenane, L. Thijs and J. Strating, J. Chem. Soc. Perkin I, 73 (1973).

39. Numbers in parentheses indicate estimated standard deviation in the least significant digit(s).

40. The reported cell parameters are for the reduced cell.

41. Programs used were: R. Dewar and A. Stone's FAME; Peter Main and M. M. Woolfson's MULTAN light atom program; Zalkin's FORDAP fourier summation program; Iber's NUCLS modification of K. O. Martin, W. R. Busing and H. A. Levy's least squares program; FINDH is a geometric prediction program which calculates atomic positions based on expected bond length, hybridization and position of other bonded atoms; and various other local porgrams.

42. M. J. S. Dewar, R. C. Bingham, and D. H. Lu, J. Amer. Chem. Soc., 97, 1285 (1975).

43. D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, New York, 1966.

VITAE

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