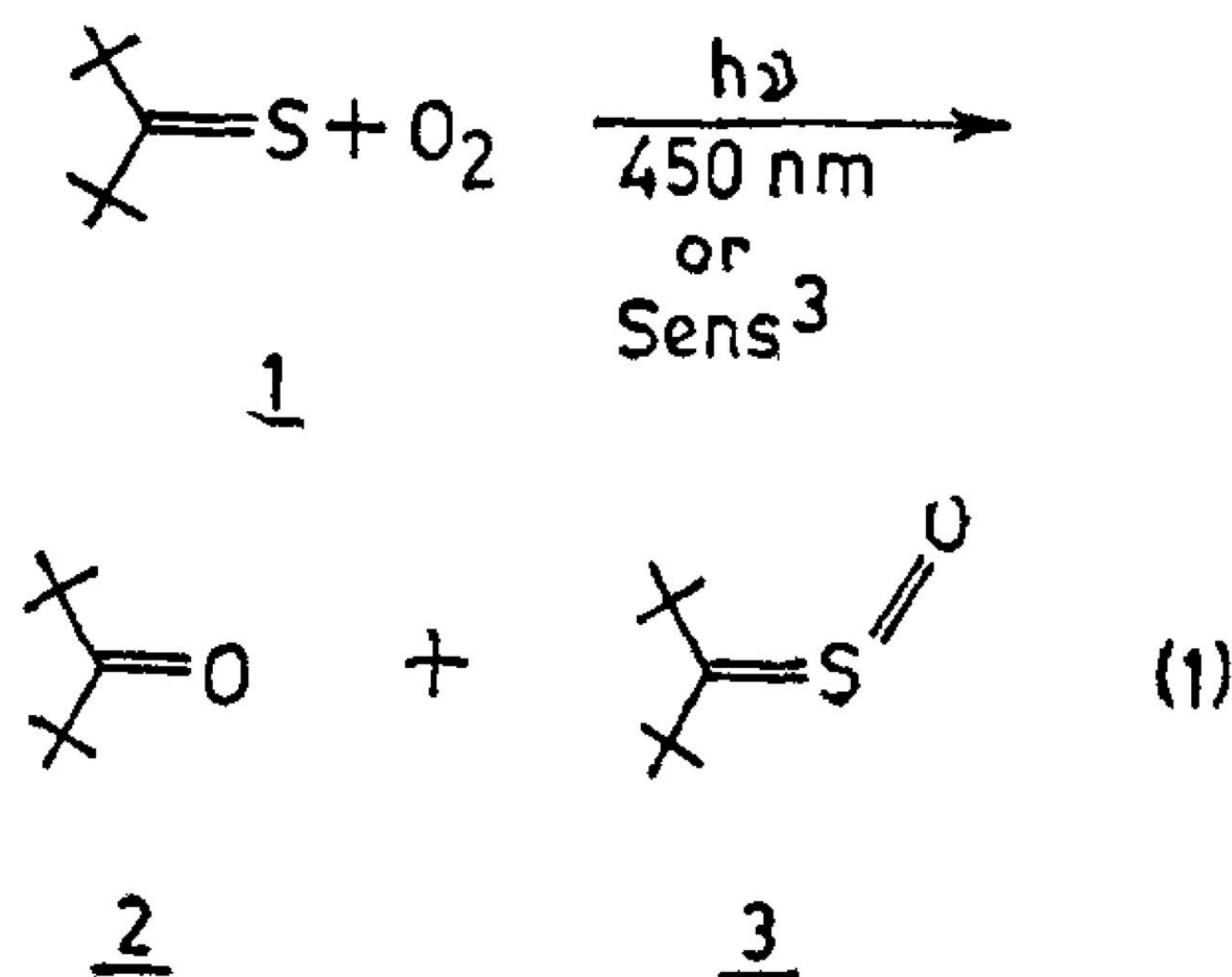


diethylether, diglyme and methanol in an atmosphere of oxygen resulted in rapid decolorisation. Purification of the product by column chromatography (silicagel-benzene) gave di-*t*-butyl ketone and a nice crystalline material (mp 47-48° C) having the following spectral properties:

IR (CCl <sub>4</sub> )	1380, 1280, 1260, 1180, 1080, 1020 cm <sup>-1</sup>
PMR (CDCl <sub>3</sub> )	1.536 (s); 1.369 (s).
CMR (CDCl <sub>3</sub> )	216.49 (s); 43.525 (s); 40.425 (s); 30.691 (q); 29.543 (q).
Mass Spec	m/e 174, 158, 131, 118, 112, 111, 101, 91, 84, 69, 57.
Analysis	Found C: 61.06%; H: 10.50% Calculated C: 62.04% for C <sub>8</sub> H <sub>18</sub> SO H: 10.41%

Based on the above spectral data the product is identified as di-*t*-butyl sulfine. The product ratio in various solvents as obtained from PMR spectra is shown in eq. 1.



### PHOTOOXIDATION OF DI-T-BUTYLTHIOKETONE

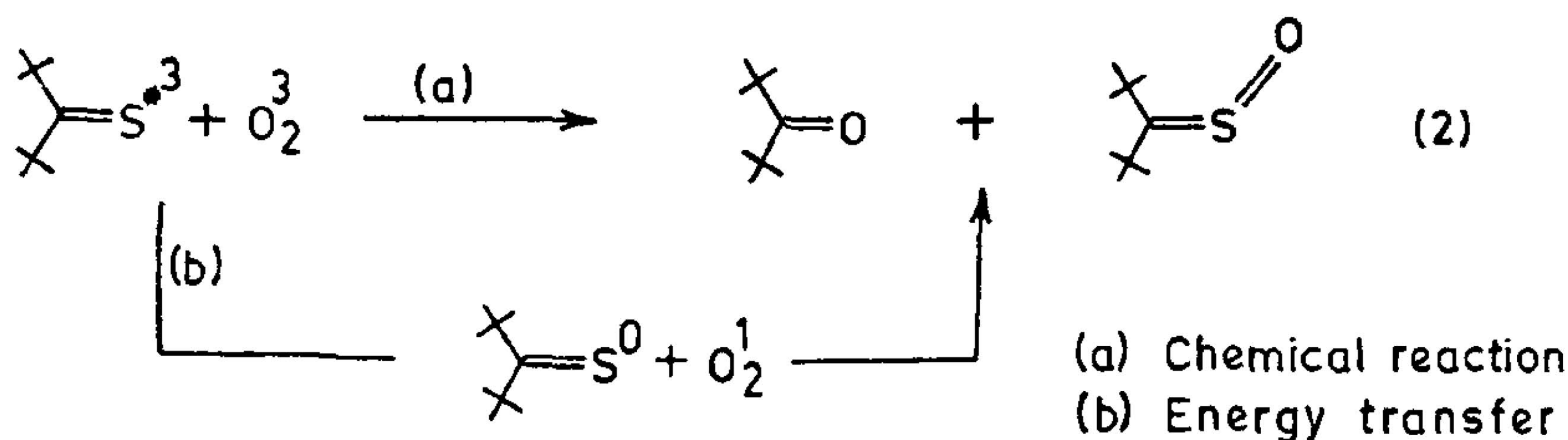
RECENTLY we had reported that thioketones are converted into the corresponding ketones by singlet and triplet oxygen<sup>1</sup>. As an exception, we have now found that di-*t*-butylthioketone(1)<sup>2</sup> is converted by triplet oxygen in the presence of light to an unexpected product -sulfine (3)- along with the expected di-*t*-butylketone (2). Irradiation of 1 (0.1 M) using a medium pressure mercury lamp and corning glass filters (> 450 nm) in cyclohexane dioxane, tetrahydrofuran,

Solvent	% of 2	% of 3
Tetrahydrofuran*	81.5	18.5
Dioxane	70.0	30.0
Cyclohexane	54.0	46.0
Diglyme	53.3	46.7
Benzene	46.0	54.0
Acetonitrile	33.3	66.7
Methanol*	10%	90%
Ethanol*	10%	90%

\* accompanied by polymer.

The formation of 3 is novel, considering the fact that thiobenzophenone is converted to the corresponding sulfine in the absence of light in oxygen atmosphere<sup>3,4</sup>. As the formation of 2 and 3 is sensitised by triplet sensitizers such as 4,4'-dibromobiphenyl and 1,4-dibromonaphthalene and quenched by triplet quenchers such as anthracene and allene, the





reactive state in the case of 1 is suggested to be the first excited triplet state of 1. In the above oxidation of 1, either singlet or triplet oxygen may be involved as illustrated in eq. 2. The mechanism of the above anomalous oxidation of 1 is being actively pursued in our laboratory<sup>5</sup>.

Authors are grateful to the Department of Science and Technology for financial support and to Prof. R. S. H. Liu for mass spectra. J. R. Thanks the Department of Atomic Energy Commission for a Junior Research Fellowship.

Department of Organic  
Chemistry,  
Indian Institute of Science,  
Bangalore 560 012,  
November 6, 1979.

V. JAYATHERTHA RAO,  
V. RAMAMURTHY.

during self-sensitised oxidation it is suggested that 2 is produced by path *a* and *b*. The origin of solvent dependence is traced to the competition between path *a* and *b*. As most of the thioketone we are investigating gives only the corresponding ketone, we believe that di-*t*-butylthioketone is an exception to our original general mechanism (Ref. 1). Full details on the oxidation of hindered and unhindered thioketone will be published at a later date. Our thanks are due to the referee for bringing our attention to the above paper.

1. Rajee, R. and Ramamurthy, V., *Tetrahedron Lett.*, 1978, p. 5127.
2. Ohno, A., Nakamura, K., Nakazima, Y. and Oka, S., *Bull. Chem. Soc. Japan*, 1975, 48, 2403; Barton, D. H. R., Guziec, F. S. and Shahak, J., *J. Chem. Soc., Perkin I*, 1974, (1974).
3. Carlsen, L., *J. Org. Chem.*, 1976, 41, 2971.
4. 1 is found to be stable in presence of oxygen in the absence of light.
5. Since the submission of our manuscript a publication on the same subject has appeared. Tamagaki, S., Akatsuka, R., Nakamura, M. and Kozuka, S., *Tetrahedron Lett.*, 1979, p. 3665. Results of these two studies are broadly similar. But, we wish to emphasise that the ratio of sulfine to ketone is solvent dependent. We have demonstrated the generation of singlet oxygen in this system by the isolation of oxidative products of dimethylsulphide, 1,3-diphenylisobenzofuran and cyclohexadiene upon excitation of 1 in their presence. Sulfine formation is quenched by singlet oxygen quenchers, such as Dabco, dimethylsulphide, cyclohexadiene and 1,3-diphenylisobenzofuran. Based on these it is suggested that sulphine formation proceeds through path *b*. Since di-*t*-butylketone is also produced by the dye sensitised oxidation but not quenched by singlet oxygen quenchers