

The Photochemical SO Extrusion of 2,2,4,4-Tetraacylthietane 1-Oxides

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Synopsis. The irradiation of a benzene solution of 2,2,4,4-tetraacylthietane 1-oxides, which had been prepared from dimedone-aldehyde derivatives with SCl_2 , followed by oxidation with peracid, was carried out to give the corresponding 1,1,2,2-tetraacylcyclopropanes (**4**) or a mixture of **4** and the corresponding dihydrofuran derivative, depending on the C_3 substituent on the 1-oxides and wavelength.

Photochemical studies of various sulfoxides, one of them is the photoisomerization of 2-phenyl-2*H*-naphtho-[1,8-*b,c*]thiophene 1-oxide to the corresponding sulfenate, have been undertaken.¹⁾ However, few attempts seem to have been made for the photolysis of thietane 1-oxides.

An attempt to prepare an 3,3,5,5-tetraacyl-1,2-oxathiolane by the photoisomerization of the corresponding 2,2,4,4-tetraacylthietane 1-oxide was carried out. However, no 1,2-oxathiolane was obtained, although photodesulfurization occurred.

In this paper we wish to describe the photochemical reactions of 2,2,4,4-tetraacylthietane 1-oxide using 3,3,11,11-tetramethyl-7-thiadispiro[5.1.5.1]teradecane-1,5,9,13-tetrone 7-oxide (**3a**) and its 14-methyl (**3b**) and 14-isopropyl (**3c**) derivatives as model compounds.

The reaction of 2,2'-methylenebis[5,5-dimethyl-1,3-cyclohexanedione] (**1a**) and its derivatives (**1b**—**1d**) with an equimolar amount of sulfur dichloride in ethyl acetate or dichloromethane gave thietane derivatives (**2a**—**2d**) in good yields. The conversion of **2** into the dioxide was unsuccessful except for the case of **2d**, which also failed to be converted into the monoxide.

A water-cooling dilute solution of **3a** in benzene open to air was irradiated with a Toshiba 75 W high-pressure mercury lamp for 1 h through a Pyrex filter. The product was identified as 3,3,10,10-tetramethyldispiro[5.0.5.1]tridecane-1,5,8,12-tetrone (**4a**) by comparison with the reported spectral data²⁾ and the elemental analysis. The photolysis of **2a** was also carried out in oxygen-free benzene both in a sealed vessel and in an atmosphere of nitrogen in a manner similar to that describes above to afford **4a** quantitatively.

Therefore, the possibility of sulfur monoxide extrusion upon the irradiation open to air *via* the formation of sulfone by photooxidation, followed by sulfur dioxide extrusion, can be ruled out.

On the other hand, the exposure of a dilute benzene solution of **2a** to light through a quartz filter open to air for 1 h gave **3a**, together with 4,5,6,7-tetrahydro-4',4',6,6'-tetramethylspiro[benzofuran-2 (3*H*), 1'-cyclohexane]-2',4,6'-trione (**5a**), which was readily formed by the treatment of **1a** with bromine in acetic acid. These results are summarized in Table 1, together

TABLE 1. PHOTOREACTIONS OF **3**

No.	Products (%)		No.	Products (%)	
	4	5		4	5
3a (P)	100		3b (P)	50	15
3a (P) ^a)	100		3b (Q)	50	20
3a (P) ^b)	100		3c (P)	100	
3a (Q)	70	20	3c (Q)	50	20

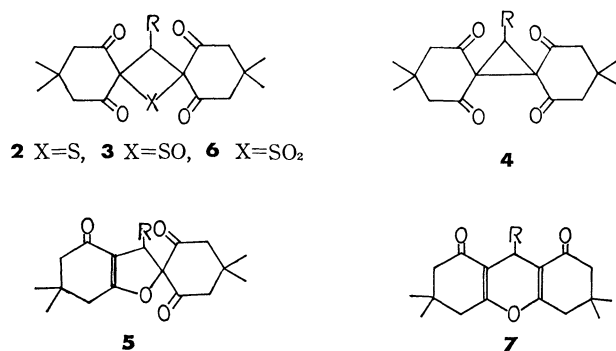
P: Pyrex filter, Q: Quartz filter, a) In oxygen-free benzene (in a sealed vessel). b) Under nitrogen.

with the results for other 1-oxides (**3b** and **3c**). Unfortunately, a comparative study with the corresponding 1,1-dioxides (**6a**—**6c**) was not undertaken because of the failure to prepare the dioxides. Thietane **2a** gave only a resinous substance under similar reaction conditions.

On the other hand, sulfone **6d** afforded neither the corresponding cyclopropane (**4d**) nor dihydrofuran (**5d**), but gave the octahydroxanthene derivative (**7d**) under similar reaction conditions.

No decomposition of **3a** occurred upon prolonged heating in boiling xylene, while the pyrolysis of **3a** in a sealed tube at the melting point resulted in the formation of only a resinous substance which could not be purified by column chromatography.

Chow *et al.* reported that the SO moiety of dibenzo-[*b,f*][1,4,6]thiadiazepin 1-oxide (**8**) was extruded in benzene or chloroform under reflux to give benzocinnoline, but no decomposition was observed when a benzene solution of **8** was irradiated in a Pyrex apparatus.³⁾ The difference in photolysis between **3** and **8** may be attributed to the low bond-dissociation energy of the carbon-sulfur bond of **3** caused by the four acyl groups. The photolysis of **3** presumably proceeds *via* a sulfenate-intermediate which, upon further photolysis, gives **4** and **5**, with SO extrusion by means of a concerted mechanism. Furthermore, the inability of compound **3** to form a thiiran 1-oxide may be responsible for the thermal stability of the compound.



2 X=S, **3** X=SO, **6** X=SO₂

4

a: R=H, **b:** R=CH₃, **c:** R=CH(CH₃)₂, **d:** R=C₆H₅.

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TABLE 2. MELTING POINTS AND ELEMENTAL ANALYSES OF **2**—**4** AND **6d**

Compd No.	IR (KBr) (cm ⁻¹)	MS (70 eV) (m/e)	NMR (in CDCl ₃) (δ)
2a	1700, 1730	322 (M ⁺)	0.82 (6H, s), 1.09 (6H, s), 2.38—2.65 (8H, m), 3.83 (2H, s)
2b	1700, 1720	336 (M ⁺)	0.97 (12H, s), 1.52 (3H, d, <i>J</i> = 7.5 Hz), 2.25—3.01 (8H, m), 4.34 (1H, q, <i>J</i> = 7.5 Hz)
2c	1705, 1730	364 (M ⁺)	0.65 (6H, d, <i>J</i> = 6.0 Hz), 1.08 (12H, s), 2.28—2.78 (8H, m), 3.65 (1H, m), 4.65 (1H, d, <i>J</i> = 11.5 Hz)
2d	1705, 1730	398 (M ⁺)	0.90 (12H, s), 1.85—2.93 (8H, m), 5.01 (1H, s), 7.35 (5H, s)
3a	1720, 1740	338 (M ⁺)	0.84 (6H, s), 1.25 (6H, s), 2.73 (8H, s), 3.50 (2H, s)
3b	1720, 1740	352 (M ⁺)	0.85 (6H, s), 1.22 (6H, s), 1.66 (3H, d, <i>J</i> = 7.5 Hz), 2.40—3.04 (8H, m), 4.55 (1H, q, <i>J</i> = 7.5 Hz)
3c	1720, 1740	380 (M ⁺)	0.75 (6H, d, <i>J</i> = 6.0 Hz), 0.89 (6H, s), 1.19 (6H, s), 2.40—3.04 (8H, m), 3.83 (1H, m), 4.30 (1H, <i>J</i> = 11.5 Hz)
4a	1690 (sh), 1705* 290 (M ⁺)	1720, 1730	1.03 (6H, s), 1.15 (6H, s), 2.23 (2H, s), 2.60 (8H, s)
4b	1690 (sh), 1705* 304 (M ⁺)	1735	1.00 (6H, s), 1.08 (6H, s), 1.38 (3H, d, <i>J</i> = 7.5 Hz), 2.13—2.50 (1H, m), 2.58 (8H, s)
4c	1688 (sh), 1705* 332 (M ⁺)	1735	1.06 (6H, d, <i>J</i> = 6.0 Hz), 1.09 (12H, s), 1.90—2.32 (2H, m), 2.50 (8H, s)
6d	1690, 1720	430 (M ⁺)	1.01 (6H, s), 1.24 (6H, s), 2.50—3.10 (8H, m), 5.78 (1H, s), 6.45—7.20 (5H, m)

(sh) shoulder, * the strongest peak. UV: λ_{max} **2a** 245 (ε 3000), 258 (max, 3200), 270 (2510), 300 nm (1000). **3a** 230 (sh, ε 3500), 270 (900), 300 nm (700)

TABLE 3. SPECTRAL DATA OF **2**—**4** AND **6d**

No.	Mp, °C (a)	Molecular formula	Found (Calcd), %	
			C	H
2a	220—221 (Ethanol)	C ₁₇ H ₂₂ O ₄ S	63.21 (63.34)	6.76 (6.88)
2b	179—180 (Ethyl acetate)	C ₁₈ H ₂₄ O ₄ S	63.92 (64.27)	7.35 (7.19)
2c	198—199 (Ethanol)	C ₂₀ H ₂₈ O ₄ S	65.62 (65.91)	7.85 (7.74)
2d	201—202 (Ethanol)	C ₂₂ H ₃₀ O ₄ S	69.05 (69.33)	6.62 (6.58)
3a	238—240 (Benzene)	C ₁₇ H ₂₂ O ₃ S	60.05 (60.34)	6.42 (6.55)
3d	215—217 (Benzene)	C ₁₈ H ₂₄ O ₃ S	61.64 (61.35)	6.99 (6.86)
3c	218—220 (Benzene)	C ₂₀ H ₂₈ O ₃ S	63.42 (63.14)	7.34 (7.42)
4a	175—176 (Ethanol) ^b	C ₁₇ H ₂₂ O ₄	70.54 (70.32)	7.82 (7.64)
4b	110—111 (Methanol) ^c	C ₁₈ H ₂₄ O ₄	71.42 (71.02)	8.05 (7.95)
4c	167—168 (Ethanol)	C ₂₀ H ₂₈ O ₄	72.17 (72.26)	8.36 (8.49)
6d	183—184 (Benzene)	C ₂₂ H ₃₀ O ₄ S	63.95 (64.17)	6.12 (6.09)

a) Recrystallization solvent. b) Lit.⁹ 147—148 °C. c) Lit.⁹ 109—110 °C.

Experimental

General. All the melting points are uncorrected. The IR spectra were recorded with a JASCO-DS-601F spectrophotometer. The UV spectra were obtained on a Hitachi EPS-2 spectrophotometer. The NMR spectra were obtained on a JNM-C-60HL spectrometer, using TMS as the internal standard. The mass spectra were measured on a Hitachi RMU-6 spectrometer.

Materials. The *m*-chloroperbenzoic acid and sulfur dichloride were obtained commercially. The purity of *m*-chloroperbenzoic acid was determined by iodometry.

Irradiation. All the irradiations were carried out externally with a high-pressure mercury lamp (Toshiba SHL-100UV, 75 W) at the temperature of running water.

Preparation of 2. *General Procedure:* To a stirred solution of the aldehyde-dimedone derivative (0.01 mol) in ethyl acetate (100 ml), cooled in an ice bath, a solution of sulfur dichloride (0.01 ml) in ethyl acetate (10 ml) was added, drop by drop, over a 20-min period. After additional stirring for 2 h at this temperature, the mixture was stirred

at room temperature for 10 h. The evaporation of the solvent under reduced pressure afforded white crystals. Yields: **2a** (80%); **2b** (80%); **2c** (80%); **2d** (75%). The recrystallization solvents, mps, and elemental analyses are summarized in Table 2.

Oxidation of 2 with m-Chloroperbenzoic Acid. *General Procedure:*

To a stirred solution of **2** (2 mmol) in benzene (100 ml), cooled in an ice bath, a solution of *m*-chloroperbenzoic acid (2 mmol) in benzene (50 ml) was added, drop by drop, over a 10-min period. After additional stirring for 1 h at this temperature, the mixture was stirred at room temperature for 19 h. The precipitate (*m*-chlorobenzoic acid) was then filtered off, and the filtrate was washed with a 5% cold NaHCO₃ solution and then with cold water. The evaporation of the solvent from the dried solution (Na₂SO₄) gave a solid substance which was fractionated by recrystallization. Yields: **3a** (63%); **3b** (30%); **3c** (45%); **6d** (20%). The recrystallization solvents, mps, and elemental analyses of the monoxides **3a**—**3c** and the dioxide **6d** are summarized in Table 2.

Preparation of 5. Compounds **5a**—**5c** were prepared according to the previously reported method.⁴ **5a**: Mp 210—212 °C (lit, 211—213 °C), **5b**: mp 197—198 °C (lit, 197—198 °C), **5c**: mp 186—187 °C, Found: C, 71.52; H, 9.06%. Calcd for C₂₀H₃₀O₄: C, 71.82; H, 9.04%.

Irradiation of Thietane Monoxide (3) in Benzene. *General Procedure:*

A solution of **3** in benzene (0.006 M) was irradiated in a Pyrex vessel or a quartz vessel for 1 h. The subsequent evaporation of the solvent afforded a white solid, which was then recrystallized from an appropriate solvent. When a mixture was given, it was chromatographed on silica gel, using hexane, hexane-benzene, and then benzene. The results are summarized in Table 1.

Irradiation of 3a in Oxygen-free Benzene. A benzene solution of **3a** was degassed at -70 °C under a high vacuum and then sealed. The irradiation of the solution was carried out in a manner similar to that described above.

Irradiation of 3a under Nitrogen. Nitrogen gas was allowed to pass through a benzene solution of **3a** during the course of irradiation.

Irradiation of 6d in Benzene. A solution of **6d** in benzene (0.006 M) was irradiated in a Pyrex vessel for 1 h. The subsequent evaporation of the solvent afforded a white solid, which was identified as the corresponding octahydroxanthene derivative (**7d**) by direct comparison with an authentic sample (yield, 95%).

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