enone 3 contaminated by approximately 12–15% of the $\alpha,\beta$-isomeric ketone (1) as determined by NMR analysis. Octalone 1 was characterized by an absorption band at $\delta$ 5.65 (vinyl H), whereas the corresponding signal for the $\beta,\gamma$-enone 3 occurred at $\delta$ 5.41 (m, 1 vinyl H).

**Acknowledgments.** The authors wish to thank the Loyola University of Chicago Committee on Research for partial financial support of this project in the form of a summer research assistantship to one of us (M.J.C.).

**Registry No.**—1, 826-56-2; 2, 3287-60-3; 3, 22789-80-6; $\alpha,\beta$-unsaturated 4c, 2047-97-4; 1-methylcyclohexene, 591-49-1; acetyl chloride, 75-36-5.

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(8) Preparation of ketone **4c** has been reported several times in the Chemical literature. See N. Dufort and J. LaFontaine, *Can. J. Chem.*, **46**, 1065 (1968), and references therein.
(9) Isomerization of the double bond occurs subsequent to ethylene ketal formation. This was demonstrated by isolation of the reaction products (**5a** and **6a**) obtained from mesityl oxide (**4a**) after 3.5 h and discovering it to be a 40:60 mixture of $\alpha,\beta$-unsaturated ketal (**6a**) and the isomeric ketal (**5a**).
(10) On a large scale, fractional distillation would be more convenient to separate $\beta,\gamma$-unsaturated ketal **5** from enone **4**.
(11) For previous syntheses of enone **7b**, see J. Meinwald and L. Hendry, *J. Org. Chem.*, **36**, 1446 (1971), and references therein.
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(13) No attempt was made to recover $\alpha,\beta$-unsaturated ketone **4** after selective hydrolysis of ketal **6** in the presence of $\beta,\gamma$-unsaturated ketal **5**. However, NMR analysis of the crude hydrolysis product, prior to chromatography on Florisil, indicated the expected mixture of ketal **5** and enone **4**, accompanied by minor (1–9%) amounts of the corresponding $\beta,\gamma$-enone **7**.
(14) Due to their volatility, ketals **5a** and **6a**, as well as enone **7a**, were recovered from the extracts by fractional distillation of the solvent at atmospheric pressure
(15) The apparatus described by W. S. Johnson and W. P. Schneider [*Org. Synth.*, **30**, 18 (1950)] was used to maintain a nitrogen atmosphere.

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# Photolysis of *o*-Phenylene Oxalate. A High-Yield Photodecarbonylation Reaction

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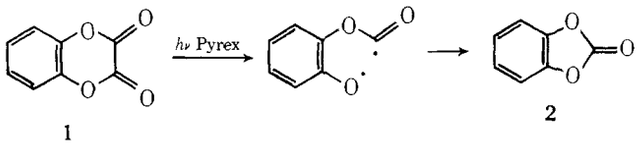
*Received November 8, 1977*

The photolysis of aryl esters in solution generally results in their rearrangement to isomeric phenolic ketones via the photo-Fries pathway.[2] Acyclic aryl oxalates, in particular, have been observed to undergo the photo-Fries rearrangement, with the simultaneous formation of phenols.[3,4] The photochemistry of cyclic oxalate esters, however, has not been studied thoroughly. We therefore have investigated the photolysis of *o*-phenylene oxalate (1).

In contrast to the photolysis of aryl esters in general and acyclic oxalate esters in particular, the photolysis of 1 induced the formation of no photo-Fries products. Instead, nearly quantitative decarbonylation resulted. Irradiation of deaerated hexane solutions of 1 afforded *o*-phenylene oxalate (2)

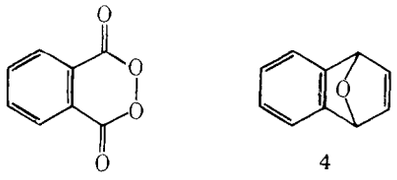



1 2

as the exclusive observed product (by NMR, VPC), identified by comparison of physical and spectral properties with an authentic sample.[5] The chemical yield of 2 was 94% (by VPC) and was found to be independent of the presence of either oxygen or acrylonitrile.

The primary photochemical reaction is evidently an $\alpha$ cleavage of either the acyl–oxygen bond, as is postulated for other aryl esters,[2] or the acyl–acyl bond, as is common in $\alpha$-dicarbonyl compounds.[6] In any event, decarbonylation of the biradical intermediate, followed by reclosure, results in the observed carbonate **2.** The formation of the typical photo-Fries product is probably precluded due to geometrical constraints.

Interestingly, *o*-phenylene oxalate, unlike its structural isomer phthaloyl peroxide (3), does not photodecarboxylate to benzyne.[7] Thus, photolysis of 1 in the presence of furan did not lead to a detectable amount of the known benzyne adduct **4.**



3 4

As is often the case, the mass spectrum of 1, which has been reported previously,[8] parallels the photochemical results. Thus, expulsion of CO is the important initial process for 1 as well as other cyclic oxalates, while no loss of $CO_2$ from the molecular ion was observed.

In summary, our findings demonstrate that the photolysis of *o*-phenylene oxalate is qualitatively different from that of other aryl esters, in that $\alpha$ cleavage, followed by decarbonylation, is the exclusive reactive pathway.

## Experimental Section

Melting points are uncorrected. Infrared spectra were recorded using a Perkin-Elmer 237-B instrument. NMR spectra were obtained with a Varian EM-390 spectrometer. Gas chromatography analyses were performed using a Varian Aerograph Series 2700 flame ionization instrument. Mallinckrodt spectrograde hexane was used as received.

**o-Phenylene Oxalate (1).** In a modification of the procedure of Gosh,[9] this compound was prepared by the dropwise addition of oxalyl chloride (1.7 mL, 20 mmol) in 5 mL of dry ether to 2.0 g (18 mmol) of catechol and 5.1 mL (36 mmol) of triethylamine in 40 mL of ether. After being stirred vigorously for 3 h, the mixture was filtered and the residue was thoroughly ether extracted. Concentration in vacuo of the combined organic materials afforded crude product, which was sublimed (90–95 °C (0.5 mm)) to give *o*-phenylene oxalate (2.4 g 79%), mp 185.5–186.5 °C (lit.[8] mp 185 °C), after recrystalization from benzene under nitrogen. The previously unreported spectral data were: IR ($CHCl_3$) 3010, 1805, 1790, 1495, 1740, and 1285 $cm^{-1}$; NMR (acetone-$d_6$) $\delta$ 7.28 (pseudo-s); UV (hexane) $\lambda_{max}$ ($\epsilon$) 277 broad (3060), 320 tail (990).

**Photolysis of *o*-Phenylene Oxalate (1).** Preparative runs were performed using an immersion well apparatus with a 450 W medium pressure Hg arc and a Pyrex filter sleeve. The solution was purged with dry nitrogen for 1 h prior to and then throughout the photolysis. In a typical run, 1 (90 mg, 0.54 mmol in 400 mL of hexane) was irradiated for 4 h. The course of the reaction was monitored conveniently by UV spectroscopy. Removal of solvent afforded 54 mg of *o*-phenylene carbonate (2).[4]

Chemical yield and quenching runs were performed using a merry-go-round apparatus with irradiation of ca. 5-mL samples in capped test tubes. Solutions were purged with nitrogen, if appropriate,

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for 20 min prior to photolysis. The photolysate was analyzed directly by VPC (6 ft column of 3% SE-30 on Chromosorb G, operating between 90 and 120 °C), using dodecane as internal standard. Relative response ratios were obtained from pure authentic samples.

**Acknowledgment.** This work was supported in part by grants from the Research Corporation and the office of Naval Research and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

**Registry No.**—1, 16536-36-0; 2, 2171-74-6; oxalyl, 79-37-8; catechal, 120-80-9.

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# Synthesis and Thermal Decomposition of 1-Methyl-1*H*,3*H*-1,2-benzisothiazole 1-Oxide Hydrochloride[1]

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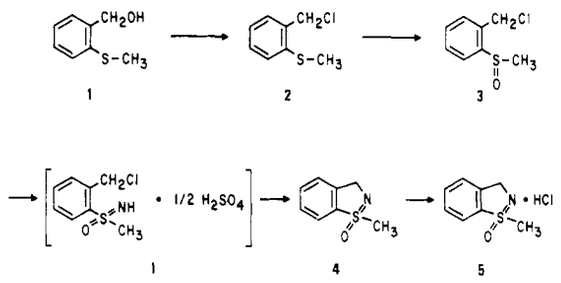
*Received June 9, 1977*

Recently there has been much interest in the sulfoximine function as a synthon and in sulfoximines which possess biological activity.[2] We wish to report the synthesis of a new heterocyclic ring system which contains the sulfoximine function, 1-methyl-1*H*,3*H*-1,2-benzisothiazole 1-oxide hydrochloride, and its thermal decomposition to afford 1,2-benzisothiazole. Experiments pertaining to the mechanism of this thermal decomposition are discussed.

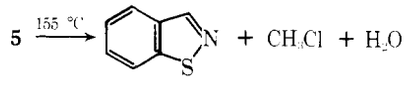
## Results and Discussion

The synthesis of 1-methyl-1*H*,3*H*-1,2-benzisothiazole 1-oxide (**4**) and its corresponding hydrochloride (**5**) were accomplished by the sequence of reactions shown in Scheme I. Treatment of *o*-(methylthio)benzyl alcohol (**1**)[3] with thionyl chloride in benzene, according to the procedure of Grice and Owen,[4] afforded *α*-chloro-*o*-tolyl methyl sulfide (**2**) in 73% yield. Oxidation of **2** with *m*-chloroperoxybenzoic acid afforded the corresponding sulfoxide **3** in 54% yield. The conversion of sulfoxide **3** to the sulfoximine proved initially baffling. Treatment of **3** with sodium azide in sulfuric acid and chloroform[5] followed by a basic workup afforded a mixture of the cyclized sulfoximine free base (**4**) and its corresponding hydrochloride (**5**). Isolation of the hydrochloride from a basic workup was confusing. We were subsequently able to isolate the open ring sulfoximine intermediate as the hemi sulfuric acid salt I. Rapid basic treatment of I afforded the hydrochloride **5** in good yield; however, a more prolonged, 20 to 30 min, treatment with base afforded only the free base **4**. This results from the fact that the ring closure of the free base of I in basic medium requires 20 to 30 min for completion. If it is quickly removed from the basic medium, spontaneous ring closure occurs to afford the hydrochloride **5**. The best procedure for the preparation of **4** involves the isolation of I which is subsequently dissolved in water, made basic (pH 12), and stirred at ambient temperature for 0.5 h. Treatment of **4** with ethereal hydrogen chloride afforded the hydrochloride **5**. The structures of **4** and **5** were confirmed by elemental analyses, IR, NMR, and mass spectra (Experimental Section).

Scheme I



When the melting point of **5** was taken, it underwent a smooth gaseous decomposition at ca. 140 °C leaving a clear oil which solidified upon cooling. As a result, this decomposition was carried out on a preparative scale. Compound **5** was heated at 155 °C for 20 min in a small flask to afford a 94% yield of 1,2-benzisothiazole (**6**). 1,2-Benzisothiazole was



identified by elemental analyses, IR, NMR, and mass spectra (Experimental Section). The organic component of the evolved gas was identified as methyl chloride by infrared and the other component was identified as water by NMR. It was found that this reaction also occurred when **5** was heated at reflux in acetonitrile and in $Me_2SO$ at 110 °C.

The demethylation of *S*-methyl sulfoximines represents a unique reaction of the sulfoximine function. Cram and coworkers[6] observed a similar demethylation when (−)-(*R*)-methyl *p*-tolyl *N*-methylsulfoximide was treated with tosyl chloride in pyridine to afford (−)-(*R*)-*N*-methyl-*N*-tosyl-*p*-toluenesulfinamide.

Johnson and co-workers[7] reported that the reaction of *N,N*-dimethylaminomethylphenyloxosulfonium fluoroborate with sodium methoxide in refluxing methanol afforded *N,N*-dimethylphenylsulfinamide, presumably by attack of the methoxide on the *S*-methyl or by decomposition of the methylide intermediate. The thermolysis of **5** affords a new and simpler method for the preparation of 1,2-benzisothiazole.[8,9]

In an attempt to elucidate the mechanism of the thermal decomposition of **5**, the following experiments were performed. When the decomposition was terminated at about one-half completion and the reaction mixture was analyzed, only starting material and 1,2-benzisothiazole were present. The reaction was also carried out in $Me_2SO$-$d_6$ at 110 °C in an effort to detect any transient intermediate by NMR and TLC; however, none was observed. The thermal decomposition of the deuteriochloride salt of **4** afforded 1,2-benzisothiazole which had incorporated 4 to 5% deuterium at the 3 position (mass spectrum analysis). A kinetic study comparing the relative rates of 1,2-benzisothiazole formation from **5** and the corresponding hydrobromide salt (**5a**) in dimethyl sulfoxide at 110 ± 3 °C showed that the hydrobromide reacted approximately four times more rapidly than did the hydrochloride. These observations are consistent with a mechanism in which the halide ion attacks the methyl group of **4**. The rate-determining step involves the attack of the halide ion on the methyl group of **4**.

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