

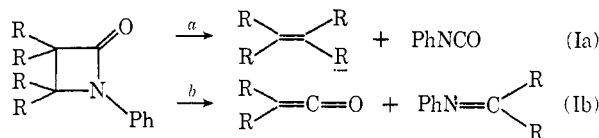
Photochemistry of 3-Thietanone 1,1-Dioxide

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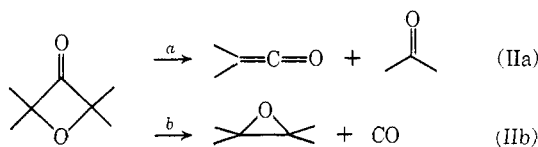
Contribution from the Department of Chemistry, Universiteit te Leuven, Heverlee B-3030, Belgium, and the Photochemistry Unit of the Department of Chemistry, University of Western Ontario, London, Canada. Received September 10, 1973

Abstract: Irradiation of 3-thietanone 1,1-dioxide in acetonitrile or in a 90:10 (v/v) mixture of acetonitrile-methanol results in the formation of ketene and sulfene. The intermediacy of the reactive sulfene was proved by trapping with alcohols and by ir spectroscopy at low temperature. Quenching experiments showed that reaction occurred from both the singlet and the triplet manifold with a total quantum yield of 0.91. The quantum yields of the important photochemical and photophysical processes were determined.

Considerable interest has been and still is shown in the liquid phase photolysis of four-membered rings containing one^{2a-m} or two carbonyl groups.³ The main modes of reaction are decarbonylation, cycloreversion, and ring expansion. Much less attention has been paid to the heterocyclic analogs.⁴ *N*-Arylazetidines^{4a} on irradiation undergo cycloreversion along either path a (eq Ia) or b (eq Ib) and, to a



small extent, decarbonylation.^{4d} Photolysis of tetramethyloxetanone^{4b} leads to cycloreversion (eq IIa) and decarbonylation (eq IIb). Irradiation of azetidine-2,4-



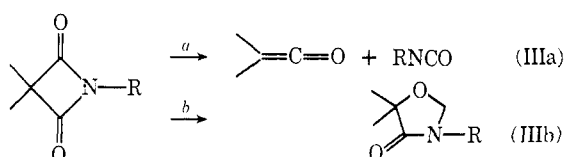
(1) (a) IWONL doctoral fellow 1969-1973; (b) Universiteit te Leuven; (c) University of Western Ontario.

(2) (a) N. J. Turro and P. M. Southam, *Tetrahedron Lett.*, 545 (1967); (b) D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4343 (1970); (c) R. F. Klemm, *Can. J. Chem.*, **48**, 3320 (1970); (d) N. J. Turro and D. M. McDaniel, *J. Amer. Chem. Soc.*, **92**, 5727 (1970); (e) P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **92**, 5724 (1970); (f) N. J. Turro and D. R. Morton, *ibid.*, **93**, 2569 (1971); (g) D. M. McDaniel and N. J. Turro, *Tetrahedron Lett.*, 3035 (1972); (h) G. Quinckert, G. Cimbollek, and G. Buhr, *ibid.*, 4573 (1966); (i) D. R. Morton, *Diss. Abstr. B*, **32** (9), 511 (1972); (j) M. J. Turro, *Angew. Chem., Int. Ed. Engl.*, **11**, 331 (1972); (k) R. D. Miller and V. Y. Abraitys, *J. Amer. Chem. Soc.*, **94**, 663 (1972); (l) J. C. Hemminger, C. F. Rusbalt, and E. K. C. Lee, *ibid.*, **93**, 1867 (1971); (m) N. J. Turro, J. C. Dalton, K. Dawes, G. Farmington, R. Hautala, D. R. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, **5**, 92 (1972); (n) O. L. Chapman and O. S. Weiss, "Organic Photochemistry," Vol. III, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1973, pp 197-280.

(3) (a) N. J. Turro, P. A. Leermakers, M. R. Wilson, D. C. Neckers, G. W. Beyers, and G. F. Vesley, *J. Amer. Chem. Soc.*, **87**, 2613 (1965); (b) R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc., London*, 144 (1964); (c) H. G. Richey, J. M. Richey, and D. C. Clagett, *J. Amer. Chem. Soc.*, **86**, 3906 (1964); (d) I. Haller and R. Srinivasan, *ibid.*, **87**, 1144 (1965); (e) N. J. Turro, G. W. Byers, and P. A. Leermakers, *ibid.*, **86**, 955 (1964); (f) P. A. Leermakers, G. F. Vesley, N. J. Turro, and D. C. Neckers, *ibid.*, **86**, 4213 (1964); (g) N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D'Angelo, *ibid.*, **87**, 4097 (1965).

(4) (a) M. Fisher, *Chem. Ber.*, **101**, 2663 (1968); (b) P. J. Wagner, C. A. Stout, S. Scarles, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1242 (1966); (c) J. Schutyser and F. C. De Schryver, in press; (d) J. Schutyser, Ph.D. Thesis, Leuven, 1973.

diones results mainly in cycloreversion (eq IIIa) and/or ring expansion (eq IIIb) depending on the nature of the substituents.^{4c}



The aim of the present work was to study the photochemical reactivity of 3-thietanone 1,1-dioxide and in particular to look into the possibility that such activation might lead to the formation of sulfene. The intermediacy of substituted sulfenes has been put forward in the flash thermolysis of thiete 1,1-dioxides,^{5a-c} demonstrated by chemical trapping in the photolysis of sultones,^{6a} sultams,^{6b} and thiete 1,1-dioxides⁷ and has been postulated in a variety of reactions.⁸

Results and Discussion

1. Spectroscopic Data. 3-Thietanone 1,1-dioxide (**1**)⁹ shows an n, π^* transition with a maximum at 302.5 nm (ϵ 27) in acetonitrile. Addition of methanol (10 vol %) resulted in a small hypochromic effect (ϵ 17), while in pure methanol the n, π^* transition in the 300-nm region disappeared.

An nmr study indicated that, upon addition of methanol to an acetonitrile solution of **1**, the hemiketal **2** was formed.¹⁰ In a solvent mixture acetonitrile-methanol (90 vol %-10 vol %) an equilibrium consisting

(5) (a) J. F. King, K. Piers, D. J. H. Smith, C. L. McIntosh, and P. de Mayo, *Chem. Commun.*, 31 (1969); (b) C. L. McIntosh and P. de Mayo, *ibid.*, 32 (1969); (c) J. F. King, P. de Mayo, C. L. McIntosh, K. Piers, and D. J. H. Smith, *Can. J. Chem.*, **48**, 3704 (1970).

(6) (a) J. F. King, P. de Mayo, E. Morkved, A. B. M. A. Satter, and A. Stossel, *Can. J. Chem.*, **41**, 100 (1963); (b) T. Dürst and J. F. King, *ibid.*, **44**, 1859 (1966); (c) E. Lee, "Excited State Chemistry," J. N. Pitts, Ed., Gordon and Breach, New York, N. Y., 1970, p 78.

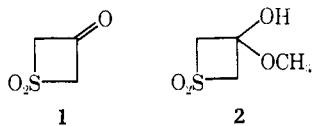
(7) R. Langendries and F. C. De Schryver, *Tetrahedron Lett.*, 4781 (1972).

(8) G. Opitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967).

(9) (a) W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc.*, **85**, 3236 (1963); (b) *Tetrahedron Lett.*, 1297 (1963).

(10) In acetonitrile the methylene protons of **1** absorb as a singlet at δ 4.95 (lit.⁹ dioxane δ 4.92). Upon addition of methanol (10 vol %), absorptions of the hemiketal appear at δ 3.13 (3 H, OCH₂) and at δ 4.28 (4 H, CH₂, m, AA'-BB' system). Upon evaporation of this solvent mixture the compound is recovered as **1** in 100%. It should also be pointed out that all photolysis solutions were freshly prepared. The time of irradiation in the kinetic runs (*vide infra*) is very short and within this time no changes in concentration of **1** due to hemiketal formation were observed.

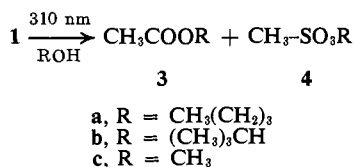
of 10% **1** and of 90% **2** was obtained after 4 days at 25°.



A broad emission from the singlet excited state of **1** is observed and neither its maximum (350 nm) nor its quantum yield¹¹ ($\phi_F = 0.001 \pm 0.0005$)^{2c,12} is dependent on the excitation wavelength in the 290–320-nm region or on the solvent system (acetonitrile or acetonitrile–methanol 90 vol %–10 vol %).

At 77°K in methanol broad emission from the triplet manifold, with onset of emission at 405 nm (~ 70 kcal/mol⁻¹) and maximum at 470 nm, was observed.

2. Photochemistry of 1. In the photolysis^{14a} of **1** after irradiation in acetonitrile containing 1 vol % water and evaporation of the solvent under reduced pressure, a viscous oil was obtained. Treatment of an ether solution of this oil with ammonia gas yielded a solid which, on comparison with an authentic sample, was found to be the ammonium salt of methanesulfonic acid (ir 3100, 1400 cm⁻¹ NH₄⁺, 1200 and 1050 cm⁻¹ -SO₃⁻; nmr in H₂O δ 2.85 (s, CH₃)). Similar photolysis of **1** in acetonitrile containing respectively 5 vol % butyl alcohol, 10 vol % 2-propanol, and 10 vol % methanol yielded a mixture of the acetic acid esters **3a–c** and the methanesulfonic acid esters **4a–c** as shown by tlc and by ir (C=O 1750 cm⁻¹; -SO₃- 1360 and 1176 cm⁻¹)^{14b} in comparison with authentic samples. Nmr analysis of a crude photolysis mixture in acetonitrile–methanol 90 vol %–10 vol % showed by the integration of the signals of the respective methyl ester groups C(=O)OCH₃, δ 3.6, 3 H; SO₂OCH₃, δ 3.8, in CD₃CN) that these esters were formed in equal amounts.



In contrast with the above, ester formation irradiation of a 0.08 *M* solution of **1a** in acetonitrile in the presence of 0.16 *M* benzhydrol resulted in the formation of benzyhydril ether **5** as was demonstrated by comparison with an authentic sample. The interpretation of this, at first, surprising result was readily arrived at in the following way. On the supposition that sulfene was an intermediate, the formation of **5** could be explained by nucleophilic substitution by benzhydrol on the so-formed sulfonic acid ester **8**. Generation of this same ester by other means should lead to the same result.

(11) The quantum yield of fluorescence is measured relative to a solution of quinine sulfate in 0.1 *N* sulfuric acid with an identical optical density as in the sample of **1** at the excitation wavelength. ϕ_F of quinine sulfate was taken as 0.5.

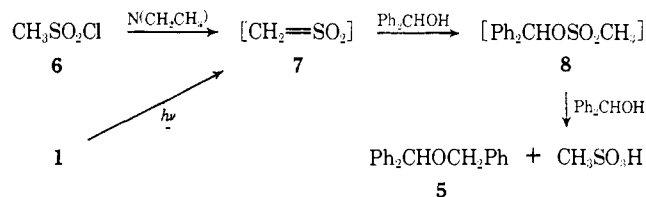
(12) In comparison the quantum yield of fluorescence of cyclobutanone is reported^{2b} to be 10⁻⁴ at 310 nm and is wavelength dependent. The triplet energy for cyclobutanone is reported^{2c} to be 75 kcal/mol⁻¹ in solution and 80 \pm 5 kcal mol⁻¹ in the gas phase.¹³

(13) E. Lee in "Excited State Chemistry," J. N. Pitts, Ed., Gordon and Breach, New York, N. Y., 1970.

(14) (a) All preparative photolyses, unless mentioned otherwise, were carried out in a Pyrex vessel in a Rayonet Preparative Reactor equipped with eight RUL-3100 Å lamps. (b) Since the boiling points of the alcohols are very close to those of their respective acetic acid esters, they were, on evaporation of the solvent, eliminated.

Since reaction of methanesulfonyl chloride and methylamine also generates sulfene, this reaction, in the presence of benzhydrol, should produce **5**; and this was, indeed, observed.¹⁵

The data so far presented provide indirect evidence that **1** does undergo cycloreversion to sulfene and ketene. Direct evidence for these conclusions was obtained in the following way.



Thietanone dioxide was irradiated in a pentane matrix at liquid nitrogen temperature with light ($\lambda > 280$ nm). The reaction was monitored by infrared spectroscopy in a cryostat.¹⁶ Five new bands appeared with time (3170, 3030, 1230, 950, and 2130 cm⁻¹) and attained constant intensity after 40 hr (see Figures 1 and 2). The first four of these bands were in excellent agreement with those we have previously observed for sulfene,¹⁷ while the final one was assigned to ketene. This latter assignment was substantiated as follows.

A film of **1** containing a small amount of pentane was irradiated in the cryostat for 12 hr and then slowly warmed. The volatile products were then analyzed by passage into a quadrupole mass spectrometer (operating at low electron energy) while the infrared spectrum was simultaneously monitored. Concomitant with the disappearance of the band at 2130 cm⁻¹ in the infrared spectrum the signal at 42 amu in the mass spectrum increased greatly. Similarly, the disappearance of the bands assigned to sulfene was accompanied by the appearance of a weak signal at mass 78 and a much stronger one (*ca.* times 8) at mass 76 in the mass spectrum. A mass spectroscopic study of the thermolysis of methanesulfonyl chloride also detected the generation of a species that gave both a 78 and 76 signal in the same ratio as above. This strongly suggests that these signals arise from sulfene, some of which is distilling from the matrix in the above irradiation experiment, though most of it is probably reacting in the condensed phase.

When light of shorter wavelength ($\lambda > 220$ nm) was used no sulfene bands were seen, but the band at 2130 cm⁻¹ was still produced. However, under these conditions sulfene (generated by the thermolysis of chlorosulfonyl acetic acid, **7b**) was observed to be completely decomposed in 0.5 hr, while it was observably unaffected by the longer wavelength light ($\lambda > 280$ nm). This suggests that the primary reaction of ketene and sulfene generation is still occurring but that the latter compound then undergoes photochemical decomposition.

Irradiation of Nujol mulls of **1** gave similar results;

(15) That the dibenzhydrol ether did not arise from the benzhydrol under influence of traces of acid present in the solution during work-up was ascertained by addition of benzhydrol, after irradiation, to a solution of **1** in acetonitrile irradiated in the presence of ethanol. Nmr analysis of this mixture did not reveal the presence of the dibenzhydrol ether even after 2 days.

(16) R. Bloch, R. A. Marty, and P. de Mayo, *Bull. Soc. Chim. Fr.*, 2031 (1972).

(17) J. F. King, R. A. Marty, and P. de Mayo, *J. Amer. Chem. Soc.*, 93, 6304 (1971).

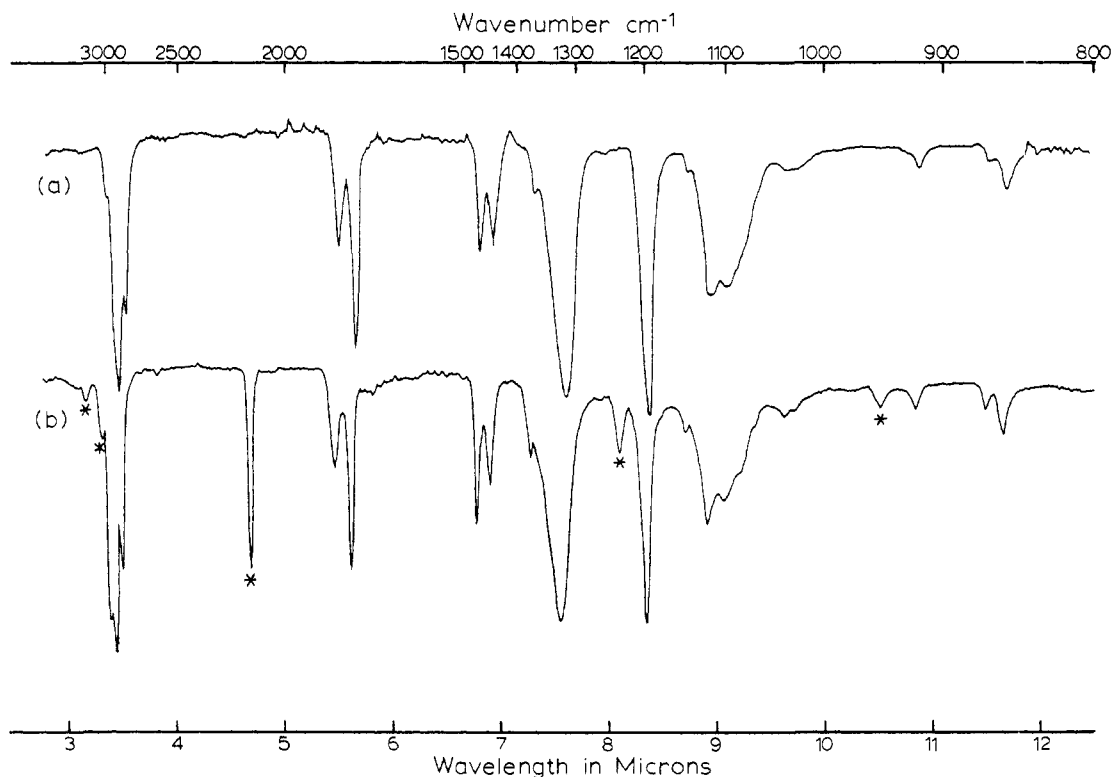


Figure 1. (a) Ir spectrum of **1** in pentane matrix. (b) Ir spectrum of matrix after irradiation.

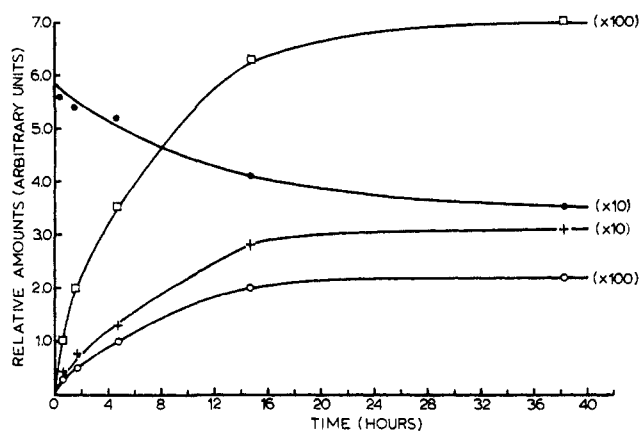


Figure 2. Changes with time of characteristic ir bands: (●) 1200 cm^{-1} , (□) 1230 cm^{-1} , (+) 2130 cm^{-1} , (○) 950 cm^{-1} .

however, the yields of sulfene at the longer wavelength irradiation were extremely small.

3. Photochemical Kinetics. Kinetic analysis of the photolysis of **1** in acetonitrile-methanol (90 vol %–10 vol %) yields a quantum yield of disappearance, Φ^0 , at 310 nm of 0.91 in the absence of quencher. Addition of piperlyene in a concentration range from 2×10^{-5} to 4×10^{-3} M resulted in partial quenching of the reaction. Plotting of the ratio Φ^0/Φ_Q as a function of the quencher concentration [Q] indicated that the reaction occurred from two excited states only one of which could be quenched (Figure 3).¹⁸ The assumption that the two states involved are the singlet and the triplet excited states could be substantiated in the

(18) (a) P. J. Wagner, "Creation and Detection of the Excited State," Vol. 1, Part A, A. A. Lamola, Ed., Marcel Dekker, New York, N. Y., 1971, p 192; (b) J. C. Dalton and N. J. Turro, *Mol. Photochem.*, **2**, 133 (1970).

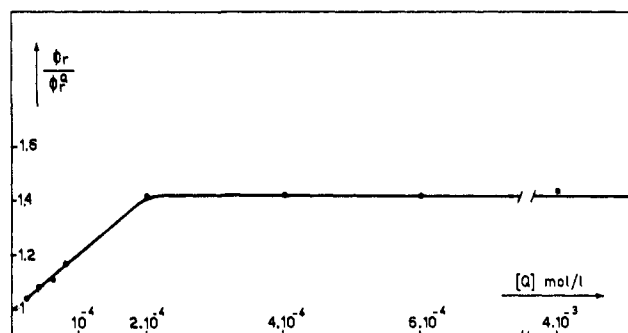


Figure 3. Quenching of the photolysis of 3-thiete 1,1-dioxide.

following way. The quantum yield of intersystem crossing, Φ_{ic} , was measured by *cis-trans* isomerization of *cis*-piperlyene¹⁹ and found to equal 0.28. Since the total quantum yield of product disappearance, $\Phi_r^s + \Phi_r^t$, equals 0.91, part of the reaction has to occur from the first excited singlet state.

Furthermore, photolysis of **1** in acetonitrile-methanol (90 vol %–10 vol %) at 350 nm in the presence of a sensitizer,²⁰ benzophenone, leads to the same products as are formed in the direct irradiation.

From the horizontal asymptote of the Stern-Volmer plot the ratio between the singlet and the triplet state in the reaction can be calculated¹⁸ (eq IV)

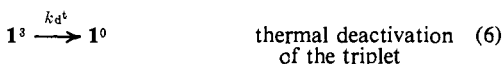
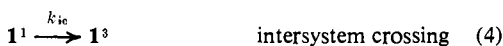
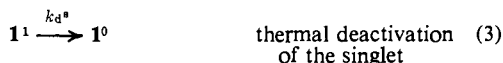
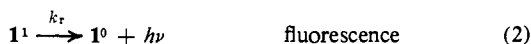
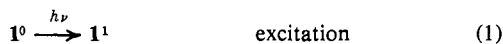
$$\text{horizontal asymptote} = 1 + \Phi_r^t/\Phi_r^s \quad (\text{IV})$$

Φ_r^s , the quantum yield of reaction from the singlet manifold, equals 0.64, while Φ_r^t , the quantum yield of

(19) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(20) A 1 cm thick filter solution of 3 g/l. of lead acetate and 479 g/l. of sodium bromide was used. Under these conditions all light below 340 nm is cut off and benzophenone is the only absorbing species.

reaction from the triplet manifold, equals 0.27. The latter value is in close agreement with the independently measured Φ_{ic} , which implies that the quantum yield per unit triplet is very close to unity. On this basis the following reaction scheme can be proposed.



The radiative lifetime, τ_s^0 , of the singlet excited state was calculated from the absorption spectrum,²¹ and its reciprocal, k_f , is equal to $5 \times 10^5 \text{ sec}^{-1}$. From the fluorescence quantum yield Φ_f and from τ_s^0 , the inherent lifetime, τ_s , of the singlet was obtained and found to be equal to $2 \times 10^{-9} \text{ sec}$.²² Using this value of τ_s the rate of singlet reaction, k_r^s , and the rate of intersystem crossing, k_{ic} , could be calculated according to eq 8 and 9. Values of respectively 3.2×10^8 and $1.3 \times 10^8 \text{ sec}^{-1}$

$$\Phi_f = k_r^s \tau_s \quad (8)$$

$$\Phi_{ic} = k_{ic} \tau_s \quad (9)$$

were found. From the initial slope of the Stern-Volmer curve¹⁸ the triplet lifetime τ^t could be obtained using eq 10, and assuming a diffusion-controlled quenching

$$\text{initial slope} = k_q^t \tau^t \Phi_r^t / (\Phi_r^t + \Phi_r^s) \quad (10)$$

rate constant of $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$.^{23,24} Using this value ($\tau^t = 0.7 \times 10^{-6} \text{ sec}$) the rate constant for reaction from the triplet manifold can be calculated according to eq 11.

$$\Phi_r^t = k_r^t \tau^t \Phi_{ic} \quad (11)$$

The order of magnitude of this value and of those of the other rate constants is assembled in Table I.

From these results it can be concluded that **1**, on irradiation at 300 nm, leads to the formation of sulfene and ketene. This cycloreversion occurs from both the singlet and triplet manifolds and could go either by a concerted pathway $2_s + 2_a$ or through a 1-4 biradical. The unimportance of either photodecarbonylation and ring expansion in this system suggests further work on substituted derivatives of **1**, which could lead to better comprehension of this photofragmentation.

(21) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 48. This value should be taken $\pm 100\%$. Consequently all other rate constants contain at least this error.

(22) Only negative direct experimental evidence for this value could be obtained. Using a single photon counting method (Applied Photo-physics Ltd.) with a resolution of $5 \times 10^{-9} \text{ sec}$ no meaningful decay could be obtained for **1** in the nanosecond range indicating that its lifetime has to be less than $5 \times 10^{-9} \text{ sec}$. The singlet lifetime τ_s of cyclobutanone is wavelength dependent and equals $2 \times 10^{-10} \text{ sec}$ above 320 nm.²¹

(23) A value of $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ can be calculated for the quenching rate constant in pure acetonitrile at 20° while for methanol a value of $1.1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ was proposed.^{4b}

(24) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 627.

Table I. Order of Magnitude of the Rate Constants of the Important Photochemical and Photophysical Processes of **1** in Acetonitrile-Methanol (90 vol % \approx 10 vol %)

Rate constants	10^6 sec^{-1}
k_f	5
k_{ic}	1300
k_r^s	3200
k_r^t	150

Table II

[3-Thietanone 1,1-dioxide], mol/l.	[<i>cis</i> -Piperylene], mol/l.	Φ_f/Φ_r^0
0.0075	0	1
0.0075	2×10^{-5}	1.044
0.0075	4×10^{-5}	1.084
0.0075	6×10^{-5}	1.114
0.0075	8×10^{-5}	1.220
0.0075	2×10^{-4}	1.420
0.0075	4×10^{-4}	1.420
0.0075	6×10^{-4}	1.420
0.0075	8×10^{-4}	1.450
0.0075	1×10^{-3}	1.450
0.0075	2×10^{-3}	1.470
0.0075	3×10^{-3}	1.440
0.0075	4×10^{-3}	1.440

Experimental Section

Apparatus. Infrared spectra were recorded with a Perkin-Elmer Model 521 grating spectrophotometer; uv spectra were recorded with a Cary 14 spectrophotometer while a Perkin-Elmer Model 124 was used for kinetic runs. Fluorescence spectra were measured with a Fica "spectrofluorimètre différentiel absolu," while phosphorescence spectra were obtained with an Aminco-Bowman. Nmr spectra were measured with a Varian A60. Mass spectral data were obtained with an AEI MS 902 S apparatus.

Materials. All solvents and reagents are p.a. grade and used without further purification.

3-Thietanone 1,1-dioxide (**1**) was synthesized as reported.⁹

Direct Photolysis. A 0.08 M solution of **1** in acetonitrile-methanol 90 vol %–10 vol % was degassed under high vacuum. The solution was irradiated in a Rayonet reactor¹² using RUL-3100 Å lamps. After completion of the reaction, as indicated by the absence of starting material on tlc (silica gel, CHCl_3 eluent), the solvent was evaporated under reduced pressure at room temperature. The residual liquid could be identified as the sulfonic acid ester **4c** (yield 100%, ir 1375 and 1175 cm^{-1} (str v SO_2); nmr in CDCl_3 δ 3 (s, CH_3SO_3), 3.9 (s, CH_3OSO_2) as compared with an authentic sample).²⁵

Analogously, the reaction was carried out in acetonitrile-2-propanol 90 vol %–10 vol % and the resulting ester **4b** was identified (yield 100%; ir 1335 and 1175 cm^{-1} (str v SO_2); nmr in CDCl_3 δ 1.4 (d, 6 H, $(\text{CH}_3)_2\text{C}$), 3 (s, 3 H, $\text{CH}_3\text{SO}_2\text{O}$), 4.9 (sep, 1 H, CH) in comparison with an authentic sample.²⁶

On irradiation in acetonitrile-butanol 95 vol %–5 vol % the sulfonic acid ester **4a** was not isolated but its presence was indicated by the typical ir bands at 1335 and 1175 cm^{-1} .²⁷ A 0.08 M solution of **1** was irradiated in the presence of 0.16 M of benzhydrol under analogous reaction conditions. The solvent was evaporated under reduced pressure. The resulting viscous oil solidified on standing and was recrystallized from ethanol. The crystalline product was identified as **5**, mp 109–110° (lit. 109–111°); $\text{M} \cdot + 350$; nmr in CDCl_3 δ 5.43 (s, 2, H), 7–7.5 (m, 10 H). The same reaction product **5** was obtained in 80–90% yield on addition of 0.1 mol of methane-sulfonyl chloride dissolved in 50 ml of ethyl ether, to a mixture of

(25) W. E. Truce, R. W. Campbell, and G. D. Madding, *J. Org. Chem.*, **32**, 308 (1967).

(26) R. E. Robertson and P. M. Langton, *Can. J. Chem.*, **35**, 1319 (1957).

(27) A. Nervassian and P. R. Johnson, *J. Appl. Polym. Sci.*, **9**, 1653 (1965).

0.1 mol of benzhydrol and 0.11 mol of methylamine in 150 ml of diethyl ether at 0° under a nitrogen atmosphere.

Sensitized Photolysis. A 0.08 M solution of **1** in acetonitrile-methanol (90 vol %–10 vol %) containing 0.08 M benzophenone was prepared. The solution was degassed and irradiated in a Rayonet Preparative Reactor equipped with 8 RUL-3500 Å lamps, using a cut-off filter.²⁰ After completion of the reaction, the solvent was evaporated and the residual benzophenone and sulfonic acid ester **4c** were separated by column chromatography (silica gel, eluent CHCl₃). **4c** was identified by comparison with an authentic sample.

Kinetic Experiments. All kinetic experiments were carried out on 3-thietanone 1,1-dioxide in acetonitrile-methanol (90 vol %–10 vol %).

Quantum Yield. Appropriate samples with an optical density greater than 2 were irradiated with monochromatic light of 300 nm ± 4 nm (Bausch and Lomb high intensity monochromator) from 5 to 10 min without depassing 15% conversion. The disappearance of starting compound was followed spectrophotometrically. Potassium ferrioxalate was used as a chemical actinometer²⁸ to measure light intensity before and after reaction.

Quenching Experiments. A number of freshly prepared samples with equal concentration of 3-thietanone 1,1-dioxide (0.0075 mol/l.) and varying concentrations of *cis*-piperylene (from 2 × 10⁻⁶ to 4 × 10⁻³ mol/l.) were degassed and irradiated for 10 min. No change in optical density of the ketosulfone could be observed in a dark run during this period of time. The decrease in concentration of starting compound **1** was determined spectrophotometrically.

Intersystem Crossing Quantum Yield. The quantum yield of intersystem crossing was determined as described,²⁹ using the sensitized isomerization of *cis*-piperylene as triplet counter. The degree of isomerization was determined by vapor phase chromatography using a Perkin-Elmer F11 (flame ionization chromatograph). The isomers were separated at room temperature using a 4-m column filled with silver nitrate-benzyl cyanide on a Chromosorb Q 60–80 mesh carrier. The system benzophenone-*cis*-piperylene was used as the actinometer.

(28) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(29) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

Thermal and Photochemical Ring Openings of Lithium Keteniminates of 2,3-Diphenylcyclopropane-1-carbonitriles¹

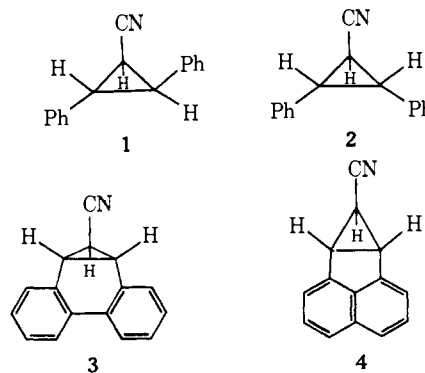
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Abstract: Treatments of *cis,trans*- and *trans,trans*-2,3-diphenylcyclopropane-1-carbonitrile (**1** and **2**), 2,3:4,5-dibenzonorcaradiene-*anti*-7-carbonitrile (**3**), and 7a,7b-dihydrocycloprop[*a*]acenaphthalene-*anti*-7-carbonitrile (**4**) with lithium diisopropylamide or lithium *tert*-butylamide in tetrahydrofuran at -78° give stable lithium keteniminates (α -cyano carbanions). On warming to -25° the keteniminates of **1** and **2** undergo electrocyclic opening to 2-cyano-1,3-diphenylallyllithium in high yield. At 25° or above the keteniminate of **4** opens to 2-cyanophenalenyllithium in modest yield and gives other unidentified products. At 36° the keteniminate of **2** opens 1.1 × 10⁴ faster than the keteniminate of **4**. The relative rates of opening of the keteniminates of **1**, **2**, and **4** support conrotatory orbital symmetry controlled thermal opening of **1** and **2**. Photolyses of the keteniminate of **1** and the lithium enolate of methyl *cis,trans*-2,3-diphenylcyclopropane-1-carboxylate at <-65° also lead to 2-substituted 1,3-diphenylallyllithiums.

Although thermal electrocyclic rearrangement of cyclopropyl anions to allyl anions is predicted to be conrotatory,² experimental evidence for its stereochemical course has been difficult to obtain.³ The structure of the cycloadduct of *trans*-stilbene and the 1,3-diphenyl-2-azaallyl anion, formed by electrocyclic opening of *cis*-2,3-diphenyl-*N*-lithioaziridine, supports the conrotatory mode.⁵ However, there are three examples of conversions of polycyclic cyclopropyl anions to allyl anions in which the conrotatory mode is impossible geometrically.^{6,7} To determine the extent

of orbital symmetry control of the stereochemistry of cyclopropyl anion opening, we have measured rates of reaction of cyclopropanecarbonitriles **1–4** in strong base.



Prior to our investigation Boche and Martens⁸ reported that **1** opened readily at -25° when treated with lithium diisopropylamide (LDIA) in tetrahydrofuran (THF) and that the resulting 2-cyano-1,3-diphenylallyl anion

(8) G. Boche and D. Martens, *Angew. Chem., Int. Ed. Engl.*, **11**, 724 (1972).

(1) Part of this research was reported in a preliminary communication: M. Newcomb and W. T. Ford, *J. Amer. Chem. Soc.*, **95**, 7186 (1973).

(2) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); (b) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **14**, 370 (1969); (c) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4290, 4291 (1971).

(3) A concise summary of this problem is available.⁴

(4) W. T. Ford and M. Newcomb, *J. Amer. Chem. Soc.*, **95**, 6277 (1973).

(5) T. Kauffmann, K. Habersaat, and E. Köppelmann, *Angew. Chem., Int. Ed. Engl.*, **11**, 291 (1972).

(6) G. Wittig, V. Rautenstrauch, and F. Wingler, *Tetrahedron, Suppl.*, **7**, 189 (1966).

(7) M. E. Londrigan and J. E. Mulvaney, *J. Org. Chem.*, **37**, 2823 (1972).