from those in water (12). While we can offer no plausible explanation, the difference in isotope effects for the hydrolysis in 39.6 and in 96.3%

plausible explanation, the difference in isotope effects for the hydrolysis in 39.6 and in 96.3% acid points to a difference in mechanism, in agreement with arguments based on other criteria (1).

#### Experimental

Acetic anhydride- $d_6$  and acetic acid- $d_4$  were purchased from Stohler Isotope of Canada and used in the general procedure of Johnson and Nicolet (13) for the preparation of 1-acyl-2-thiohydantoins. 1-Acetyl-5,5-dimethyl-2-thiohydantoin was characterized by m.p. (uncorrected) 186–187 °C, in agreement with Carrington (14), and by n.m.r. (3Hsinglet at 7.33 and 6H-singlet  $8.5 \tau$ ). 1-Acetyl- $d_3$ -5,5dimethyl-2-thiohydantoin had the same m.p. and n.m.r. spectrum, except that the peak at 7.33  $\tau$  was missing. Both compounds in water showed the same u.v. absorption spectrum. Experimental methods for following the hydrolysis and for working-up the data have been described (1, 2).

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### A New Photochemical Reaction of Unconjugated Thioketones<sup>1,2,3</sup>

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Tetramethyl-3-thio-1,3-cyclobutanedione (1) and tetramethyl-1,3-cyclobutanedithione (6) react with oxygen in the presence of light to yield tetramethyl-1,3-cyclobutanedione (2). A mechanism involving singlet oxygen is suggested. 1,3-Diphenyl-2-propanethione (3) undergoes accelerated dimerization in the presence of visible radiation to yield tetrabenzyl-1,3-dithietane (4).

La tétraméthylthio-3 cyclobutanedione-1,3 (1) et la tétraméthylcyclobutanedithione-1,3 (6) réagissent avec l'oxygène en présence de lumière pour conduire à la tétraméthylcyclobutanedione-1,3 (2). Un mécanisme faisant intervenir l'oxygène singulet est suggéré. La diphényl-1,3 propanethione-2 (3) subit une dimérisation accélérée en présence de radiation visible pour conduire au tétrabenzyldithiétane-1,3 (4).

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In a continuing attempt to understand the chemical differences between unconjugated

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ketones, imines and thioketones, (1) we have investigated the photochemistry of compounds containing the thiocarbonyl chromophore. There were no documented photochemical reports in the literature concerning this unconjugated chromophore until adamantanethione very recently (2) was shown to dimerize and add to alkenes probably through an  $n \rightarrow \pi^*$  triplet state. 3924

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We wish to report the first example of an unconjugated thioketone reacting photochemically with oxygen. Tetramethyl-3-thio-1,3-cyclobutanedione (1) (3) when irradiated in isopropyl alcohol at wavelengths > 400 nm in the presence of oxygen gave tetramethyl-1,3-cyclobutanedione (2) and most likely sulfur monoxide (eq. 1). The reaction was complete in 3 days and there was no evidence for the formation of a dimer even in the absence of oxygen. It would appear the resulting dimer is structurally unfavorable in this case.

Dibenzyl thione (3) photochemically does give tetrabenzyl-1,3-dithietane (4) in quantitative yield (eq. 2). This dimerization also occurs in the dark but is definitely accelerated by light. These results are consistent with those reported on the dark reactions of cyclohexanethione (4), in which it was shown that the ground state reaction possessed both ionic and free radical character.

In an attempt to determine the mechanism for the photochemical reaction of the monothione (1) with oxygen we encountered once again the importance of singlet oxygen. Because the reaction occurs in the absence of a dye photosensitizer it might be suggested that the reaction proceeds via the triplet  $n \rightarrow \pi^*$  state of the thione and triplet oxygen to give a cyclic intermediate (5), which then collapses to give the desired products. Our kinetic data obviate this pathway. The reaction is first order in monothione, at low concentration of 1 (0.01-0.1 M), and yet the rate decreases dramatically at high concentrations of 1 (1 M). This suggests a competitive excited state reaction, photochemical quenching, or substantially decreased oxygen solubility. We are hypothesizing that the excited state thione itself photosensitizes the formation of singlet oxygen from triplet oxygen in a spin forbidden process (5). Singlet oxygen then reacts with ground state thione to give the cyclic intermediate (5) which collapses to give



the products (eq. 3). Ground state thione (1) does react in the dark with singlet oxygen generated thermally (6) to give the same products. This reaction occurs at a faster rate than the photochemical reaction and this is consistent with our hypothesis. A mechanism similar to ours has been shown to occur in the dye-photosensitized photooxygenation of 4H-pyran-4-thiones and 4H-thiopyran-4-thiones (7).

We examined the photochemistry of tetramethyl-1,3-cyclobutanedithione (6) under identical conditions to those used for the monothione (1) and the same products resulted (eq. 4). Experimental evidence suggests that there is no transannular participation in the dithione (6) or in (1) (8). We feel therefore that the presence of the carbonyl chromophone has no significant effect when irradiation is carried out on (1) at wavelengths greater than 400 nm.

Although only a few examples are present in the literature, it would appear that simple unconjugated thicketones are to some extent unlike their oxygen or nitrogen analogs. The thicketones absorb light and react through an

NOTES



 $n \rightarrow \pi^*$  state to add to alkenes or dimerize in the absence of alkenes if the spirothietane is sterically favorable. A third reaction results in the formation of ketones by reaction of the excited state thione with oxygen.

The mechanisms of these reactions are somewhat aberrant. We are presently investigating the feasibility of the monothione (1) acting as a dye type photosensitizer for the production of singlet oxygen.

#### Experimental

Melting points are uncorrected. The i.r. spectra were recorded with a Perkin-Elmer 521 grating i.r. spectrometer. Visible and u.v. spectra were run on a Beckman DK-2A ratio recording spectrophotometer. The n.m.r. spectra were obtained from a Varian A-60A instrument. Samples were dissolved in CCl<sub>4</sub> solution using tetramethylsilane as the internal standard. Molecular weight data were obtained by use of a Mechrolab Model 301A vapor phase osmometer. Samples were run as solutions in benzene. Mass spectra were run on both the Varian CH-5 and CEC-103-C mass spectrometers at the University of Wyoming, Laramie, Wyoming. Vapor phase chromatography was performed on an Aerograph Autoprep Model A-700 using 30% SE30 on 45/60 Chrom-P. The aluminum column dimensions were 3/8 in.  $\times$ 20 ft and the operating temperature was 100 °C. Analytical v.p.c. was performed on a Beckman GC-2A using 15% SE-30 on 45/60 Chrom-P. The dimensions of the column were 1/4 in.  $\times$  10 ft and the operating temperature was 160 °C. Chemical analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

#### Tetramethyl-3-thio-1,3-cyclobutanedione (1) and

Tetramethyl-1,3-cyclobutanedithione (6)

The procedure used here was a modification of the one described by Elam and Davis (3).

To 210 g (1.50 mol) of tetramethyl-1,3-cyclobutanedione (2) (Aldrich Chemical Co.) dissolved in 500 ml of pyridine was added 150 g (0.67 mol) of phosphorus pentasulfide (Fisher Scientific Co.) and the mixture refluxed for 40 min. After cooling to room temperature the pyridine was decanted and saved. The remaining solid was heated to boiling with 125 ml of fresh pyridine and once again decanted. The combined pyridine solutions were distilled rapidly without fractionating *in vacuo* (35–50 mm Hg). The pyridine was then removed *in vacuo* (30 mm Hg) by fractional distillation until the temperature reached 60 °C. The resulting residue was extracted with 150 ml of warm hexane and then cooled to 20 °C. At this point the majority of unreacted 2 would crystallize. The compound was collected on a Büchner and washed with hexane to remove the last traces of red color. The mother liquor and the hexane washings were

combined and distilled and a fraction collected at 160-170 °C. This heavy red liquid was subjected to column chromatography on silicic acid (Matheson Coleman and Bell) with hexane as the eluting solvent. Column dimensions were  $80 \text{ cm} \log \times 3 \text{ cm}$  diameter and the column was packed about half full. After 1 h, three distinct layers appeared. The layers were collected, solvent evaporated, and the compound identified.

Tetramethyl-1,3-cyclobutanedithione (6), the first layer, was an orange solid, m.p.  $123-125^{\circ}$  (lit.  $124-125^{\circ}$ ) (3); i.r.: 1460, 1256, and 1075 cm<sup>-1</sup>; n.m.r.: 1.40  $\delta$  (12H, S); visible and u.v. absorptions in hexane,  $\lambda_{max}$  227 ( $\epsilon$  21 600), 298 (409), 500 nm (22.4); *m/e* 172; yield 10%.

Tetramethyl-3-thio-1,3-cyclobutanedione (1), the second layer, was a red solid, m.p.  $57-58^{\circ}$  (lit.  $57-58^{\circ}$ ) (3); i.r.: 1800, 1700, 1450, 1290, and 1125 cm<sup>-1</sup>; n.m.r.: 1.33  $\delta$  (12H, S); visible and u.v. absorptions in hexane,  $\lambda_{max}$  228 nm ( $\epsilon$  8700), 270 (300), 318 (100), and 520 nm (9.65); m/e 156; yield 50%.

The third layer was unreacted tetramethyl-1,3-cyclobutanedione.

#### Photolysis of Tetramethyl-3-thio-1,3-cyclobutanedione (1)

A solution of 1, 0.096 M in isopropyl alcohol was irradiated through a Kimax sleeve using a 250 W R40/3 Westinghouse lamp. The reaction was followed by u.v. spectroscopy and v.p.c. There was no apparent reaction after 10 days.

Any oxygen stream was introduced and after 3 days the monothione 1 had completely reacted. The hexane solution was evaporated to give a white solid which was purified by sublimation. The compound was identical in all respects to that of an authentic sample of tetramethyl-1,3-cyclo-butanedione (2); yield 75%.

The effluent oxygen stream from the photoreaction was trapped using 100 ml of 1% sodium hydroxide. The excess sodium hydroxide was neutralized with hydrochloric acid and the solution titrated with iodine to indicate the presence of sodium sulfite, thus the presence of SO<sub>2</sub> in the oxygen stream.

A second method for the detection of sulfur dioxide was to precipitate and identify barium sulfite from a portion of the non-neutralized sodium hydroxide solution.

The photolysis was carried out in hexane and in carbon tetrachloride and the times for complete reaction were 5 and 1 days respectively.

#### Reaction of Tetramethyl-3-thio-1,3-cyclobutanedione (1) with Singlet Oxygen

Tetramethyl-3-thio-1,3-cyclobutanedione (1), 0.10 M in isopropyl alcohol was placed in a 250 ml separatory funnel and 50 ml of 5.25% sodium hypochlorite solution (Hilex) was placed in another separatory funnel. Both funnels were attached to a 250 ml three-neck flask containing 50 ml of 30% hydrogen peroxide (J. T. Baker) which was being stirred magnetically. The sodium hypochlorite solution was added slowly and completely, followed by the dropwise

[4]

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3925

addition of the monothione 1 solution. The reaction was complete in 5 min. The gas evolving from the reaction was trapped using 100 ml of 1% sodium hydroxide. A positive analysis for SO<sub>2</sub> was obtained as described above. The diketone 2 was obtained by evaporation of the isopropyl alcohol, yield 90%.

There was no apparent reaction (by visible spectroscopy or v.p.c.) when the monothione 1 was added separately to hydrogen peroxide or to sodium hypochlorite solution.

#### Photolysis of Tetramethyl-1,3-cyclobutanedithione (6)

A 0.10 M solution of the dithione 6 in hexane was irradiated under identical conditions as reported for the monothione 1. Sulfur dioxide and the diketone 2 were identified as reported above. The reaction was complete in 3 days.

#### 1,3-Diphenyl-2-propanethione (3)

Modified procedure of Mayer and Berthold (9).

To 27.2 g (0.10 mol) of 2,2-diethoxy-1,3-diphenylpropane (10) was added 0.05 g of *p*-toluenesulfonic acid. Hydrogen sulfide gas was passed through the solution for 8 h or until the solution was a consistent brilliant red. The solution was evaporated *in vacuo* to remove excess ketal, hydrogen sulfide, and ethanol. The condensate was a viscous red liquid, n.m.r.: 4.17 (4H, S), 7.19  $\delta$  (10H, m), visible absorptions in cyclohexane,  $\lambda_{max}$  510 nm ( $\epsilon$  10); *m/e* 226, P + 2 228 (1 sulfur).

#### Tetrabenzyl-1,3-dithietane (4)

1,3-Diphenyl-2-propanethione (3) was irradiated using direct sunlight and a Pyrex container. The red color began to disappear and a white precipitate began to form after 2 h. The red color was completely gone after 2 days. The solution was filtered with solution and the precipitate washed with ethanol and acetone. The crude product was then recrystallized from carbon tetrachloride collected and dried in an oven at 120° for 24 h; m.p. 247–248°; i.r.: 3080, 3050, 3025, 2925, 2900, 2825, 1947, 1880, 1810, 1765, 1600, 1577, 1488, 1449, 1426, 1379, 1321, 1309, 1211, 1172, 1150, 1141, 1075, 1039, 1025, 1000, 992, 982, 970, 954, 911, 900, 879, 850, 827, 808, 752, 740, 702, 690, 608, 590, 565, 510 and 460 cm<sup>-1</sup>; n.m.r.: 7.25  $\delta$  (20H, S); *m/e* 452 P + 2 454 (2 sulfur); v.p.o. 442 g/mol.

Anal. Calcd. for  $C_{30}H_{28}S_2$ : C, 79.59; H, 6.23. Found: C, 79.18; H, 6.39.

1,3-Diphenyl-2-propanethione (3) will also dimerize in the dark to give tetrabenzyl-1,3-dithietane (4) but the reaction is not nearly complete even after 8 days.

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## The Investigation of Cation-Anion Interactions by <sup>39</sup>K Nuclear Magnetic Resonance

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# AND

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The  $^{39}$ K chemical shifts in a number of aqueous electrolyte solutions have been determined. These arise from the overlapping of the outer electron orbitals of the anion and cation during random ionic collisions. The magnitudes of the chemical shifts are shown to be directly proportional to the effectiveness of this overlap interaction.

Nous avons déterminé les déplacements chimiques du <sup>39</sup>K dans différentes solutions électrolytiques aqueuses. Ceux-ci proviennent du recouvrement des orbitales des électrons externes de l'anion et du cation lors de collisions ioniques aléatoires. Nous avons montré que l'importance de ces déplacements chimiques est directement proportionnelle à cette interaction de recouvrement.

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