that it also contained some chloroform, and an acidic gas (presumably HBr) was detected when the reaction flask was opened.

Adduct **2** distilled at 111–112° (0.08 mm). Its 60-MHz nmr spectrum included narrow multiplets at −5.19 (m, 1 H, HCBr) and −3.16 ppm (m, 1 H, $HCCCl_3$) which were not resolved at 100 and 220 MHz. Decoupling experiments led to the assignment of coupling constants summarized in Figure 1. *Anal.* Calcd for $C_{11}H_{16}BrCl_3$: C, 39.50; H, 4.82. Found: C, 39.75; H, 4.98.

The lower boiling components of the product mixture were not cleanly resolved by distillation, but the nearly pure distillate fractions were identified by nmr spectra. Compound **3** was the principal component in the fraction distilling at 56–60° (0.08 mm): nmr −5.72 (bm, 2 H, C=CH) and −4.52 ppm (bm, 1 H, HCBr). Compound **4** was obtained mixed with **2** and was identified by its nmr absorption at −4.67 ppm (m, HCBr); a small authentic sample for comparison was prepared in solution by the addition of hydrogen bromide to **1**.

Addition to Cycloheptene.—Irradiation of a mixture of cycloheptene (1.0 mol) and $BrCCl_3$ (4.0 mol) for 16 hr led to the formation of three products. In addition to lower boiling products tentatively identified as 3-bromo-1-cycloheptene [20% yield; decolorized Br_2 in CCl_4; ir 3.31 and 6.06 μ (olefin); nmr −5.83 (bm, 2 H, C=CH) and −4.90 ppm (m, 1 H, HCBr)] and trichloromethylcycloheptane [23% yield; did not decolorize Br_2 in CCl_4; ir 12.9–13.0 μ (intense, CCl_3)], the adduct, *cis*-1-bromo-2-trichloromethylcycloheptane, was obtained (26% yield) at 89–103° (0.1 mm). It was characterized by its ir (12.95 μ, intense, CCl_3) and nmr [C_6D_6, −4.78 (m, 1 H, HCBr) and −3.27 ppm (bm, 1 H, $HCCCl_3$)] spectra. The narrow multiplet absorption for HCBr was not resolved at 220 MHz.

Anal. Calcd for $C_8H_{12}BrCl_3$: C, 32.54; H, 4.37. Found: C, 32.89; H, 4.21.

Treatment of a sample of this adduct with a deficiency of potassium hydroxide in mixed solvent as described for the cyclohexene adduct led to a single dehydrohalogenation product, 1-bromo-2-dichloromethylenecycloheptane [ir 6.2 and 10.85 μ ($C{=}CCl_2$); nmr −5.15 ppm (m, HCBr), no absorption for C=CH], which was not separated from unconsumed adduct.

Addition to Cyclopentene.—A mixture of cyclopentene (0.18 mol) and $BrCCl_3$ (0.71 mol) afforded an 84% yield of *trans*-1-bromo-2-trichloromethylcyclopentane: bp 60° (0.05 mm); nmr −4.46 (m, 1 H, HCBr), −3.69 (m, 1 H, $HCCCl_3$), and −2.96 ppm (bm, 6 H, CH_2). Gc analysis of the product mixture revealed the presence of three minor products of significantly shorter retention time than the adduct; these products were not further characterized but are presumably hydrogen-abstraction products corresponding to those obtained from cyclohexene. When a portion of the adduct was treated with a deficiency of potassium hydroxide in mixed solvent as described for the cyclohexene adduct, it was partially dehydrochlorinated to 1-bromo-2-dichloromethylenecyclopentane: ir 6.23 and 11.1 μ ($C{=}Cl_2$); nmr −4.9 ppm (nm, HCBr). Gc analysis indicated that a single dehydrohalogenation product had been formed.

Addition to Indene.—When a mixture of indene (0.215 mol) and $BrCCl_3$ (0.86 mol) was irradiated for 6 hr, the nmr spectrum of the mixture revealed only a single component containing hydrogen, *trans*-1-bromo-2-trichloromethylindane: bp 125–129° (0.1 mm); nmr −5.72 (d, J = 3.2 Hz, 1 H, HCBr) and −4.02 ppm (m, 1 H, $HCCCl_3$).

Addition to Norbornene.—Periodic nmr spectra revealed that the addition of $BrCCl_3$ (0.64 mol) to norbornene (0.16 mol) was essentially complete after 15 min. Distillation of the mixture afforded a 95% yield of the adduct, *trans*-2-*endo*-bromo-3-trichloromethylnorbornane: bp 90–95° (0.4 mm); n^{25}D 1.5516; nmr (C_6D_6) −4.06 (m, 1 H, HCBr), −2.63 (q, 1 H, $HCCCl_3$), −2.33 (m, 1 H, H-4), −2.19 (m, 1 H, H-1), −2.1 to −1.68 (bm, 2 H, H-5 *endo* + H-6 *endo*), −1.5 to −1.0 (bm, 3 H, H-5 *exo* + H-6 *endo* + H-7 *syn*), and −0.92 ppm (dq, 1 H, H-7 anti).

Anal. Calcd for $C_8H_{10}Cl_3Br$: C, 32.85; H, 3.45. Found: C, 33.01; 3.64.

Registry No.—Bromotrichloromethane, 75-62-7; *cis*-1-bromo-2-trichloromethylcyclohexane 17831-07-1; *trans*-1-bromo-2-trichloromethylcyclohexane, 17831-06-0; **2**, 19640-04-1; *cis*-1-bromo-2-trichloromethylcycloheptane, 19640-05-2; *trans*-1-bromo-2-trichloromethylcyclopentane, 19640-06-3; *trans*-1-bromo-2-trichloromethylindan, 19640-07-4; *trans*-2-*endo*-bromo-3-trichloromethylnorbornane, 19640-08-5.

Laser Photolysis of 2-Chloro-2-nitrosobutane. Kinetics and Mechanism

LINDA CREAGH[1] AND ISAAC TRACHTENBERG

Texas Instruments Inc., Dallas, Texas 75222

Received August 26, 1968

The kinetics and mechanism of the photolysis of 2-chloro-2-nitrosobutane have been investigated using the 6328-Å emission from helium–neon lasers. Concentration, oxygen, and solvent have been found to affect the mechanism and kinetics of the photodecomposition. The use of a laser as light source simplified experimental problems and reduced total irradiation time so that complications from slow dark reactions were reduced. Selective production of 2-chloro-2-nitrobutane occurred on photolysis in the presence of oxygen.

The photochemistry of 2-chloro-2-nitrosobutane and similar compounds has been previously investigated[2,3] and reviewed.[4-6] Products of the photolysis in methanol of *gem*-chloronitrosoalkanes have been reported to be 2-butanone oxime, 2,3-butanedione monoxime, and a compound with $C_8H_{16}O_3N_2 \cdot HCl$ as the molecular formula,[2b] but Baldwin and Rogers[3] isolated a compound ($C_8H_{16}O_2N_2HCl$) which was shown to have a dinitrone structure. For 4-chloro-4-nitrosovaleric acid and 2-chloro-2-nitroso-1,4-diphenylbutane, Mitchell and coworkers[2a] found the primary products of the photolysis in methanol to be the respective oxime hydrochlorides. Kosinski[5] contended since experiments were carried out using light absorbed by the nitroso chromophore that the initial step of the photolysis must be the activation of the nitroso group and then its splitting off. A major role for the solvent was postulated. Artemiev[7] considered the initial step to be the formation of chlorine and nitrosoalkyl radicals. These radicals then participated in further reactions.

The photolysis of 2-chloro-2-nitrosobutane was reexamined to clarify the mechanism of the photodecom-

---

[1] Address inquiries to this author at Texas Woman's University, Box 3686, TWU Station, Denton, Texas 76204.

[2] (a) S. Mitchell, K. Schwarzwald, and G. K. Simpson, *J. Chem. Soc.*, 602 (1941); (b) S. Mitchell and J. Cameron, *ibid.*, 1964 (1938).

[3] J. E. Baldwin and N. H. Rogers, *Chem. Commun.*, 524 (1965).

[4] B. G. Gowenlock and W. Luttke, *Quart. Rev.* (London), **12**, 321 (1958).

[5] M. Kosinski, *Lodz. Towarz. Nauk., Wydzial III, Acta Chim.*, **9**, 93 (1964).

[6] J. H. Boyer, NASA-CR-79491, 1966, NASA Access N-67-11725.

[7] A. A. Artemiev and A. A. Stvelcova, *Khim. Nauka i Promy.*, **3**, 629 (1958).

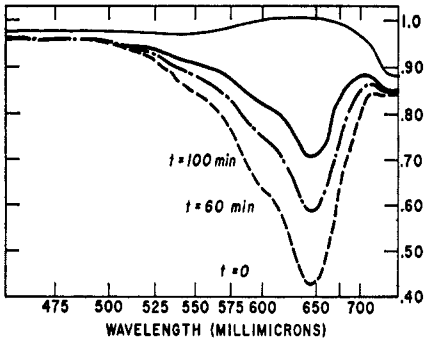


Figure 1.—Change in transmission of 2-chloro-2-nitrosobutane solution on irradiation (methanol, absence of oxygen).

position and to develop techniques for using lasers in photochemistry. Although it was not expected that the low power laser would produce photochemical effects different from other monochromatic light sources, it was anticipated that greater selectivity in products would be observed because of the narrow band width of the exciting light. The effect of coherence was presumed to be unimportant in this case. One of the major advantages of using a laser light source is the high-power density. Ordinary light sources usually provide intensities on the order of 10^{13} quanta/cm^3 sec.[8] An unfocused 3-mW helium–neon laser offers intensities greater than 10^{17} quanta/cm^3 sec. In a 1.0-cm cell containing 10^{-2} *M* solutions of 2-chloro-2-nitrosobutane, the change in absorption throughout a typical run was small so that the Lambert–Beer approximation for photobleaching systems gave accurate results.[9] The relatively high power density not only simplified the calculations but reduced the experimental time resulting in elimination of most interference from slow dark reactions that have been reported[2] to occur.

Experimental Section

Light sources were a Spectra Physics helium–neon laser Model 122 with emission at 6328 Å TEM$_{00}$ with beam diameter of 0.7 mm at $1/e^2$ points and a Spectra Physics hilium–neon Model 125 with emission at 6328 Å TEM$_{09}$ and a beam diameter of 2.0 mm at $1/e^2$ points. The detector was a Spectra Physics Model 401 power meter connected to an E. H. Sargent Model SR recorder. Beckman DK-2 and Perkin-Elmer 250 spectrophotometers were used to record ultraviolet and visible spectra. Infrared spectra were determined on a Perkin-Elmer 337 infrared spectrophotometer equipped with a specular reflectance attachment. An F & M Model 700 gas chromatograph with dual flame and electron capture detectors and F & M Model 200 gas chromatograph with flame and themistor detectors were used in analysis of reactants and products. An AEI MS 7 mass spectrometer was used to analyze gaseous products.

2-Chloro-2-nitrosobutane and 2-chloro-2-nitrobutane were prepared in good yield and purity by the method of Kosinski.[5] A variety of chlorinated butanes and butenes including 2,2-dichlorobutane were purchased from K & K Laboratories, Inc., Plainview, N. Y., for use as standards in the gas chromatographs and infrared instrument.

Experiments using the Model 122 laser were conducted in 1.0-cm quartz cells stirred magnetically. Temperatures were lowered by passing chilled water through a baffled brass block; temperatures were raised by heating the block with a hot plate while water circulated slowly through the block. The temperature was monitored with an iron–constantan thermocouple and maintained ±1° of the desired temperature. The block was fitted with two cell compartments with a hole 3 mm in diameter drilled through each compartment for the admission of the laser beam. The purpose of the second cell was to provide a comparison for the behavior of the solutions in the absence of laser irradiation.

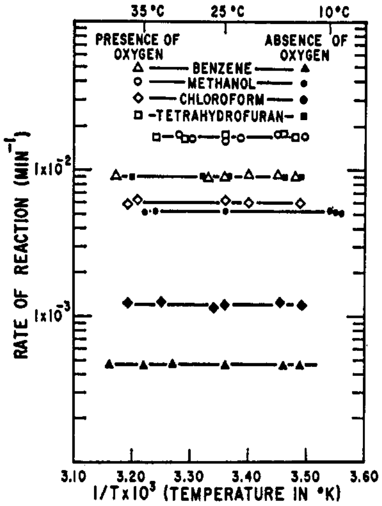


Figure 2.—Effect of changing temperature on rate of reaction.

Experiments using the Model 125 laser were conducted in cylindrical cells 6-mm i.d., varying in length, with ends ground optically flat.

As the rates of reaction and product distribution were markedly dependent on the concentration of oxygen in the system, precautions were taken to eliminate thoroughly dissolved oxygen by repeated vacuum freezing of stirred ampoules.[10] Cells were filled in a dry nitrogen atmosphere and sealed. Reactions conducted in the presence of oxygen were maintained saturated by constantly bubbling oxygen through the reaction cell.

Relative quantum yields were determined by comparing the yield of products to the number of quanta that could be absorbed by 2-chloro-2-nitrosobutane in the elapsed time.[11]

The photomultiplier was calibrated by reference to National Bureau of Standards calibrated tungsten–iodine standard light source. Calibration was checked at frequent intervals to maintain accuracy.

Discussion and Results

Not only were the experimental techniques simplified by using the laser source, but the progress of the reaction could be followed directly by means of a photomultiplier system coupled directly to a recorder.

The applications of nulling potential at the start of each experiment permitted the use of maximum recorder sensitivity. When comparing recorder output with spectrophotometer measurements, the former was at least as accurate as the latter in determining changes in optical density on irradiation. The laser, after proper warm-up, proved to be a very constant source of energy.

The absorption spectrum of 2-chloro-2-nitrosobutane in the visible region was little affected by changes in solvent. Figure 1 illustrates the change in transmission of dilute solutions of 2-chloro-2-nitrosobutane in methanol on irradiation in the absence of oxygen. Spectrophotometric measurements on other dilute solutions were found to be very similar.

The kinetics of the photodecomposition of 2-chloro-2-nitrosobutane in dilute solution can be treated as first or pseudo first order. The rate of decomposition and quantum yield depend on the nature of the solvent as well as the presence or absence of oxygen (see Table I).

---

(8) J. G. Calvert, J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 722.

(9) H. C. Kessler, Jr., *J. Phys. Chem.*, **71**, 2736 (1967).

(10) See ref 8, p 583.

(11) See ref 8, p 588.

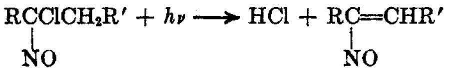
TABLE I

IRRADIATION OF 2-CHLORO-2-NITROSOBUTANE AT 6328 Å (3 mW)

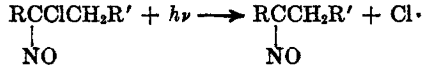
Solvent	Concn, *M*	*k*, min^{-1} Presence of O_2	*k*, min^{-1} Absence of O_2	Quantum yield Presence of O_2	Quantum yield Absence of O_2	Product analysis (absence of O_2)
Benzene	$(1–9) \times 10^{-2}$	9×10^{-3}	4.6×10^{-4}	0.6	0.2	25% 2,2-dichlorobutane, 40% 2-chloro-2-nitrobutane
Benzene	8.25					0.4 mol of N_2/mol of 2-chloro-2-nitrobutane
Methanol	$(1–9) \times 10^{-2}$	1.6×10^{-2}	5.6×10^{-3}	1.3	0.6	90% 2-butanone oxime hydrochloride, trace of formaldehyde
Methanol	9.0					60% 2-butanone oxime hydrochloride, 24% 2,3-butanedione monoxime hydrochloride
Chloroform	$(3–9) \times 10^{-2}$	6.1×10^{-3}	1.2×10^{-3}	0.6	0.2	23% 2,2-dichlorobutane, 37% 2-chloro-2-nitrobutane
Tetrahydrofuran	$(3–6) \times 10^{-2}$	1.7×10^{-2}	9×10^{-3}	2.0	1.0	82% 2-butanone oxime hydrochloride, 12% complex mixture of unidentified compounds

That the rate-determining step of the photodecomposition is probably a primary process was indicated by the fact that the rate of reaction was observed to be independent of temperature[12] over the range of 8–45° in all solvents employed (Figure 2) and that the rate of reaction is found to be directly proportional to the intensity of light (Figure 3).[13] The rate of reaction is dependent on solvent and oxygen concentration and independent of temperature over the range investigated.

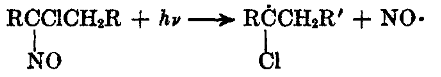
Three types of primary photochemical processes have been postulated for the photodecomposition of *gem*-chloronitrosoalkanes.[14]



$$\underset{\mathrm{NO}}{\mathrm{RCCl}}\mathrm{CH_2R'} + h\nu \longrightarrow \mathrm{HCl} + \underset{\mathrm{NO}}{\mathrm{RC}}\mathrm{{=}CHR'} \qquad (1)$$



$$\underset{\mathrm{NO}}{\mathrm{RCCl}}\mathrm{CH_2R'} + h\nu \longrightarrow \underset{\mathrm{NO}}{\mathrm{RC}}\mathrm{CH_2R'} + \mathrm{Cl}\cdot \qquad (2)$$



$$\underset{\mathrm{NO}}{\mathrm{RCCl}}\mathrm{CH_2R} + h\nu \longrightarrow \underset{\mathrm{Cl}}{\mathrm{R\dot{C}}}\mathrm{CH_2R'} + \mathrm{NO}\cdot \qquad (3)$$

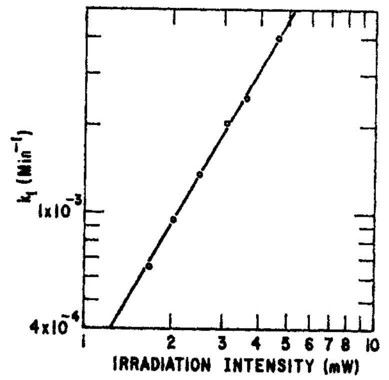
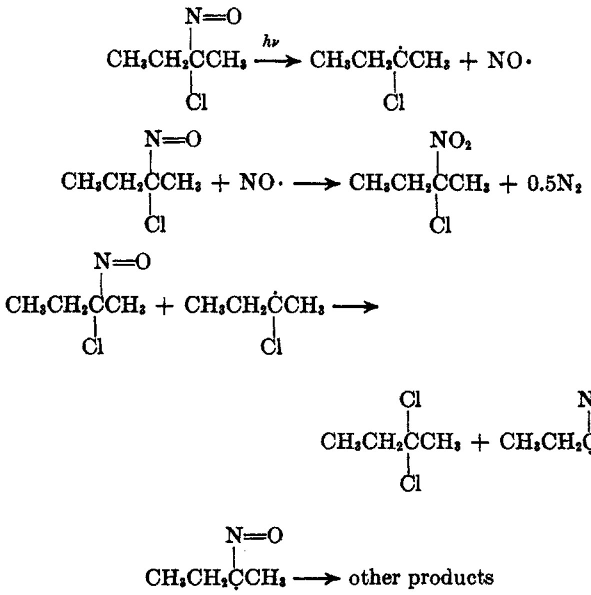


Figure 3.—Typical effect of intensity of light on the rate of reaction for chloroform solutions of 2-chloro-2-nitrosobutane in the absence of oxygen.

In solutions high in concentration with respect to 2-chloro-2-nitrosobutane and in solvents from which hydrogen atoms are not readily abstracted, eq 3 appears to be the important primary process. That NO is the oxidizing agent in such solutions is shown by the effect of added nitric oxide on the reaction[15] (see Figure 4). The rate is increased 30-fold and the yield of 2-chloro-2-nitrobutane relative to 2,2-dichlorobutane approaches 100%. In experiments in which the solution was 1:1 2-chloro-2-nitrosobutane–benzene, nitrogen formation could be detected; analysis by mass spectrograph gave a ratio of about 0.4 mol of nitrogen for each mole of 2-chloro-2-nitrobutane produced. The addition of nitrosyl chloride to dilute benzene solutions affected the rate of reaction very little (see Figure 4) but increased the ratio of 2,2-dichlorobutane to 2-chloro-2-nitrobutane; the combined yield of 2,2-dichlorobutane and 2-chloro-2-nitrobutane changed from 65% in the absence of nitrosyl chloride to 97% on addition of nitrosyl chloride. These data support the mechanism given in Scheme I for the disproportionation of 2-chloro-2-nitrosobutane in benzene in the absence of oxygen.

SCHEME I



$$\mathrm{CH_3CH_2}\overset{\mathrm{N=O}}{\underset{\mathrm{Cl}}{\mathrm{C}}}\mathrm{CH_3} \xrightarrow{h\nu} \mathrm{CH_3CH_2}\underset{\mathrm{Cl}}{\dot{\mathrm{C}}}\mathrm{CH_3} + \mathrm{NO}\cdot$$

$$\mathrm{CH_3CH_2}\overset{\mathrm{N=O}}{\underset{\mathrm{Cl}}{\mathrm{C}}}\mathrm{CH_3} + \mathrm{NO}\cdot \longrightarrow \mathrm{CH_3CH_2}\overset{\mathrm{NO_2}}{\underset{\mathrm{Cl}}{\mathrm{C}}}\mathrm{CH_3} + 0.5\mathrm{N_2}$$

$$\mathrm{CH_3CH_2}\overset{\mathrm{N=O}}{\underset{\mathrm{Cl}}{\mathrm{C}}}\mathrm{CH_3} + \mathrm{CH_3CH_2}\underset{\mathrm{Cl}}{\dot{\mathrm{C}}}\mathrm{CH_3} \longrightarrow \mathrm{CH_3CH_2}\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}\mathrm{CH_3} + \mathrm{CH_3CH_2}\overset{\mathrm{NO}}{\dot{\mathrm{C}}}\mathrm{CH_3}$$

$$\mathrm{CH_3CH_2}\overset{\mathrm{N=O}}{\dot{\mathrm{C}}}\mathrm{CH_3} \longrightarrow \text{other products}$$

---

[12] See ref 8, p 646.

[13] See ref 8, p 651.

[14] See ref 8, pp 475, 476.

[15] D. E. O'Connor and P. Tarrant, *J. Org. Chem.*, **29**, 1793 (1964).

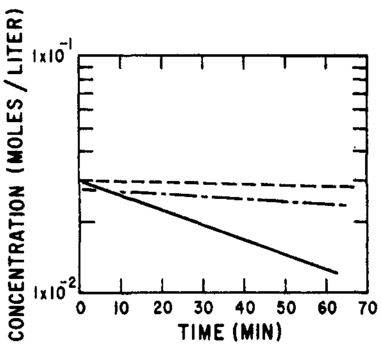


Figure 4.—Effect of the addition of nitric oxide and nitrosyl chloride on the rate of reaction of 2-chloro-2-nitrosobutane in benzene: ———, NO, $k = 1.4 \times 10^{-2}$ min^{-1}; – – – –, NOCl, $k = 4.3 \times 10^{-4}$ min^{-1}; –·–·–·, no addition, $k = 4.6 \times 10^{-4}$ min^{-1}. Experiments were conducted in the absence of oxygen.

In dilute solutions of 2-chloro-2-nitrosobutane in oxygen-free methanol, the primary process of greatest importance is eq 2. The radicals abstract hydrogen from the solvent to produce the oxime and hydrogen chloride. Not only is the oxime hydrochloride the dominant product, but traces of formaldehyde can be detected by gas chromatography of the reaction products.

In concentrated oxygen-free methanol solutions of 2-chloro-2-nitrosobutane, 2,3-butanedione monooxime was formed as well as 2-butanone oxime. The dinitrone reported by Baldwin and Rogers[3] was detected only if the photolysis products were not analyzed immediately.

In tetrahydrofuran the primary process of importance is probably eq 2. The rate of reaction and quantum yields are increased relative to the other solvents (see Table I). The abstraction of hydrogen from cyclic ethers results in the formation of an intermediate α-alkoxy radical which can then combine with another radical to form a stable product or ring opening can occur with the formation of a carbonyl compound.[16] These free-radical pathways result in the increase in reaction rate and apparent quantum efficiency.

The mechanism for the photodecomposition of 2-chloro-2-nitrosobutane solutions proceeds in essentially the same manner as the reaction in benzene (see Table I).

In summary, the fate of the excited 2-chloro-2-nitrosobutane molecule depends on solvent and concentration. The competing paths, eq 2 and 3, are the important primary processes. Selectivity in product occurs in oxygen-saturated solutions, but not in oxygen-free systems. In the absence of oxygen the excited molecule can either experience deactivating collisions or react to form free radicals. These free radicals undergo further reactions to produce products dependent on the nature of the radical, not the source of the free radical. In the presence of oxygen the excited molecule reacts very rapidly with oxygen to form 2-chloro-2-nitrobutane and only traces of products of free-radical origin.

The use of laser light sources removes many experimental problems encountered in ordinary photochemical work. As was to be expected, the low-power lasers used did not directly give rise to products different from common light sources, but the fact that the time of photolysis could be drastically shortened lessened the interference from dark side reactions and simplified product analysis.

Registry No.—2-Chloro-2-nitrosobutane, 681-01-6.

[16] R. S. Davidson, *Quart. Rev.* (London), **21**, 249 (1967).

Derivatives of Thiacyclobutene (Thiete). IV.[1] Thermal Decomposition of a Naphthothiete Sulfone. An Oxidation–Reduction Reaction and Formation of a Cyclic Sulfinate Ester (Sultine)[2-4]

Donald C. Dittmer, Richard S. Henion, and Naomitsu Takashina

Department of Chemistry, Bowne Hall, Syracuse University, Syracuse, New York 13210

Received October 16, 1968

Pyrolysis of 3,8-diphenyl-2H-naphtho[2,3-*b*]thiete 1,1-dioxide, **1**, at 360–400° for 5 min in a nitrogen atmosphere gives two principal organic products which are thiophene derivatives: 14H-benzo[*b*]benzo[3,4]fluoreno-[2,1-*d*]thiophen-14-one (**2**) and 14H-benzo[*b*]benzo[3,4]fluoreno[2,1-*d*]thiophene (**3**). Sulfur dioxide is not evolved in any significant amounts and no evidence for formation of a naphthocyclopropene was observed. When the pyrolysis is done in the presence of 9,10-dihydroanthracene, the reaction took a completely different course yielding 78–81% cyclic sulfinate ester or sultine, 4,9-diphenyl-3H-naphth[2,3-*c*]-2,1-oxathiole 1-oxide (**6**). The cyclic sulfinate by itself decomposes on pyrolysis to the two thiophene derivatives obtained from the naphthothiete sulfone.

Pyrolysis of sulfones usually gives sulfur dioxide and products derived formally from radicals formed on the departure of sulfur dioxide.[5] Examples of pyrolysis of four-membered-ring sulfones (thietane sulfones) are limited. Dodson and Klose found that sulfur dioxide was lost from either *cis*- or *trans*-2,4-diphenylthietane 1,1-dioxide to give a mixture of *cis*- and *trans*-1,2-diphenylcyclopropane in which the *trans* isomer predom-

---

[1] Paper III: D. C. Dittmer and J. M. Balquist, *J. Org. Chem.*, **33**, 1364 (1968).

[2] This work was aided by Grant GP 5513 of the National Science Foundation and Grant CA08250 of the National Cancer Institute, National Institutes of Health.

[3] Reported at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p 101-O.

[4] For further details, see R. S. Henion, Ph.D. Thesis, Syracuse University, 1967.

[5] Reviewed in ref 4 and by J. L. Kice, "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, London, England, 1966, p 115.