$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.032$$

$$R = [\sum(w|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.043$$

Atomic scattering factors and anomalous dispersion components for sulfur were taken from the "International Tables for X-ray Crystallography".[50] The largest residual peak in the final electron density difference map was 0.4 eÅ^{-3}.

The labeling of atoms is shown in Figure 1 and the bond lengths and angles are in Table I. The coordinates of atoms with thermal parameters are listed in Table Ia (supplementary material) along with observed and calculated structure factors.

2,2,4,4-Tetramethyl-1,3-dithietane 1,1,3,3-Tetraoxide (14). To 1.908 g of 60% NaH dispersion (48 mmol) rinsed with pentane and placed under argon in a 25-mL three-necked flask equipped with a condenser with a three-way stopcock, thermometer, and septum was added a solution of 1g 1,3-dithietane 1,1,3,3-tetraoxide (7, 6.4 mmol) in 30 mL of anhydrous dimethyl sulfoxide. With cooling, 4.56 g (32 mmol) of methyl iodide was added slowly. An immediate exothermic reaction occurred with gas evolution; ice-water cooling was necessary to maintain a temperature of 35-50 °C. After the reaction had subsided, an additional 4.6 g of methyl iodide (32 mmol) was added and stirring was continued overnight. The mixture was poured onto water and the precipitate collected and dried at 130 °C affording 0.7641 g (56% yield) of the title compound. Fine white crystals decomposing at 270-274 °C were obtained by recrystallization from hot dimethylformamide. These showed IR (KBr) 1460 (s), 1340 (vs), 1165 (vs), 1090 (vs), 920 (s), 703 (s), 664 (s), and 490 (s) cm^{-1}; NMR (CF_3CO_2H) δ 2.0 (s); mass spectral mol wt 212; calcd for $C_6H_{12}S_2O_4$, 212.

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Registry No. 1, 287-53-6; **2**, 58816-63-0; **3**, 60743-07-9; **4**, 60743-08-0; **5**, 60743-09-1; **6**, 60743-10-4; **7**, 21511-46-6.

Supplementary Material Available: Figure of stereoscopic view of the unit cell of **7**, table of final positional and thermal parameters of **7**, and structure factor table (9 pages). Ordering information is given on any current masthead page.

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(49) Local versions of the following programs were used for crystallographic calculations: (1) SYNCOR, W. Schmonsees' program for data reduction; MULTAN, Germain, Main, and Woolfson's program for structure solutions; FORDAP, A. Zalkin's Fourier program; ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; ORTEP, C. K. Johnson's program for drawing crystal models.

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(51) **Note Added in Proof.** Following submission of this work a report appeared (Rheude, U.; Sundermeyer, W. *Chem. Ber.* **1981**, *114*, 3378-3384) on the twofold and threefold silylation of **7** with trimethylsilyl nonafluorobutanesulfonate, using triethylamine as base. Metalation of the threefold silylated product with *n*-butyllithium followed by silylation led to O-silylation, giving a product which the authors claim is "the first enol ether of a sulfone". In our opinion their O-silylated product would be more appropriately described as a cyclic sulfoxonium ylide.

The Efficiency of Benzil-Sensitized Photoepoxidation: A Correction

Paul D. Bartlett,*[1] Antonius A. M. Roof,[1] and Nobujiro Shimizu[2]

Contribution from the Departments of Chemistry, Texas Christian University, Fort Worth, Texas 76129, and Faculty of Science, Kyushu University, Hakozaki, Fukuoka, Japan.

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Abstract: Photosensitized epoxidation of norbornene by benzil leads to about two epoxide molecules or less per diketone molecule consumed, not the larger numbers previously reported.[3] It is not necessary to postulate a chain mechanism for this epoxidation, although side reactions still complicate the process in many cases.

In the original report[3] of photoepoxidation of olefins by α-diketones, a survey was made of a number of olefins in reaction chiefly with biacetyl and benzil, comparing the yields and sensitizer efficiencies. Whereas the biacetyl-sensitized epoxidation always required 1 mol of biacetyl to produce up to 2 mol of epoxide, much higher recoveries of benzil were reported, indicating epoxidation efficiencies up to 16 mol of epoxide per mol of benzil consumed.

Table I. Epoxide Yields in Benzil-Sensitized Epoxidation of Norbornene, 7-10 °C, in Benzene

vol of benzene, mL	initial mmol of olefin	initial mmol of benzil	*t*, h	mmol of epoxide	mmol of benzil recovered	epoxide/ benzil consumed	ref
20	3.0	2.0	1.5	1.92	1.02	1.96	1
18	2.7	1.8	1.5	1.81	0.82	1.85	1
20	2.0	2.0	1.5	0.92	1.10	1.02	1
15	4.0	2.0	1.0	1.23	1.15	1.45	1[a]
15	4.0	2.0	0.58	1.78	1.18	2.17	2
15	3.0	2.0	0.58	1.78	1.12	2.02	2

[a] Average of four analyses.

In the course of following up the implications of these material balances for the reaction mechanism, we have found a serious error in the analytical procedure for the benzil photosensitizations, amounting to nonseparation of benzil from its photolysis products, phenyl benzoate and biphenyl. Careful repetition of the relevant analyses in our two laboratories has shown that with benzil, as with biacetyl, 2 mol of epoxide is an approximate upper limit to the product of photosensitization from 1 mol of diketone. The lowest yields of epoxide were in the reactions with low norbornene

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[1] Department of Chemistry, Texas Christian University.

[2] Department of Chemistry, Faculty of Science, Kyushu University.

[3] Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4193.

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Table II. Corrected Efficiencies of Benzil-Sensitized Photoepoxidations (0.1 M Solutions in Benzene, 5 °C)

olefin	*t*, h	% epoxide	% benzil recovered	epoxide/ benzil consumed	ref
$Ph_2C{=}CMe_2$	0.25	80	42	1.4	2
PhCH=CHMe					
trans	0.25	96	48	1.8	2
cis	0.25	89	45	1.6	2
norbornene	0.25	98	50	2.0	2
t-$BuCH{=}CH_2$	2	69	35	1.1	2

concentrations, where the conditions permitted loss of olefin in the oxygen stream. When benzene was the solvent, the yield of phenyl benzoate was between 29 and 45%, with biphenyl in approximately 5% yield.

Table I shows the results of VPC analyses of a series of benzil-sensitized photoepoxidations in benzene as solvent. Table II gives the corrected results in benzene for epoxidations of five olefins previously reported.[3]

There is an extreme variation of about twofold in the epoxide yields from norbornene in benzene over a range of concentrations in our two laboratories. The experimental condition most difficult to standardize is the light source; in a series of experiments[1] in methylene chloride, the light source was varied from a projection lamp (48 h, (epoxide)/(benzil consumed) = 0.42) to a 450-W Hanovia arc with a Corning 3387 filter, λ_{max} 436–466 nm (5.25 h, (epoxide)/(benzil consumed) = 1.11). Irradiation with the latter lamp with a potassium chromate filter, λ_{max} 313 nm, for 0.75 h consumed 10.6% of the benzil but yielded no epoxide.

Experimental Section

The irradiations in benzene were carried out at temperatures between 7 and 10 °C, with oxygen being constantly bubbled through the solution. Vapor chromatography was carried out with hexadecane[1] or diphenylmethane[2] as internal standard on a 5-ft 5% SE-30 column[1] or a 1-m 25% SE-30 column on Chromosorb W 60–80 mesh).[2] The light source was a Hanovia[1] or Eiko-sha[2] 450-W lamp in a Pyrex jacket.

In addition to the products mentioned above, the norbornene epoxidations[2] yielded about 4% of a product with longer retention time than benzil and with IR and ^1H NMR spectra suggesting a norbornanediol monobenzoate: IR (neat) 3470 (br), 1720, 1705, 1205, 1110, 780, 750, 700 cm^{-1}; ^1H NMR (CCl_4) δ 0.8–2.7 (br m), 3.7–4.8 (br m), 7.0–7.6 (m), 7.7–8.2 (m); ratio ca. 5:1:1.5:1.

Conclusions

The present results confirm[4] that no chain character is inherent in the benzil-sensitized epoxidation reaction. However, a number of facts about this and related processes bear witness to the occurrence of competing reactions: the self-sensitized photoepoxidation of methoxymethylenefluorene,[5] the frequent competition of epoxidation with singlet oxygen reactions, and the general capability of benzophenone as an epoxidation sensitizer. Most of these competing processes are not understood, and they cannot be accounted for as incidental to a simple epoxidation by benzoylperoxy radicals. The authors concerned[3] deeply regret having made an erroneous report in this field, and efforts are being continued to arrive at a comprehensive view of the process.

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Registry No. Norbornene, 498-66-8; benzil, 134-81-6; $Ph_2C{=}CMe_2$, 781-33-9; *trans*-PhCH=CHMe, 873-66-5; *cis*-PhCH=CHMe, 766-90-5; *t*-BuCH=CH_2, 558-37-2.

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Reactivities of Norbornene-Type Double Bonds in Propellane Derivatives and Their Precursors; Furan as a Diene

Paul D. Bartlett,* Gerald L. Combs, Jr., Ai-Xuan Thi Le, William H. Watson,*[1] Jean Galloy,[1] and Michio Kimura[1]

Contribution from the Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129. *Received November 9, 1981*

Abstract: Some of the factors determining reactivity of a norbornenic double bond have been investigated by measuring the rates of epoxidation of the syn and anti adducts (**3** and **4**) of cyclopentadiene to norbornene-2,3-dicarboxylic anhydride, the syn adduct **10** of furan to the same dienophile, and the anti adduct **5** of cyclopentadiene to norbornadiene-2,3-dicarboxylic anhydride. In this series the major determinant of double-bond reactivity is proximity in space to the anhydride group. Structures of the monounsaturated syn and anti adducts **10** and **15**, the anti cyclopentadiene adduct **4**, and its epoxide **6** have been determined by X-ray crystallography. In additions to dienophiles **1** and **2**, the use of furan rather than cyclopentadiene strongly favors the exo Alder's rule products **13** and **10**.

The effect of bicyclic ring structures, notably that of norbornene, on the reactivity of the double bond has been of interest for some time.[2] In this rigid system the angle strain and positions in space of neighboring groups can be precisely specified and correlations sought with the observed rates of reaction.[3] In a growing number of systems,[4-13] it has appeared that interactions between the π orbital of the double bond and the σ or n orbitals of neighboring

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