6.20 (d, J = 3 Hz, 1 H), 6.60 (d, J = 2 Hz, 1 H). *Anal.* Calcd for $C_7H_5O_6Cl_3$: C, 28.85; H, 1.73. Found: C, 29.01; H, 1.69.

Bromoform.—Carbon tetrabromide (0.65 g, 1.95 mmol) was dissolved in THF (10 ml) and irradiated through a Pyrex filter with a high-pressure mercury lamp for 6 min. The major product (78% yield by glc analysis) was identified as bromoform by direct comparison.

7-Bromonorcarane.—7,7-Dibromonorcarane[5] (4.9 g, 19.1 mmol) was dissolved in THF (1000 ml) and irradiated with a low-pressure mercury lamp under an argon atmosphere for 6 hr. Removal of the solvent followed by chromatography on silica gel (n-hexane) gave a mixture of *cis-* and *trans*-7-bromonorcarane in a ratio of 2.2:1 (0.8 g, 24%) as a colorless liquid in addition to the starting material (0.66 g): bp 78° (16 mm); nmr δ 1.35 (m, 10 H), 2.55 (t, J = 3 Hz, 0.3 H, trans isomer), 3.25 (t, J = 8 Hz, 0.7 H, cis isomer); glc retention time (120°), trans isomer 5.1 min, cis isomer 6.2 min. The nmr and glc data were identical with those of the authentic sample prepared by the literature method.[7]

1,1,2,2-Tetrachloro-1,2-diphenylethane.—A solution of benzotrichloride (2.35 g, 12 mmol) in THF (100 ml) was irradiated in a Pyrex vessel with a high-pressure mercury lamp for 4 hr. Purification of the product by chromatography on silica gel gave dimeric compound, 1,1,2,2-tetrachloro-1,2-diphenylethane (0.77 g, 40%), together with a trace of benzal chloride and the unchanged material (156 mg). The dimer was recrystallized from n-hexane to give colorless prisms, mp 163°, whose ir spectrum was identical with that of the authentic sample.[9]

Registry No.—**1a**, 39010-29-2; **1b**, 39010-30-5; **2a**, 39010-31-6; **2b**, 39010-32-7; 1-heptene, 592-76-7; carbon tetrachloride, 56-23-5.

(9) G. Sanna, *Chem. Zentr.*, *II*, 2345 (1937).

Photolysis of Sultones. Conversion to Butenolides and to Dimeric Sultones

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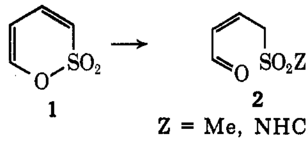
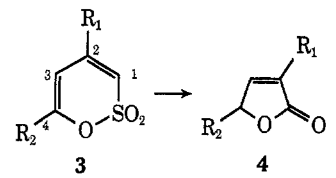
Received November 9, 1972

Photolysis of unsaturated sultones of general structure **1**, when carried out in methanol solution or in ether solutions containing benzylamine, has been shown to give ketosulfonic acid derivatives (**2**).[2,3]



Z = Me, NHCH$_2$Ph

We have found that when photolysis is carried out in the absence of a nucleophile the product is a butenolide. Thus, irradiation of 4-hydroxy-2-methyl-1,3-pentadiene-1-sulfonic acid sultone (**3a**)[4] in ether solution employing a medium-pressure mercury lamp yielded 2-methyl-4-hydroxy-2-pentenoic acid lactone (**4a**)[5] in 65% yield. Similarly irradiation of the sultone **3b**[4] gave the butenolide **4b**[6] in 53% yield. The loss of sulfur monoxide in these reactions is evidenced

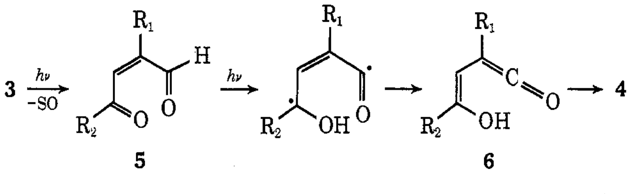


a, R$_1$ = R$_2$ = Me

b, R$_1$ = Me; R$_2$ = Ph

by the formation of both sulfur dioxide and monoclinic sulfur.[7,8]

Although the detailed mechanism of this transformation has not been defined, initial formation of a dicarbonyl intermediate **5** through photochemically induced loss of sulfur monoxide from **3** seems likely.[9] Further transformation of the unsaturated keto aldehyde through photochemical γ-hydrogen abstraction, decay to the ground state, and cyclization of the ketene **6** has a close parallel in the photochemical conversion of 2-formylbenzophenone,[13] 2-formylacetophenone,[14] and phthalaldehyde[15,16] to the corresponding pthalides. In these reactions clear evidence has been adduced for γ-hydrogen abstraction in the keto aldehyde and for the intermediary of an enol ketene.[15,16]



Sensitized photolysis of these sultones, carried out in the presence of benzophenone, leads to the formation of dimeric products. The infrared spectra of these dimers preserved the moderately intense band near 1680 cm^{-1}, present in the starting material, which is assigned to the enol sulfonate grouping.[17] However, a second moderately intense absorption band in the starting material near 1580 cm^{-1}, assigned to the remaining double bond, is uniformly absent from the dimers.[18] These observations eliminate all possible

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(1) Taken in part from the Ph.D. Thesis of B. Gorewit, Brandeis University, 1973.

(2) E. Henmo, P. de Mayo, A. B. M. A. Sattar, and A. Stoessl, *Proc. Chem. Soc.*, 238 (1961).

(3) J. F. King, P. de Mayo, E. Morkved, A. B. M. A. Sattar, and A. Stoessl, *Can. J. Chem.*, **41**, 100 (1963).

(4) T. Morel and P. E. Verkade, *Recl. Trav. Chim. Pays-Bas*, **68**, 539 (1949).

(5) H. C. Volger, W. Brackman, and J. W. F. M. Lemmers, *ibid.*, **84**, 1203 (1965).

(6) F. Ramirez and M. B. Rubin, *J. Amer. Chem. Soc.*, **77**, 3768 (1955).

(7) P. W. Schenk and R. Steudel, *Angew. Chem., Int. Ed. Engl.*, **4**, 402 (1965).

(8) The loss of SO$_2$ on irradiation of a similarly constituted sultone in dyglyme solution has previously been reported by J. L. Charlton and P. de Mayo, *Can. J. Chem.*, **46**, 55 (1968).

(9) Sulfenes may be intermediates in this reaction. The photochemical rearrangement of the closely related sulfines to carbonyl compounds through an excited singlet state[10] has been reported for a number of such compounds.[10,11] Although the corresponding photochemical rearrangement of a sulfene has hitherto not been observed, high-temperature thermolysis of thiete 1,1-dioxides is reported to give α,β-unsaturated ketones or aldehydes formed apparently through initial cycloreversion to a vinyl sulfene followed by loss of SO.[12]

(10) A. G. Schultz and R. H. Schlessinger, *Chem. Commun.*, 1483 (1969); R. H. Schlessinger and A. G. Schultz, *Tetrahedron Lett.*, 4513 (1969).

(11) R. Zwanenburg, L. Thys, and J. Strating, *ibid.*, 3453 (1967). J. F. King and T. Durst, *J. Amer. Chem. Soc.*, **85**, 2676 (1963); *Can. J. Chem.*, **44**, 819 (1966).

(12) C. L. McIntosh and P. de Mayo, *Chem. Commun.*, 32 (1969).

(13) M. Pfau, E. W. Sarver, and N. D. Heindel, *C. R. Acad. Sci., Ser. C*, **268**, 1167 (1969).

(14) P. Yates, A. C. Mackay, and F. X. Garneau, *Tetrahedron Lett.*, 5389 (1968).

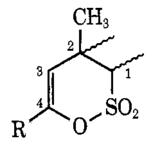
(15) S. P. Pappas and J. E. Blackwell, *ibid.*, 3337 (1968).

(16) K. F. Cohen, J. T. Pinhey, and R. J. Smith, *ibid.*, 4729 (1968).

(17) P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **90**, 6515 (1968), have reported absorption near 1680 cm^{-1} for a number of enol tosylates and brosylates.

(18) Divinyl sulfone exhibits absorption at 1613 cm^{-1} (Satler ir no. 13512).

structures for the dimers, except for the 1,2-dimeric structure **7**.



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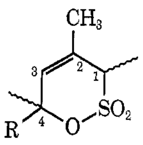

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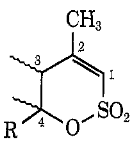

9

a, R = CH_3
b, R = C_6H_5

These conclusions are supported by the following further observations. The relative simplicity of the nmr spectra of the dimers rules out structures resulting from [2 + 2] cycloadditions of $C_{1,2}$ with $C_{3,4}$ or of [2 + 4] cycloadditions. The assignment of the multiplets at τ 3.74 and 4.38 to H_1 and H_3, respectively, in the spectrum of **3a** is based on the spectra of trisubstituted sultones reported by Barnett and McCormack.[19] These absorptions shift to τ 5.3 [broad singlet) and 4.8 (singlet) in the photodimer, consistent with a 1,2 or 1,4 dimer structure (**7** or **8**) in which these resonances are assigned to H_1 and H_3, respectively. The data are not in accord with a 3,4 dimer structure (**9**), which would require assigning the absorption at τ 4.8 to H_1. The changes observed in the dimerization of **3b** are more instructive. The nmr spectrum of this substance exhibits two one-proton signals, one a multiplet at τ 3.53 and the second a singlet at τ 3.60, which can be assigned to H_1 and H_3, respectively, in addition to a methyl doublet signal at τ 7.85 (J = 1.5 Hz). Dimerization results in the collapse of the methyl doublet to a sharp singlet at τ 8.6. The two one-proton signals now both appear as singlets at τ 3.80 and 4.89. Taken together with the spectral data of **3a** and its photodimer, neither of these observations are compatible with either a 3,4 or a 1,4 dimer, since each such structure preserves a –CH=CMe– grouping which should give rise, as it does in the dimer of **3a**, to readily detectable allylic coupling. A 1,2 dimer structure is alone compatible with the absence of such coupling and with the chemical shift of the methyl protons.

Thus, in contrast to α-pyridones and 2-aminopyridines, which give rise only to 1,4 photodimers, these sultones afford only 1,2 dimers on photolysis. Their behavior is more closely paralleled by that of α-pyrones. The parent substance is reported[20] to yield a mixture of 1,4 and 1,2 dimers on photolysis, while 4,6-diphenyl-α-pyrone yields only a mixture of 1,2 dimers under these conditions.[21]

The present evidence does not allow us to define the structures of the photodimers more closely, but the failure of **7a** to react with a variety of olefin reagents such as bromine, diimide, diborane, *m*-chloroperbenzoic acid, and potassium permanganate and its resistance to catalytic hydrogenation suggests that it has one of the two possible syn 1,2-dimeric structures.[22]

Experimental Section

All reactions were carried out under nitrogen in a flame-dried apparatus. Photolyses were carried out using a medium-pressure quartz mercury-vapor lamp (Hanovia Type L, 450 W). Infrared spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer. Nuclear magnetic resonance spectra were obtained using a Varian Model A-60A spectrometer. Mass spectra were obtained with an AEI Model MS-12 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Column chromatography was carried out using Camag neutral alumina adjusted to Brockman II activity.

Preparation of 4-Hydroxy-2-methyl-1,3-pentadiene-1-sulfonic Acid Sultone (3a).—This material was prepared from mesityl oxide following the procedure of Morel and Verkade:[4] mp 70–71°; ir (KBr) 1667 (C=CO), 1587 (C=CS), 1335, 1155 cm^{-1} (SO_2); uv max (95% C_2H_5OH) 267.5 nm (ε 5250); nmr ($CDCl_3$) τ 3.74 (m, 1, SCH=), 4.38 (m, 1, CH=), 7.87 [d, 3, J = 1 Hz, $OC(CH_3)$=], 7.98 (d, 3, J = 2 Hz, $=CCH_3$).

Preparation of 4-Hydroxy-2-methyl-4-phenyl-1,3-butadiene-1-sulfonic Acid Sultone (3b).—This material was prepared from β,β-dimethylvinyl phenyl ketone following the procedure of Morel and Verkade:[4] mp 83–84°; ir (KBr) 1640 (C=CO), 1555 (C=CS), 1345, 1180 cm^{-1} (SO_2); uv max (95% C_2H_5OH) 307.0 nm (ε 15,200), 219.0 (10,400); nmr ($CDCl_3$) τ 3.53 (m, 1, SCH=), 3.60 (s, 1, CH=), 7.85 (d, 3, J = 1.5 Hz).

Unsensitized Photolyses of Sultone 3a.—A solution of 2.50 g (15.6 mmol) of sultone in 220 ml of absolute ether was irradiated, under nitrogen, for 2.3 hr, through a Vycor filter. At this time infrared analysis revealed that the lactone band at 1745 cm^{-1} had reached maximum intensity. Work-up, including chromatography on alumina, yielded 1.14 g (65.4%) of lactone **4a**:[4,5] bp 30° (0.05 mm); nmr ($CDCl_3$) τ 8.63 (d, 3, J = 6.8 Hz, 4-Me), 8.10 (t, 3, J = 3.6 Hz, 2-Me), 5.06 (m, 1, 4-H), 2.96 (m, 1, 3-H).

When irradiation was carried out in benzene solution and nitrogen was passed continuously through one solution, and then into a 30% aqueous solution of H_2O_2, sulfuric acid corresponding to 11 mol % of the sultone consumed was titrated. Chromatography of the reaction solution yielded monoclinic sulfur corresponding to 29 mol % of the sultone consumed, in addition to lactone **4a**.

Unsensitized Photolysis of Sultone 3b.—Similar photolysis of **3b** in ether solution for 1 hr, employing a Corex filter, yielded lactone **4b**: mp 220–221° (lit.[6] mp 221–223°); ir (KBr) 1760 cm^{-1} (CO); nmr (DMSO) τ 8.40 (d, 3, J = 1.8 Hz, Me), 2.66 (s, 5, Ph), 1.91 (m, 1, 3-H), 1.69 (s, 1, 4-H).

Sensitized Irradiation of Sultone 3a.—A solution of 7.50 g (46.9 mmol) of **3a** and 9.0 g (49.4 mmol) of benzophenone in 100 ml of anhydrous ether was irradiated through a Pyrex filter. After 45 min of irradiation, the solution was filtered, and the white precipitate was collected. The solution was returned to the reaction vessel and irradiation was resumed. This procedure was repeated until no further precipitate was formed. Recrystallization of this product from ethyl acetate–ether gave 2.89 g of dimer: mp 258–259°; ir (KBr) 1700 (C=CO), 1360, 1190 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 4.8 (s, 2, OC=CH), 5.3 (s, 2, SCH), 8.02 [s, 6, $OC(CH_3)$=], 8.79 (s, 6, CCH_3); mass spectrum (70 eV) *m/e* 320, 176, 160, 133, 96, 43.

Anal. Calcd for $C_{12}H_{16}S_2O_6$: C, 45.00; H, 5.00; S, 20.00. Found: C, 45.16; H, 5.36; S, 19.82.

Chromatography of the reaction solution gave 7.51 g of benzpinacol, mp 190–192°, and 3.74 g of unreacted sultone.

Sensitized Irradiation of Sultone 3b.—Similar irradiation of **3b** gave the dimer **7b**: mp 218–219°; ir (KBr) 1660 (C=CO), 1375, 1180 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 2.5 (m, 10, Ph), 3.80 (s, 2, OC=CH), 4.89 (s, 2, SCH) 8.60 (s, 6, CH_3); mass spectrum (70 eV) *m/e* 444, 300, 222, 195, 158, 129, 105, 77, 64, 43, 41.

Anal. Calcd for $C_{22}H_{20}S_2O_6$: C, 59.50; H, 4.52; S, 14.48. Found: C, 59.53; H, 4.55; S, 14.38.

Registry No.—**3a**, 4941-84-8; **3b**, 39533-27-2; **4a**, 5584-69-0; **4b**, 15121-75-2; **7a**, 39533-28-3; **7b**, 39599-24-1; benzophenone, 119-61-9.

Acknowledgment.—This work was supported by a grant from the National Institutes of Health (GM-16395) which is gratefully acknowledged.

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[19] W. E. Barnett and J. A. McCormack, *Tetrahedron Lett.*, 651 (1969).

[20] P. de Mayo and R. W. Yip, *Proc. Chem. Soc.*, 84 (1964).

[21] R. D. Rieke and R. H. Copenhafer, *Tetrahedron Lett.*, 879 (1971).

[22] An example of a similar reduction in chemical reactivity owing apparently to steric crowding in the transition state is provided by the 1,4 photodimer of 2-aminopyridine, whose tetrahydro derivative resists hydrolysis by hot concentrated alkali while the monocyclic analog undergoes rapid hydrolysis in water: E. C. Taylor and R. O. Kan, *J. Amer. Chem. Soc.*, **85**, 776 (1963).