Mechanistic Investigations into the Photochemical Oxidation of Thioketones

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Summary Singlet-oxygen reaction with dialkyl, aryl alkyl, and diaryl thioketones is found to give the corresponding sulphines and ketones in proportions depending on the nature of the thioketone.

THE chemical behaviour of thiocarbonyl compounds has been explored less than that of the analogous carbonyl compounds, probably owing to their low stability. Herein, preliminary results of our systematic investigation of the

Table. Distribution of products upon oxidation of thioketones.

	Thioketone $R^1C(:S)R^2$		Direct excitation^a		O_2^1 reaction^b		Ozonolysis^c	
	R^1	R^2	Ketone	Sulphine	Ketone	Sulphine	Ketone	Sulphine
(**1**)^d	Bu^t	Bu^t	33	67	20	80	5	95
(**2**)	"	Ph	63	16	60	12	54	25
(**3**)	"	p-MeOC$_6$H$_4$	80	2	90	2	88	6
(**4**)	"	p-ClC$_6$H$_4$	52	25	51	25	4	86
(**5**)	p-MeC$_6$H$_4$	p-MeC$_6$H$_4$	97	—	97	—	99	—
(**6**)	Ph	p-MeOC$_6$H$_4$	87	—	90	—	82	—
(**7**)	p-MeOC$_6$H$_4$	p-MeOC$_6$H$_4$	57	—	61	—	61	—
(**8**)	Ph	p-ClC$_6$H$_4$	65	2	70	2	77	3
(**9**)	p-ClC$_6$H$_4$	p-ClC$_6$H$_4$	83	5	67	6	83	3

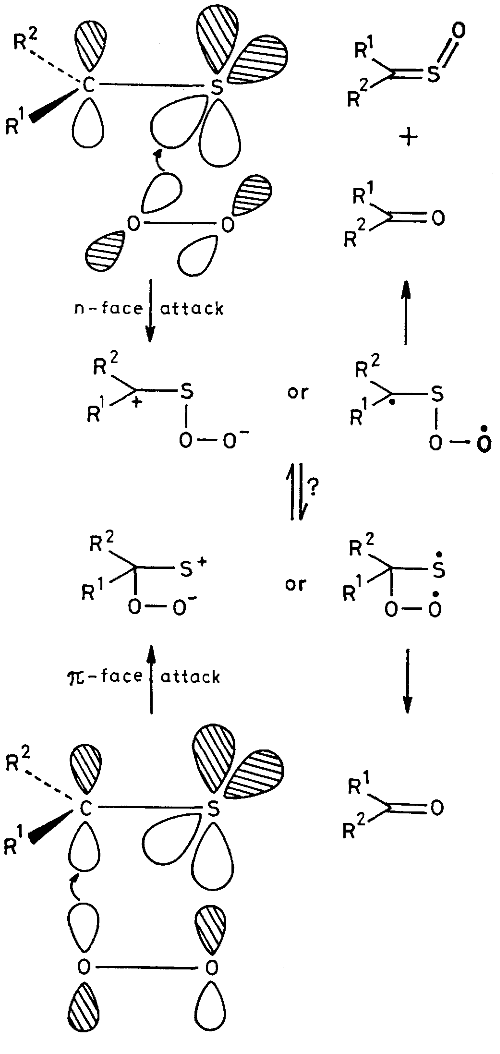
[a] Direct excitation was conducted in acetonitrile solution using a 500 W tungsten lamp. [b] Singlet oxygen was generated by Methylene Blue sensitisation and by thermal decomposition of triphenyl phosphite ozonide. [c] Ozonolysis was conducted in chloroform solution at room temperature. [d] The ratio of sulphine to ketone is solvent-dependent: V. Jayathertha Rao and V. Ramamurthy, *Indian J. Chem., Sect. B*, 1980, **19**, 43.

oxidation of thiocarbonyl compounds which, in part, is responsible for their poor stability, are presented.[1] The results reveal the formation, at least in some cases, of sulphines in addition to the corresponding carbonyl compounds. Further, the yields of sulphine and ketone vary with the substituents on the aromatic rings of the diaryl and aryl alkyl thioketones.

Diaryl and aryl alkyl thioketones with widely varying substituents were investigated (Table), and they were oxidised by three independent methods: (a) by direct excitation in aerated solvents, (b) by singlet oxygen generated by dye sensitisation and by thermal decomposition of triphenylphosphite ozonide, and (c) by ozonolysis. The products obtained from these oxidations are shown in the Table.† The oxidising agent during direct excitation is believed to be singlet oxygen (to a major extent) as product formation is quenched by singlet-oxygen quenchers such as 2,5-diphenylisobenzofuran, dimethyl sulphide, 2,3-dimethylbut-2-ene, and 1,4-diazabicyclo-[2.2.2]octane with the corresponding formation of their oxidation products.

The Table reveals that the amounts of sulphine and ketone are dependent on the nature of the thioketone. The most revealing observations are the following: (a) dialkyl and aryl alkyl thioketones give the corresponding sulphine as one of the products, whereas the diaryl systems are generally resistant towards sulphine formation [compare (**1**), (**2**), and (**5**)] and (b) in the case of diaryl and aryl alkyl thioketones, electron-releasing substituents favour the formation of ketones [(**3**), (**6**), and (**7**)], whereas electron-withdrawing substituents favour sulphine formation [(**4**), (**8**), and (**9**)]. A similar trend is also observed during ozonolysis of these thioketones.‡ This observation could be accommodated by the mechanism suggested in the Scheme.

Singlet oxygen, with its empty π^* orbital, is expected to interact with the filled n and π orbitals of the thiocarbonyl chromophore. The dominant interaction among these orbitals will be determined by the energy difference between these orbitals (n—π^* and π—π^*) and by steric factors. We suggest that in the case of dialkyl thioketones, where the energy difference between the n and π orbitals is large,



Scheme.

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† Both ketones and sulphines were characterised by their spectral properties (i.r., n.m.r., and m.s.) and were identical in all respects with authentic materials independently synthesised. In some cases elemental sulphur was also isolated. Full details will be presented elsewhere.

‡ Ozonolysis of thioketones has been reported to give sulphines and ketones: B. Zwanenburg and A. J. Janssen, *Synthesis*, 1973, 617.

the singlet oxygen interacts preferentially with the n orbital. As the energy difference between n and π orbitals is lowered as in the case of aryl alkyl and diaryl thioketones, interaction with the π orbital competes with that with the n orbital of the thione. Based on the above model, we also suggest that as the singlet oxygen attacks the π face, it preferentially forms a bond with the carbon atom of the thiocarbonyl chromophore, whereas during the n-face attack a bond is formed with the sulphur atom. As illustrated in the Scheme, following the above model, π-face attack leads to ketone formation, whereas n-face attack leads to both sulphine and ketone. The above model stems from the observation that protonation of di-t-butyl thioketone occurs on the sulphur atom (n-side attack) and that of thiobenzophenone on the carbon atom (π-side attack).[2] This model is consistent with the results obtained with substituted thioketones. As the energy of the π orbital is increased by electron-releasing substituents [(**3**), (**6**), and (**7**)], the yield of sulphine is decreased; similarly, lowering the energy of the π orbital by electron-withdrawing substituents [(**4**), (**8**), and (**9**)] favours attack on the n orbital with concomitant increase in the sulphine yield.§

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§ Attempts are underway to measure and correlate the ionisation potentials of the n and π electrons with the reactivity of the thiones.

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[2] T. Yamabe, S. Nagata, K. Akagi, R. Hashimoto, K. Yamashita, K. Fukui, A. Ohno, and K. Nakamura, *J. Chem. Soc., Perkin Trans.* 2, 1977, 1516. Similar differences in behaviour between dialkyl and diaryl thioketones have been noticed during nucleophilic attack: A. Ohno, K. Nakamura, M. Vohama, S. Oka, T. Yamabe, and S. Nagata, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3718.