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PHOTOXIDATION OF DI-t-BUTYL THIOKETONE

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Abstract: The photo-oxygenation of the title compound leads to the corresponding ketone and sulfine. A mechanism for the reaction is elucidated.

As have been well known, upon irradiation of sunlight thioketones react with oxygen to give the corresponding ketones where thioketones themselves act as photo-sensitizers.[1)] Quite recently, Rajee and Ramamurthy undertook detailed examination on the photoxidation of several types of thioketones and suggested that the reaction species involved in the air oxidation of these thiones in the presence of light is only the singlet oxygen, and proposed the following reaction scheme for the photoxidation of thioketones:[2)]

$$T \xrightarrow{h\nu} \xrightarrow{ic} {}^3T$$

$${}^3T + {}^3O_2 \longrightarrow T + {}^1O_2$$

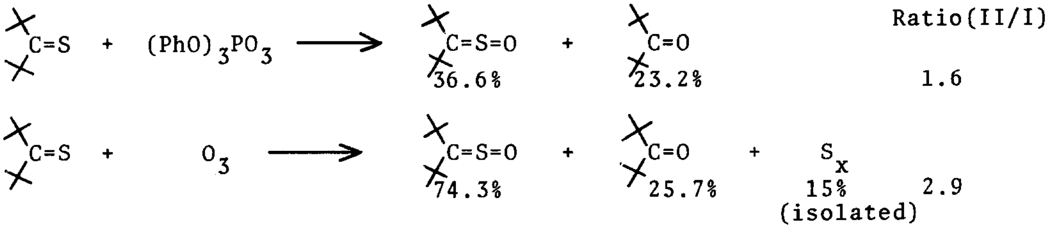
$$T + {}^1O_2 \longrightarrow K$$

T = thioketone
K = ketone

Contrary to thier suggestion, however, we have now found evidence that their scheme is not acceptable as the general one for the photoxidation of, at least, a sterically hindered thioketone.

Di-t-butyl thioketone (3.16 mmol) in 15 ml of benzene was irradiated with a tungsten-halogen lamp (500 W) in an oxygen atmosphere.[3)] A clean reaction took place. After 2.5 hrs of the irradiation, the reddish solution of the thioketone was bleached completely and then the solvent was stripped off. The distillation under a reduced pressure and chromatograpic separation of the result ing residue afforded, respectively, 48 % di-t-butyl ketone (I: 1685 cm^{-1}; 1.23 (s) ppm) and 21 % of di-t-butyl sulfine (II: 1065, 1130 cm^{-1}; 1.35(s), 1.42(s) ppm).

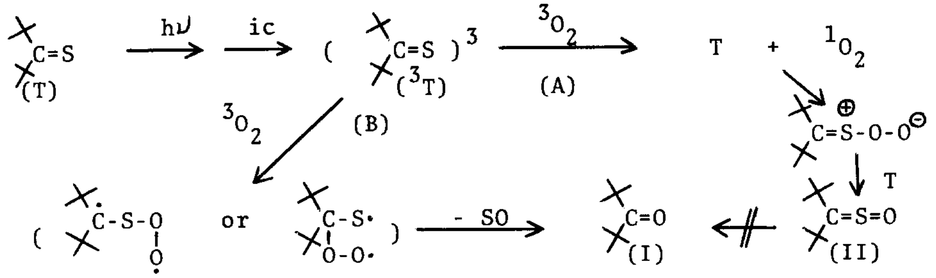
In order to shed light on the photoxidation mechanism, the reaction was carried out under a variety of conditions and the yields of the two products were evaluated by NMR spectroscopy. The results thus obtained are summarized in Table I. The table includes some interesting aspects; in every run the ketone formation is favored over the sulfine formation. In order to compare the result to that of thermal reactions, the reactions with a phosphine ozonide and ozone were examined and resulted in the preferential formation of the sulfine.



The proportion of the ketone increased only slightly in solvents with lower polarity, but the solvent effect on the product ratio was quite small, implying that the key intermediates or transition states leading to each product is essentially of non-polar nature. Further inspection of Table I reveals that the product ratios are almost independent of the progress of reaction time and hence of the concentration of the thioketone. Interestingly enough, the sulfine formation was effectively depressed by the addition of singlet oxygen quenchers such as DABCO, dimethyl sulfide,[4] thioamides,[5] while the ketone formation was not affected significantly by addition of the same quenchers. This observation strongly demonstrates that the major process leading to the ketone does not involve the reaction with singlet oxygen.

Therefore, all these observations can be most reasonably accounted for by assuming two distinct reaction paths: namely, the one leading to the sulfine by oxidation with singlet oxygen (Path A) and the other to the ketone probably through a biradicaloid intermediate (III) (Path B), as illustrated in Scheme I.

Scheme I.



In conclusion, the photoxygenation of di-t-butyl thioketone includes two different reaction paths leading to the ketone and sulfine, respectively; the former, contrary to the Rajee and Ramamurthy's suggestion, is not produced through the oxidation of the thioketone with singlet oxygen, but probably through a short-lived biradicaloid intermediate which is formed by the direct interaction of the triplet thioketone with molecular oxygen in the ground state, while the latter is indeed produced by oxidation with singlet oxygen. Previously, some stable sulfines were reported to undergo further oxidation by singlet oxygen to the corresponding ketones.$^{6)}$ The sulfine of di-t-butyl thioketone, however, is perfectly stable toward irradiation and attack of singlet oxygen.

Table I. The Photoxidation of Di-t-butyl Thioketone (1 mmol) in Various Solvents (20 ml) at Ambient Temperature.

Solvent	Reaction Time, min	Conversion %	Sulfine (II),%	Ketone (I),%	Ratio (II/I)
CH_2Cl_2	7.5	20.8	8.0	12.8	0.63
	15	39.4	15.8	23.5	0.67
	22.5	50.6	20.7	29.9	0.69
	30	66.4	26.2	40.2	0.65
	45	81.7	31.5	50.2	0.63
	60	90.1	36.1	54.0	0.67

(contined)

Solvent	Reaction Time, min	Conversion %	Sulfine (II),%	Ketone (I),%	Ratio (II/I)
CCl_4	30	75.1	20.0	55.1	0.36
	60	92.5	24.3	68.2	0.36
CS_2	30	89.3	26.8	62.5	0.43
	45	98.0	32.9	65.1	0.51
Benzene	30	57.9	17.5	40.4	0.46
	75	94.0	27.6	66.4	0.42
$CHCl_3$	30	74.7	30.5	44.2	0.69
CH_3CN	30	66.7	29.3	37.4	0.78
CH_2Cl_2[a)]	30	50.3	2.4	47.9	0.05
CH_2Cl_2[b)]	30	35.8	0.8	35.0	0.02
CH_2Cl_2[c)]	30	40.6	7.3	33.3	0.07
CH_2Cl_2[d)]	30	42.6	0.0	42.6	0.0
CH_2Cl_2[e)]	30	73.5	26.8	44.9	0.60

a), b), c), d), and e) : in the presence of DABCO(1 mmol), Me_2S(70 mmol), tetramethylthiourea(1 mmol), 1-methylpyrrolidine-2-thione(1 mmol), and 2,6-di-t-butyl-p-cresol(1 mmol), respectively.

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