

PHOTOCHEMISTRY OF HETEROCYCLES. PART IV.

PHOTOLYSIS OF THIETE-1,1-DIOXIDES

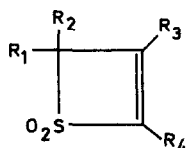
R.F.J. Langendries, F.C. De Schryver*

Dept.Scheikunde, Universiteit Leuven, Celestijnenlaan 200 F, B-3030 Heverlee

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Although the thermal behavior of some thiete-1,1-dioxides (I) has been reported (1), few data on their photochemistry have been presented (2).

We now wish to report some results on the photolysis of the thiete-1,1-dioxides I_{a-f}.



	<u>Ref.</u>
a : R ₁ =C ₆ H ₅ ; R ₂ =R ₃ =H; R ₄ =C ₆ H ₅	(3)
b : R ₁ =R ₂ =CH ₃ ; R ₃ =H; R ₄ =C ₆ H ₅	-
c : R ₁ =R ₂ =R ₃ =H; R ₄ =C ₆ H ₅	(4)
d : R ₁ =R ₂ =H; R ₃ =OH; R ₄ =C ₆ H ₅	(1c)
e : R ₁ =R ₂ =H; R ₃ =OC ₂ H ₅ ; R ₄ =C ₆ H ₅	(1c)
f : R ₁ =R ₂ =H; R ₃ =C ₆ H ₅ ; R ₄ =H	(5)

The unknown derivative I_b was synthesized from 2-phenyl-3-pyrrolidino-4,4-dimethylthietane-1,1-dioxide (6) by oxidative deamination with hydrogenperoxide in glacial acetic acid-acetic acid anhydride. m.p. : 107-108°C; yield : 66%. [IR (KBr) : 1310 and 1120 cm⁻¹ >SO₂; n.m.r. (CDCl₃): 8.3τ S 6H, 3.15τ S 1H, 2.55τ m 5H].

The data of absorption and emission spectrometry of I_{a-f} are summarized in table I.

The ultra violet spectra of the mono-phenyl substitutes derivatives correspond very well with the spectrum of 1-phenylcyclobutene [λ_{max} (alc) : 255 nm, ε = 13850 l⁽⁷⁾]. Therefore, we may suggest that the lowest π-π* transition in thiete-1,1-dioxides is due to the unsaturated system.

All the photolyses, described here, were carried out, using a Rayonet Type RS Preparative Photochemical reactor, equipped with Rayonet RUL mercury lamps.

TABLE I

Comp.	UV spectrum	E_T (b)
	λ_{max} (nm) [ϵ] solvent : CH_3CN or CH_3OH	Kcal/mole
I_a	257 [25.000]	63.9 (75.1)
I_b (a)	257 [12.000]	64.7 (74.9)
I_c (a)	253 [13.800]	64.7 (74.9)
I_d (a)	261 [13.200]	(c)
I_e (a)	265 [20.000]	(c)
I_f	262 [16.600]	60.6 (70.6)

- (a) Weak fluorescence could be obtained from these compounds ($\phi_f \sim 0.016$)
- (b) Energy of the triplet excited states. Calculated from the maximum of the unstructured phosphorescence spectra at 77°K (solvent : EPA). The values between brackets are calculated from the onset of the spectra.
- (c) No phosphorescence was observed from these compounds.

Irradiation of a degassed solution of I_a in acetonitrile or dichloromethane at 253 nm gave chalcone (benzylidene acetophenone) III_a as the main organic reaction product (> 95%) [IR (KBr) : 1660 cm^{-1} C=O; n.m.r. ($CDCl_3$) : 1.9 - 2.7 τ m 12H] ; m.p. 54-55°C (lit.: 54-55°C). A second reaction product was isolated (<5%) and identified by mass spectrometry as the tetraphenylcyclohexadiene IV [M^+ : 384; basic peak : m/e = 192 (Ph-CH=CH=C-Ph) ‡ or $M^{\ddagger\dagger}$]

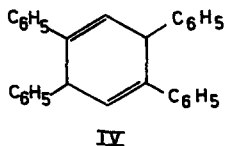
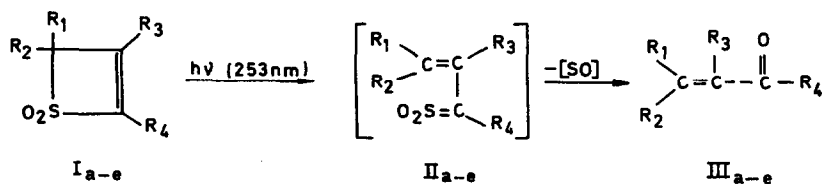
The photolysis of I_b in acetonitrile at 253 nm yielded isobutenylphenylketone III_b as the only reaction product [IR (liq.) : 1660 cm^{-1} C=O; n.m.r. ($CDCl_3$) : 7.9 τ d 6H; 3.4 τ s 1H; 2.9-2.1 m 5H].

After irradiation of I_c in acetonitrile at 253 nm, a polymeric substance, which could be characterized as the polymer derived from acrylophenone III_c was isolated [IR (KBr) : 1680 cm^{-1} $>C=O$; n.m.r. ($CDCl_3$) : 2.7τ m 5H; two broad peaks at 6τ 1H and 7τ 2H].

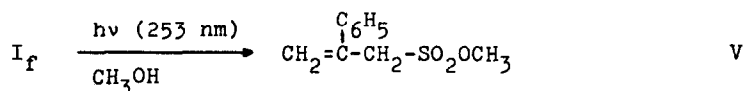
Irradiation of I_d in acetonitrile at 253 nm yielded 1-phenyl-propane-1,2-dione, the stable keto-form of III_d , as the only reaction product [IR (liq.) : 1710 and 1670 cm^{-1} $>C=O$; n.m.r. ($CDCl_3$) ; 7.48τ S3H; $1.8-2.6\tau$ m 5H].

Column chromatography of the irradiated solution of I_e in acetonitrile at 253 nm (adsorbens : silicagel; eluens : benzene) also yielded 1-phenylpropane-1,2-dione which is probably formed by hydrolysis on the column of 1-ethoxyacrylophenone III_e .

From these results , one may conclude that all derivatives of thiete-1,1-dioxides studied here, react in an analogous way. One can assume that, on irradiation, an electrocyclic ring opening occurs, with the formation of a sulfene II, which decomposes immediately into the unsaturated ketone by loss of sulfurmonooxide ($1b,c; 8$). In the case of I_a , however, a second fragmentation path is the loss of sulfur dioxide and dimerization of the intermediate thus formed, yielding a small amount of IV.



The intermediacy of a vinylsulfene in the photolysis of I_c was previously (2) excluded on the basis of lack of i.r. spectroscopic evidence under their experimental conditions but could be substantiated in the photolysis of I_f in methanol at 253 nm. The sulfonic ester V was isolated as the only reaction product [IR (liq.) : 1355 and 1177 cm^{-1} -SO₂O-; n.m.r. (CDCl₃) : 3.6 τ s 3H, 4.2 τ s 2H; 5.6 τ d 2H; 7.4 τ m 5H].



Quantum yields of disappearance of I_a and I_b were measured by n.m.r. spectroscopy in dichloromethane using Dow Corning silicone grease as internal standard (9). The values for I_a and I_b are 0.001 and 0.004 respectively. The quantum yield of disappearance of I_f in methanol, measured spectrophotometrically, was found to be 0.045.

When the photolyses of I_a and I_b in acetonitrile and of I_f in methanol were carried out at 350 nm, using benzophenone or acetophenone as sensitizer (equal concentrations for donor and acceptor) the same reaction products as in the direct irradiations were obtained.

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