BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (11), 3403—3404 (1978)

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

Shoei ITO* and Jun-ichi MORI**
Department of Chemistry, Faculty of Science, Hirosaki University, Hirosaki 036

(Received May 10, 1978)

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-tetraacylcylopropanes(**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 data[2] 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 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.

TABLE 1. PHOTOREACTIONS OF 3

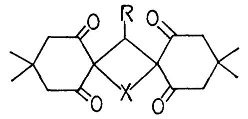
No.	Products (%)		No.	Products (%)	
	4	**5**		**4**	**5**
3a(P)	100		**3b**(P)	50	15
3a(P)[a]	100		**3b**(Q)	50	20
3a(P)[b]	100		**3c**(P)	100	
3a(Q)	70	20	**3c**(Q)	50	20

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

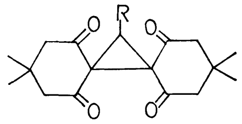
On the other hand, sulfone **6d** afforded neither the corresponding cyclopropane(**4d**) nor dihydrofuran(**5d**), but gave the octahydroxanthene derivative(**7d**) under similar reaction conditions.

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 stabitity of the compound.



2 X=S, **3** X=SO, **6** $X=SO_2$



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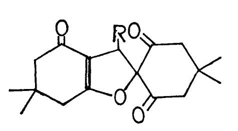

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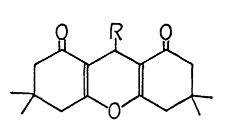

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a: R=H, **b**: $R=CH_3$, **c**: $R=CH(CH_3)_2$, **d**: $R=C_6H_5$.

** Present address: Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060.

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, *J*=7.5 Hz), 2.25—3.01(8H, m), 4.34(1H, q, *J*=7.5 Hz)
2c	1705, 1730	364(M$^+$)	0.65(6H, d, *J*=6.0 Hz), 1.08(12H, s), 2.28—2.78 (8H, m), 3.65(1H, m), 4.65(1H, d, *J*=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, *J*=7.5 Hz), 2.40—3.04(8H, m), 4.55(1H, q, *J*=7.5 Hz)
3c	1720, 1740	380(M$^+$)	0.75(6H, d, *J*=6.0 Hz), 0.89(6H, s), 1.19(6H, s), 2.40—3.04(8H, m), 3.83(1H, m), 4.30(1H, *J*=11.5 Hz)
4a	1690(sh), 1705* 1720, 1730	290(M$^+$)	1.03(6H, s), 1.15(6H, s), 2.23(2H, s), 2.60(8H, s)
4b	1690(sh), 1705* 1735	304(M$^+$)	1.00(6H, s), 1.08(6H, s), 1.38(3H, d, *J*=7.5 Hz), 2.13—2.50(1H, m), 2.58(8H, s)
4c	1688(sh), 1705* 1735	332(M$^+$)	1.06(6H, d, *J*=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^{EtOH}; **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	Found (Calcd), % H
2a	220—221 (Ethanol)	$C_{17}H_{22}O_4S$	63.21 (63.34)	6.76 (6.88)
2b	179—180 (Ethyl acetate)	$C_{18}H_{24}O_4S$	63.92 (64.27)	7.35 (7.19)
2c	198—199 (Ethanol)	$C_{20}H_{28}O_4S$	65.62 (65.91)	7.85 (7.74)
2d	201—202 (Ethanol)	$C_{23}H_{26}O_4S$	69.05 (69.33)	6.62 (6.58)
3a	238—240 (Benzene)	$C_{17}H_{22}O_5S$	60.05 (60.34)	6.42 (6.55)
3d	215—217 (Benzene)	$C_{18}H_{24}O_5S$	61.64 (61.35)	6.99 (6.86)
3c	218—220 (Benzene)	$C_{20}H_{28}O_5S$	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)	$C_{23}H_{26}O_6S$	63.95 (64.17)	6.12 (6.09)

a) Recrystallization solvent. b) Lit,[2] 147—148 °C. c) Lit,[2] 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 $NaHCO_3$ solution and then with cold water. The evaporation of the solvent from the dried solution (Na_2SO_4) 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 $C_{20}H_{30}O_4$: 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%).

References

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