Table VI. Effect of Various Sensitizers on the Reactions of Azirine Ie

Sensitizer	Concn of azirine	λ (nm)	Product distribution: Isoxazole	Oxazole	Azirine
Acetone	1.475×10^{-4}	254	42.5	0.87	46.7
Benzene	3.26×10^{-4}	254	10.3	4.0	85.7
Benzene	8.55×10^{-5}	254	11.9	4.25	83.35

was no greater than ±100 Å. The reactions were monitored by measuring the absorption spectra of the solutions. The results are shown in Table V.

Effect of Different Wavelengths of Light on 2-(1-Naphthoyl)-3-phenyl-2*H*-azirine (Ie). Approximately 10^{-4}–10^{-5} *M* solutions (100–300 ml) of the azirine in ether or acetonitrile were bubbled with nitrogen, degassed, and irradiated with a chosen wavelength of radiation. The solvent was removed *in vacuo* and the residue was analyzed by quantitative infrared spectroscopy. The results are summarized in Table III (see Results and Discussion section).

Benzene- and Acetone-Sensitized Reactions of Azirine Ie. Benzene or acetone solutions of the azirine (10^{-4}–10^{-5} *M*) were degassed and irradiated for the indicated period (Table VI). Solvent and or the sensitizer were removed *in vacuo*, and the mixture was analyzed by quantitative infrared spectroscopy.

Acknowledgments. The authors wish to thank M. Orloff for the molecular orbital calculations and J. Lancaster and Mrs. M. Neglia for the nmr measurements.

Photooxygenation (Singlet Oxygen) of Tetrathioethylenes

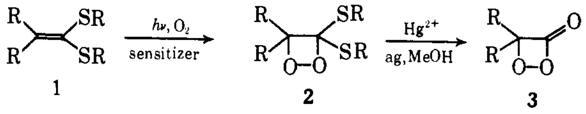
Waldemar Adam* and Ju-Chao Liu

Contribution from the Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931. *Received May 24, 1971*

Abstract: The reaction of singlet oxygen, generated photochemically by sensitization, with tetrathioethylenes **4** between −78 and +30° has been shown to afford dithiooxalates **6** and disulfides **7**, instead of the expected dithiocarbonates **8**. Control experiments showed that **4** did not react with molecular oxygen in the dark or on irradiation in the absence of sensitizer. On warming a photooxygenated reaction mixture from −78 to +30° in the dark, no chemiluminescence was observed. The tetrakis(benzylthio)ethylene (**4c**) gave the same products on exposure to singlet oxygen which was generated by decomposition of the triphenyl phosphite–ozone complex at −20°. The photooxygenation is suggested to proceed *via* the intermediary 1,2-dioxetane **5**, which suffers preferential fragmentation into **6** and **7**, rather than into the expected dithiocarbonate **8**. This unusual result is rationalized in terms of the lower bond strength of the carbon–sulfur *vs.* the carbon–carbon bond.

The recent discovery of Kopecky and Mumford that 1,2-dioxetanes can be isolated as relatively stable materials[1] has initiated a great deal of interest in the four-membered ring peroxide heterocycles during the last 3 years. Of particular interest is the observation by White, Wieko, and Roswell that the energy transfer from the electronically excited carbonyl fragments generated in the thermolysis of 1,2-dioxetanes can be utilized to carry out photochemical transformation,[2] the theoretical study of concerted fragmentation by Kearns[3] and by McCapra,[4] the thermochemical study of O'Neal and Richardson,[5] the stereospecific addition of singlet oxygen to *cis*- and *trans*-diethoxyethylene by Bartlett and Schaap,[6] and the isolation of the stable tetramethoxy-1,2-dioxetane by Mazur and Foote.[7] Of course, numerous reports of 1,2-dioxetanes as reaction intermediates in chemical and photochemical oxygenation of olefinic substrates can be cited.[3,5]

Our vested interest in α-peroxy lactones[8] encouraged us to explore the possibility of preparing 3,3-bis(alkylthio)-1,2-dioxetanes (**2**) by photooxygenation of 1,1-bis(alkylthio)ethylenes (**1**) with singlet oxygen (eq 1).



(1)

The 1,2-dioxetane **2**, at least in principle, could be hydrolyzed by mercuric salts in aqueous solvents to give α-peroxy lactones **3**.[9] Examination of the literature reveals that photooxygenation of thiones[10] and of sulfins[11] leads to ketones; presumably the 1,2-dioxetanes are precursors. To the best of our knowledge no studies on the photooxygenation of thioethylenes have been reported hitherto. In view of the ready availability of the tetrathioethylenes **4**, we have examined the photooxygenation of the electron-rich olefins and wish to report some unusual results concerning the 1,2-dioxetanes **5** derived from these ethylenes *via* addition of singlet oxygen.

Results and Discussion

Ethylenes **4** are prepared in fair yields by trialkyl phosphite desulfurization of trithiocarbonates;[12] the

---

[1] K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1968).

[2] E. H. White, J. Wieko, and D. F. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969).

[3] D. R. Kearns, *ibid.*, **91**, 6554 (1969).

[4] F. McCapra, *Chem. Commun.*, 155 (1968).

[5] H. E. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.*, **92**, 6553 (1970).

[6] P. D. Bartlett and A. P. Schaap, *ibid.*, **92**, 3223 (1970); A. P. Schaap and P. D. Bartlett, *ibid.*, **92**, 6055 (1970).

[7] S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970).

[8] F. D. Greene, W. Adam, and G. A. Knudsen, *J. Org. Chem.*, **31**, 2087 (1966); W. Adam, R. J. Ramirez, and S. C. Tsai, *J. Amer. Chem. Soc.*, **91**, 1254 (1969); W. Adam and Y. M. Cheng, *ibid.*, **91**, 2109 (1969); W. Adam, Y. M. Cheng, C. Wilkerson, and W. A. Zaidi, *ibid.*, **91**, 2111 (1969).

[9] D. Seebach, *Synthesis*, 17 (1968).

[10] N. Ishibe, M. Odani, and M. Sunami, *Chem. Commun.*, 118 (1971).

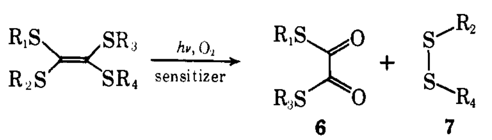
[11] B. Zwanenburg, A. Wagenaar, and J. Strating, *Tetrahedron Lett.*, 4683 (1970).

latter in turn are available by the reaction of the corresponding halides with trithiocarbonate salts.[13] *Via* this sequence **4b** and **4c** were prepared, while **4a, 4d**, and **4e** were kindly supplied as gift samples by Dr. D. Seebach (University of Giessen, Germany).

The singlet oxygen was generated *in situ* by irradiation of the reaction mixture containing the ethylene **4** and dinaphthylthiophene as sensitizer, while continuously saturating the solution with oxygen gas. The progress of the reaction was monitored by ir, nmr, or tlc (whichever was more convenient), and the photooxygenation stopped after about 95% of the ethylene was consumed. A significant difference in the reactivities of the ethylenes **4** was noted. Qualitatively, the rate of photooxygenation decreased in the order **4a** $\cong$ **4b** > **4c** > **4d** $\gg$ **4e**. Thus, under similar conditions, **4a** was consumed at about 0.5 mmol/hr, and an equivalent amount of **4c** required 10 hr until completion, while not even traces of **4e** were consumed after 10 hr. This ordering, *i.e.*, methylthio faster than phenylthio, is of course in agreement with the electrophilic nature of singlet oxygen.[14]

It is important to mention that in the dark none of the ethylenes reacted with molecular oxygen, nor could any appreciable reaction be provoked by irradiation of a solution of the ethylene continuously purged with oxygen gas, but in the absence of a sensitizer. When solutions photooxygenated at −78° were allowed to warm up to room temperature in the dark, no luminescence could be observed.

Conventional work-up of the reaction mixtures and column chromatography of the products afforded the respective dithiooxalates **6** and disulfides **7** (eq 2) in moderate yields. The structures of these products were derived on the basis of ir and nmr spectral data and comparison of physical constants with the authentic materials. No efforts were made to optimize the yields, but semiquantitative ir analysis of the crude reaction mixtures showed that better than 80% of the dithiooxalate (characteristic carbonyl band at 1660–1680 cm^{-1}) was formed in all of the photooxygenated ethylenes. Furthermore, exposure of the tetrakis(benzylthio)ethylene (**4c**) to singlet oxygen, generated from the triphenyl phosphite–ozone complex at −20°,[15] produced the dithiooxalate **6c** and disulfide **7c**, as evidenced by tlc and ir and nmr spectra. However, when this reaction was carried out in the dark no luminescence was observed. Nor was it possible to detect visibly any luminescence in the presence of rubrene or 9,10-diphenylanthracene.

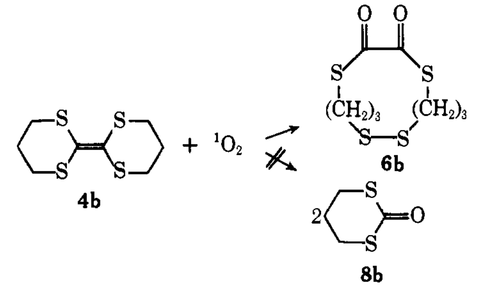


6 **7**

(2)

4a, $R_1 = R_2 = R_3 = R_4$ = methyl
4b, $R_1,R_2 = R_3,R_4$ = trimethylene
4c, $R_1 = R_2 = R_3 = R_4$ = benzyl
4d, $R_1 = R_2 = R_3 = R_4$ = *p*-anisyl
4e, $R_1 = R_2 = R_3 = R_4$ = phenyl

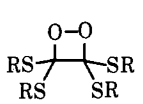
In the case of ethylene **4b**, the absence of the expected dithiocarbonate **8b** was rigorously demonstrated by independent synthesis of **8b** *via* permanganate oxidation of 1,3-dithiane-2-thione.[16] Dithiocarbonate **8b** has a strong carbonyl band at 1600 cm^{-1}, while the dithiooxalate **6b** has a strong carbonyl band at 1660–1680 cm^{-1}. In the crude reaction mixture no appreciable absorbance at 1600 cm^{-1} in the ir could be detected, nor could a spot corresponding to **8b** be found by tlc of the reaction mixture. Thus, addition of singlet oxygen to **4b** leads to dithiooxalate **6b** instead of dithiocarbonate **8b** (eq 3).



4b **6b** **8b**

(3)

The simplest account of the formation of dithiooxalate **6** and disulfide **7** in this photooxygenation is to postulate the formation of a tetrathio-1,2-dioxetane **5** as



5

precursor. However, rigorous low-temperature photooxygenations monitored by ir and/or nmr will be essential to establish the intermediacy of dioxetane **5**. Accepting the intermediacy of **5**, its preferential fragmentation into **6** and **7** rather than **8** is novel and was certainly not anticipated initially. A rationale for this unusual fragmentation of a 1,2-dioxetane can be offered in view of the average bond energies of carbon–sulfur and carbon–carbon single bonds. These are, respectively, 65 and 83 kcal/mol.[17] The 18-kcal/mol difference in the relative bond strengths is apparently sufficient to induce fragmentation of the carbon–sulfur bonds rather than the expected carbon–carbon bond.

Whether this fragmentation proceeds *via* a 1,4-dioxatetramethylene diradical or *via* a molecular path cannot be answered with certainty at this moment. The fact that mainly polymeric dithiooxalate was formed in the photooxygenation of **4b** suggests a diradical pathway. Unfortunately, no fluorescence data on dithiooxalates appear to be available in the literature to use the lack of luminescence as a mechanistic diagnostic between the diradical and molecular fragmentations of the tetrathio-1,2-dioxetanes **5**.

Finally, it is of interest to mention that the photooxygenation of ylide **9** gave essentially quantitative amounts of the expected triphenylphosphine oxide (**10**) and phenyl dithiocarbonate (**11**), as illustrated in eq 4.

$$\underset{\mathbf{9}}{Ph_3P{=}C(SPh)_2} \xrightarrow{^1O_2} \underset{\mathbf{10}}{Ph_3P{=}O} + \underset{\mathbf{11}}{O{=}C(SPh)_2} \qquad (4)$$

This photooxygenation was the most rapid of the ones studied here and no sensitizer was necessary since the

---

(12) E. J. Corey and G. Markel, *Tetrahedron Lett.*, 320 (1967).

(13) W. H. Mills and B. C. Saunders, *J. Chem. Soc.*, 537 (1931).

(14) C. S. Foote, *Accounts Chem. Res.*, 1, 104 (1968).

(15) R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **91**, 5358 (1969).

(16) B. S. Shasha, W. M. Doane, C. R. Russel, and C. E. Rist, *Nature (London)*, 210, 89 (1966).

(17) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1966, p 242.

yellow ylide **9** served as its own sensitizer. A control experiment showed that **9** does not react appreciably with oxygen in the dark under the photooxygenation condition. Again an intermediary dioxetane is the simplest way to account for the expected products.

Experimental Section

All melting points and boiling points are uncorrected. The ir spectra were measured on a Perkin-Elmer Infracord Model 237B, the nmr spectra on a Varian T-60. Elemental analyses were submitted to A. Bernhardt Analytical Labs., Germany.

General Method of Photooxygenation. A 150 × 20 mm Pyrex test tube was capped with a rubber septum which supported a sintered glass inlet tube and a hypodermic needle (22G) as gas vent. The empty test tube was submerged into a quadrangular quartz dewar. The beam of DVY 650-W Sylvania tungsten-halogen lamp, the latter supported in a Pyrex cooling sleeve through which was pumped a solution of 0.2 *M* $CuCl_2$ and 0.5 *M* $CaCl_2$ serving as infrared shield and ultraviolet filter,[18] was focused on one of the vertical surfaces of the quartz dewar. While passing a gentle stream of oxygen gas (supplied from an oxygen cylinder) through the test tube, a solution of the substance to be photooxygenated was injected by means of a syringe. After equilibration of the temperature, the light source was activated, and the sensitizer solution was injected. The progress of the photooxygenation was monitored by ir, nmr, or tlc of aliquots removed from the photovessel by a syringe. After completion, the solvent was removed at reduced pressure (30° (25 mm)) and the residue was separated into its constituents by column chromatography. The details for each system are described below.

Photooxygenation of Tetrakis(benzylthio)ethylene (4c). A solution of 1.29 g (2.5 mmol) of the ethylene **4c** (mp 112–113°, lit.[19] mp 113–114°), prepared in 28% yield from benzyl trithiocarbonate employing the method of Corey and Markel,[12] in 20 ml of chloroform-carbon tetrachloride mixture (1:3), containing 4×10^{-6} *M* dinaphthylthiophene (mp 250°, Columbia Organic), was photooxygenated for 12 hr at 30° after which time olefin **4c** was completely consumed. The crude product, 1.27 g (93%), on molecular distillation at 100° (2 mm) gave 103 mg (7.5%) of clear distillate, identified by ir and nmr as benzaldehyde. The residual oil (1.16 g) was taken up in ether and placed into a Dry Ice-acetone bath for crystallization, affording 258 mg (34%) of pale yellow crystals, which on recrystallization from ethanol gave the benzyl dithiooxalate (**6c**), mp 83–85°, mmp 83–85° with the authentic oxalate. The mother liquor, after removal of the solvent, gave 0.83 g of brown oil, which by column chromatography on silica gel, using carbon tetrachloride as eluent, gave after recrystallization from methanol 201 mg (33%) of colorless needles, mp 66–68°, mmp 66–68° with authentic benzyl disulfide (lit.[20] mp 71.5°), prepared in 85% yield from benzyl mercaptan by the method of Miller, Grossley, and Moore.[21]

Dibenzyl thiooxalate (6c) was prepared in 78% yield, greenish yellow needles from ethanol, mp 83–85°, starting with 6.2 g (50 mmol) of benzyl mercaptan (Evans Chemical Co., n^{21}D 1.5762; lit.[22] n^{20}D 1.5760), following the procedure of Jones and Tasker.[23] The spectral data are: ir (cm^{-1}, CCl_4) 1680 (thiooxalate carbonyl), 1495 and 1455 (aliphatic CH bending), and 710 (monosubstituted phenyl); nmr (60 MHz) δ (ppm, TMS, CCl_4) 7.16 (s, 5, C_6H_5) and 4.10 (s, 2, PhCH_2S).

Anal. Calcd for $C_{14}H_{10}O_2S_2$: C, 61.30; H, 3.60; O, 11.70; S, 23.40. Found: C, 61.41; H, 3.34; O, 11.53; S, 23.81.

Photooxygenation of Tetrakis(methylthio)ethylene (4a). A solution of 200 mg (0.94 mmol) of ethylene **4a** (obtained from Dr. D. Seebach, mp 60–61°; lit.[24] mp 60.5–61.5°) in 4 ml of methylene chloride, containing 2×10^{-6} *M* dinaphthylthiophene, was photooxygenated at −70° and after 2 hr the **4a** was completely consumed. Column chromatography of the 118 mg (84%) of crude product (brown semisolid) on neutral alumina, eluting with methylene chloride, gave 39 mg (28%) of orange semisolid, which on recrystallization from pentane afforded methyl dithiooxalate, mp 81.0–81.5° (lit.[23] mp 81–82°).

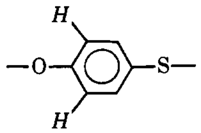
Photooxygenation of 2-(1,3-Dithia-2-cyclohexylidenyl)-1,3-dithiane (4b). A solution of 765 mg (3.24 mmol) of ethylene **4b** (mp 139–141°; lit.[25] mp 141–142°), prepared in 55% yield from 1,3-dithiane-2-thione (mp 78–79°; lit.[26] mp 80°) according to the method of Corey and Markel,[12] in 15 ml of chloroform, containing 4×10^{-6} *M* dinaphthylthiophene, was photooxygenated at −78° for 3 hr, resulting in 874 mg (100%) of brown semisolid. Several recrystallizations from methylene chloride gave 120 mg (14%) of colorless, cubic crystals, mp 109.5–110.5°. The spectral data are: ir (cm^{-1}, $CHCl_3$) 1660 (dithiooxalate carbonyl), and 1105 and 825 (sulfur-sulfur stretching); nmr (60 MHz) δ (ppm, TMS, $CDCl_3$) 2.10 (m, 2, $SCH_2CH_2CH_2S$), 2.88 (t, J = 7 Hz, 2, CH_2CH_2S), and 3.25 (t, J = 7 Hz, 2, CH_2CH_2SCO), consistent with the 1,2,5,9-tetrathiadodecane-7,8-dione (**6b**) structure; mol wt calcd for $C_8H_{12}O_2S_4$, 268; found, 265 (by osmometry in chloroform).

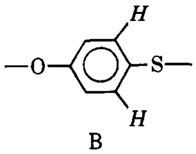
Anal. Calcd for $C_8H_{12}O_2S_4$: C, 35.80; H, 4.50: O, 11.90; S, 47.80. Found: C, 36.09; H, 4.21; O, 11.83; S, 48.07.

Attempted molecular distillation (150° (0.05 mm)) of the residue from the recrystallization failed. This residue, 750 mg (85%), is identical in its ir and nmr with the cyclic dithiooxalate **6b**, but could not be induced to crystallize. Column chromatography on neutral alumina, ethyl acetate as eluent, gave a sticky wax which exhibited a singlet spot by tlc on alumina plates and methylene chloride as eluent. On the basis of these data, a polydithiooxalate structure is proposed.

Photooxygenation of Tetrakis(phenylthio)ethylene (4e). A solution of 46 mg (0.1 mmol) of ethylene **4e** (obtained from Dr. D. Seebach, mp 153–155°; lit.[24] mp 154.5–155°) in 5 ml of benzene, containing 10^{-4} *M* dinaphthylthiophene, was photooxygenated at 25–30° for 12 hr. By means of ir and nmr no reaction could be discerned. Unreacted starting material (90%) was reisolated after column chromatography on silica gel (hexane as eluent), mp 153–155°, mmp 150–155° with the authentic material.

Photooxygenation of Tetrakis(*p*-methoxyphenylthio)ethylene (4d). A solution of 116 mg (0.2 mmol) of ethylene **4d** (obtained from Dr. D. Seebach, mp 93–94°) in 5 ml of chloroform, containing 2×10^{-6} *M* dinaphthylthiophene, was photoxygenated at 25–30° for 4 hr, after which time all of the **4d** was consumed. The crude product, 120 mg (100%), was triturated with 3 ml of hexane and the solid residue was recrystallized with benzene to give 25 mg (38%) of *p*-methoxyphenyl dithiooxalate (**6d**), yellow cubic crystals (mp 185–187°). The oxalate structure of **6d** rests on the spectral data: ir (cm^{-1}, $CHCl_3$) 1680 (dithiooxalate carbonyl), 1485 and 1460 (methoxy CH), and 830 (para disubstituted benzene); nmr (60 MHz) δ (ppm, TMS, $CDCl_3$) 7.35 (AB quartet, J = 8 Hz, 4, see structure A), 7.05 (AB quartet, J = 8 Hz, 4, see structure B), and 3.86 (s, 6, OCH_3). The hexane triturate (95 mg) was submitted to column chromatography on silica gel, and eluting with benzene gave 22 mg (40%) of disulfide **7d**, mp 41–42°, after recrystallization from ethanol (lit.[27] mp 44–45°).


A


B

Photooxygenation of Bis(phenylthio)methylenetriphenylphosphorane (9). A solution of 98.4 mg (0.2 mmol) of ylide **9** (obtained from Dr. D. Seebach, mp 170–172°) in 5 ml of methylene chloride was photooxygenated at −78° for 1 hr, resulting in 105 mg (100%) of crude product mixture. Several triturations with hot hexane and recrystallizations of the residue gave 50 mg (90%) of triphenylphosphine oxide, mp 150–151°, mmp 150–153° with authentic material (lit.[28] mp 153°). The combined triturates, after removal of the solvent, were submitted to column chromatography on silica

---

(18) C. R. Masson, *Tech. Org. Chem.*, **2**, 784 (1956).

(19) U. Schoellkopf and E. Wiscott, *Justus Liebigs Ann. Chem.*, **694**, 44 (1966).

(20) F. H. McMillan and J. A. King, *J. Amer. Chem. Soc.*, **70**, 4143 (1948).

(21) E. Miller, F. C. Grossley, and M. L. Moore, *ibid.*, **64**, 2322 (1942).

(22) W. C. Arnold, A. P. Liew, and R. M. Alm, *ibid.*, **72**, 731 (1950).

(23) H. O. Jones and H. S. Tasker, *J. Chem. Soc.*, **95**, 1904 (1909).

(24) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **6**, 442 (1967).

(25) R. N. Hurd, G. de la Mater, and J. P. McDermott, *J. Org. Chem.*, **27**, 272 (1962).

(26) O. Seipold, H. J. Renner, J. Weissflog, and H. Schneider, East German Patent 11,045 (1950); *Chem. Abstr.*, **53**, 6519 (1959).

(27) J. Tsurugi and W. W. Mayer, *J. Org. Chem.*, **26**, 2486 (1961).

(28) A. Michaelis and F. Wegener, *Chem. Ber.*, **48**, 316 (1915).

gel, and eluting with methylene chloride gave 48 mg (98%) of phenyl dithiocarbonate (**11**), mp 39–41° (lit.[29] mp 41°).

Control Experiment. All of the ethylenes **4** were shown to be photostable in the absence of sensitizer, except the yellow ylide **9** which served as its own sensitizer. Furthermore, none of the ethylenes reacted with molecular oxygen in the dark. Photooxygenation at −78° and slow warming of the solutions to room temperature in the dark were not accompanied by luminescence. In fact, treatment of tetrakis(benzylthio)ethylene (**4c**) with an excess of the triphenyl phosphite–ozone complex[15] at −20° in the dark produced benzyl dithiooxalate (**6c**) and benzyl disulfide (**7c**) in appreciable amounts, as evidenced by tlc analysis of the product mixture, but again no luminescence was observed.

Acknowledgments. We are grateful for financial support by the National Science Foundation, the Petroleum Research Fund, and the A. P. Sloan Foundation. Particular thanks goes to Dr. D. Seebach of the University of Giessen (Germany), who generously supplied several starting materials. Also, we appreciate a gift sample of benzyl mercaptan from the Evans Chemical Co.

---

(29) D. G. Crosby and C. Niemann, *J. Amer. Chem. Soc.*, **76**, 4458 (1954).

One-Electron *vs.* Two-Electron Oxidations. Cerium(IV) and Cyclobutanol[1]

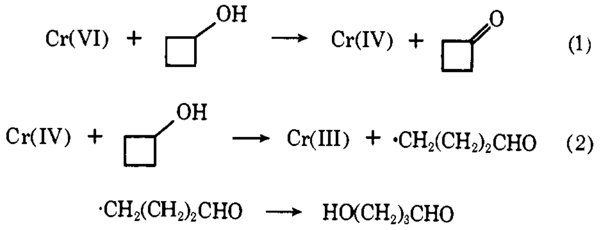
Karl Meyer and Jan Roček*

Contribution from the Department of Chemistry,
University of Illinois at Chicago Circle, Chicago, Illinois 60680.
Received July 23, 1971

Abstract: Cyclobutanol reacts with cerium(IV) 10^3–10^5 times faster than cyclopentanol to yield products derived only from the ring-opened free-radical intermediate, $\cdot CH_2(CH_2)_2CHO$ (I). Nearly all of the cyclobutanol oxidation products in water or aqueous perchloric acid solution arise from radical dimerization or disproportionation. In aqueous sulfuric acid or in acetonitrile the intermediate, I, is further oxidized through direct electron transfer or by ligand transfer from the oxidant. In the presence of molecular oxygen the ligand transfer reaction is suppressed and succinaldehyde is the only isolable product. Products from the cerium(IV) oxidation of 1-methylcyclobutanol are analogous to those from the cyclobutanol oxidation. The results of this study support the contention that oxidation of cyclobutanol by one-electron oxidants proceeds selectively with ring cleavage. These results are discussed in terms of the unique reactivity of cyclobutanol toward one-electron oxidants and the utility of cyclobutanol in classifying one- and two-electron transfer oxidations.

We have recently found that cyclobutanol reacts with chromic acid to give a mixture of two products, cyclobutanone and γ-hydroxybutyraldehyde.[2] Chromium(VI) reacts with cleavage of the carbon–hydrogen bond to give the cyclic ketone, whereas chromium(IV) yields the acyclic hydroxyaldehyde by cleavage of the carbon–carbon bond (Scheme I).

Scheme I



With these results it was tempting to speculate that cyclobutanol could serve as a useful probe for distinguishing between one- and two-electron oxidizing agents. For this purpose it would be necessary for cyclobutanol to react generally with carbon–carbon bond cleavage in one-electron oxidations and with carbon–hydrogen bond cleavage in two-electron reactions. We were encouraged by the finding that both Mn(III) and V(V), known to be one-electron oxidizing agents, easily convert cyclobutanol to γ-hydroxybutyraldehyde in high yield.[2b] In order to further test the general usefulness of cyclobutanol as a classifying agent for one- and two-electron oxidants of alcohols, we undertook this study of the Ce(IV) oxidation of cyclobutanol.

Experimental Section

Materials. All ceric solutions were prepared from ceric ammonium nitrate (CAN) (G. F. Smith Chemical Co., analyzed reagent) which was used without further purification.

Cyclobutanol was prepared from cyclopropylcarbinol,[3] and 1-methylcyclobutanol from 5-bromo-2-pentanone and magnesium.[4] Commercially available cyclopentanol (Aldrich) was used. All alcohols were purified by preparative glpc.

All carbonyl compounds, except those described below, were obtained from commercial sources. γ-Nitrobutyraldehyde was prepared from acrolein and nitromethane using Shechter's procedure.[5] γ-Hydroxybutyraldehyde was prepared *in situ* by the hydrolysis of 2,3-dihydrofuran.[6] These carbonyl compounds were

---

(1) This investigation was supported by the Petroleum Research Fund (Grant No. 1529-4A), administered by the American Chemical Society.

(2) (a) J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **90**, 2986 (1968); (b) A. E. Radkowsky, Ph.D. Thesis, The Catholic University of America, Washington, D.C., 1966.

(3) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

(4) G. W. Cannon, R. C. Ellis, and J. R. Leal, *Org. Syn.*, **31**, 74 (1951); Y. Leroux, *Bull. Soc. Chim. Fr.*, 359 (1968).

(5) H. Shechter, D. E. Ley, and L. Zeldin, *J. Amer. Chem. Soc.*, **74**, 3664 (1952).

(6) R. Paul, M. Fluchaire, and G. Collardeau, *Bull. Soc. Chim. Fr.*, 668 (1950).