

comparable NMR spectrum and MS with the reported β -sitosterol⁴.

The acetic acid elute was found to contain a mixture of acids (3500-3,000, 1720 cm⁻¹). On methylation and purification, of the methyl esters on 40% argentized silicagel, with benzene : petroleum ether (20 : 80 v/v) mixture as eluant, two fractions—a semi-solid (0.1% yield) and a liquid (0.2% yield)—were obtained. These fractions were analysed by GLC (EGSS—'X' 15% on chromosorb W, 200°C, N₂, FID) and the composition of the fatty acids given as below :

Semi-solid fraction : C₁₄ 2.5%, C₁₆ 81.6%, C₁₈ 13.4%.

Liquid fraction : C_{18:1} (Oleic) 86.9%, C₁₆ 12.9%.

The sandal bark was also estimated for its tannin content using the standard procedure⁵ and it was found to contain 14% of tannins, tannin : non-tannin ratio 2 : 1.

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1. Shankara Narayana, K. H., Ayyar, K. S. and Krishna Rao, G. S., "Insect growth inhibitor from the bark of *Santalum album* L.," (accepted for publication in *Phytochemistry*.)
2. Ayyar, K. S., Shankara Narayana, K. H., Sivaramakrishnan, V. R. and Sen Sarma, P. K., *Proceedings of the All India Sandal Seminar*, Bangalore, 7th Feb. 1977, p. 120.
3. Williams, C. M., *Scientific American*, 1967, 217, 13.
4. Jain, T. C. and Banks, C. M., *Canadian J. Chem.*, 1968, 46, 2325.
5. *Indian Standard Methods of Test for Vegetable Tanning Materials* (CSIR, New Delhi), IS : 5466—1969.

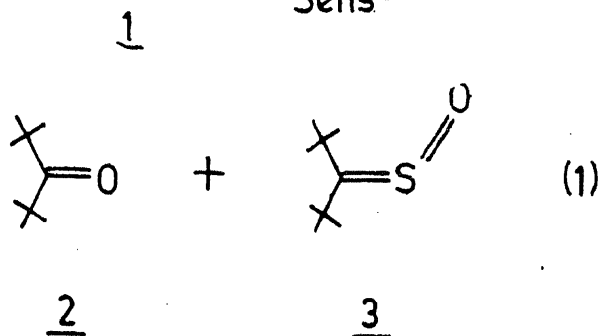
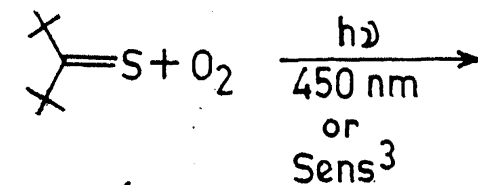
PHOTOOXIDATION OF DI-T-BUTYLTHIOKETONE

RECENTLY we had reported that thioketones are converted into the corresponding ketones by singlet and triplet oxygen¹. As an exception, we have now found that di-*t*-butylthioketone(1)² 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,

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 ₄)	1380, 1280, 1260, 1180, 1080, 1020 cm ⁻¹
PMR (CDCl ₃)	1.536 (s); 1.369 (s).
CMR (CDCl ₃)	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 ₉ H ₁₈ SO H: 10.41%

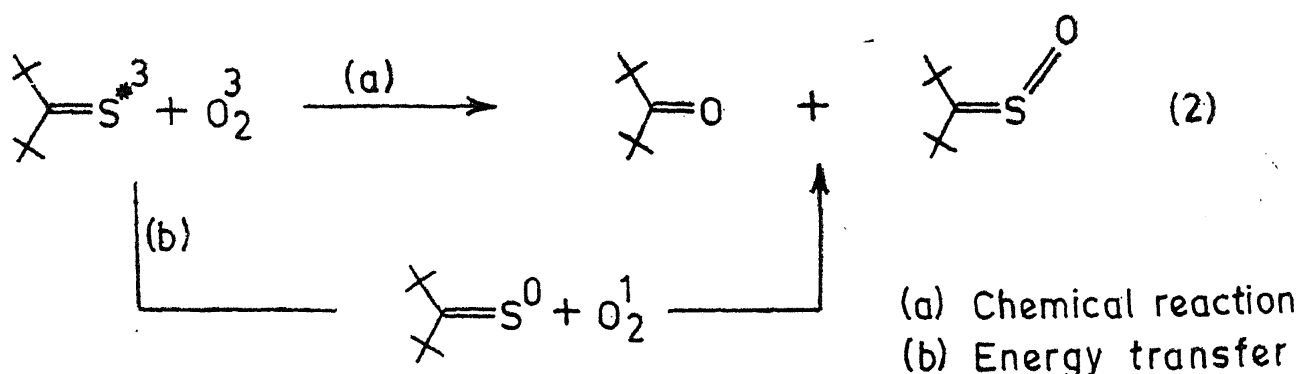
Based on the above spectral data the product is identified as di-*t*-butyl sulfine. The product ratio in various solvents as obtained from PMR spectra is shown in eq. 1.



Solvent	% of <u>2</u>	% of <u>3</u>
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^{3,4}. 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 allcocimine, 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 laboratory⁵.

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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; Barten, D. H. R., Guziac, 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-diphenyl-isobenzofuran 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

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 thioester we are investigating gives only the corresponding ketone, we believe that di-*t*-butylthioester is an exception to our original general mechanism (Ref. 1). Full details on the oxidation of hindered and unhindered thioester will be published at a later date. Our thanks are due to the referee for bringing our attention to the above paper.

INCIDENCE AND CHEMICAL CONTROL OF MITES ON MANDARIN IN HIMACHAL PRADESH

DURING the survey of the commercial citrus orchards of Himachal Pradesh, the authors observed that 64% of the Nagpur mandarin fruits were badly deformed and remained stunted in growth. On examination, the fruits showed russetting on their rind and mites were found on these areas of the fruits. The mite population ranged from 5 to 23 per fruit in December-January (Table I).

Perusal of the data reveals that the Nagpur variety was the most susceptible with 64 and 72% of fruit infestation with mite and rind disorder respectively. It was followed by Srinagar, Sylhet, Emperor, Butwal and Kinnow. Verma and Bhalla¹ got these mites identified as *Brevipalpus phoenicis* and *Tyrophagus putrescentiae* belonging to families Tetranychidae and Tyroglyphidae respectively. *B. phoenicis* was the dominant among these two species. The affected fruits showed two types of symptoms on their skin. In the majority of the cases, these fruits had a circular russetting band and vertical streaks around the fruit.

In view of this, a control trial on Nagpur mandarin with recommended doses of Kelthane and Omite was conducted. The miticides were sprayed regularly at an interval of ten days throughout the season while water was sprayed on control plants starting from pre-bloom stage. To check the migration of mites from soil to the plants a strip of thiodan granules was made, in the soil, in the basins 25 cm from the trunk