

THE PHOTOLYSIS OF β -KETOSULPHONES:
AN INTRAMOLECULAR REARRANGEMENT

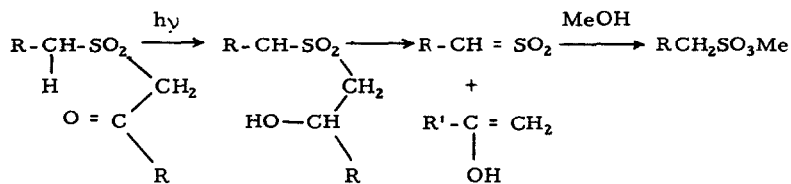
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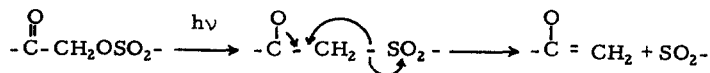
Sulphenes, $RR'C=SO_2$, were first suggested as chemical intermediates by Wedekind and Schenk in 1911.¹ Although no stable substance of this type has yet been isolated,² several studies³ have made their transient existence highly probable. There was, however, and still is, a need for a method of preparation of simple sulphenes under neutral aprotic conditions. The ultraviolet irradiation of β -ketosulphones bearing a hydrogen atom attached to the γ -carbon atom,⁴ seemed a possible route: abstraction of the γ hydrogen atom by the electron deficient oxygen of the excited carbonyl group, followed by Norrish Type II cleavage would produce a sulphene.

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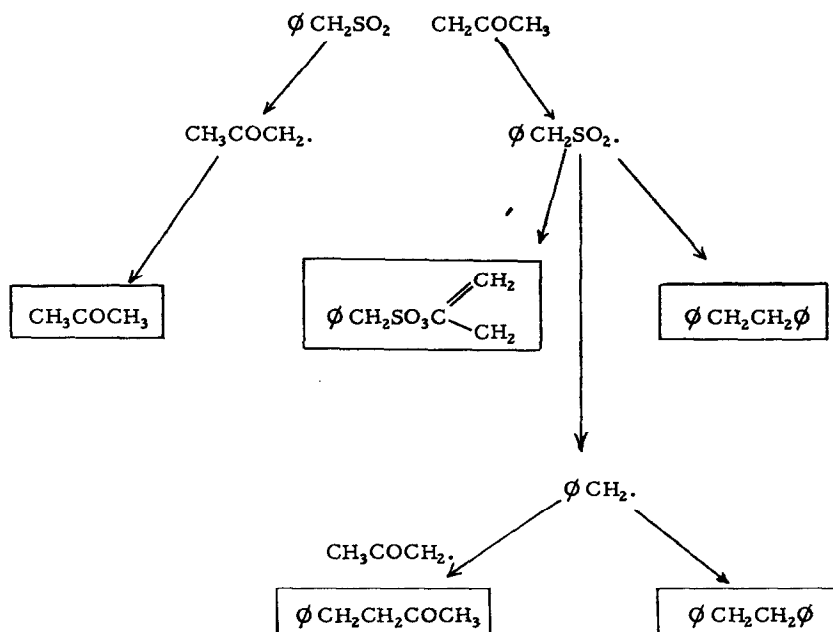


Benzyl acetonyl sulphone, I, and benzyl phenacyl sulphone, II, were prepared from the corresponding sulfides.^{5,6} Irradiation of both I and II in methanol (0.75%), using an immersed Hanovia 450 watt mercury arc and a Corex filter at 0°, gave a mixture of products as shown in Table I. Neither the N.M.R. spectra of the reaction product mixtures, nor separation by thin layer chromatography gave any evidence of the hoped for methyl α -toluene sulphonate (from the addition of methanol to the sulphene). This had previously been shown to be stable under the irradiation conditions.

It was clear that all the products formed could have arisen as the result of cleavage of the carbon-sulphur bond beta to the carbonyl group without any commitment as to the multiplicity of the species in-



involved. The radicals formed could then react further, as shown below for the case of the acetonyl compound. The formation of the vinyl sulphinate was of particular interest since only two syntheses for these substances appeared to have been recorded.^{7,8} The absence of such an ester from the phenacyl derivative is probably to be attributed to the reactivity of the styryl product.



But it appeared possible, that the vinyl ester could have been formed by the Norrish Type II cleavage, followed by rapid recombination of the so-formed sulphene and enolic ketone in a solvent cage.

In order to distinguish between this possibility and that of radical combination, *t*-butyl acetonyl sulfone, III, b.p. 106-108° was prepared from the sulfide⁹ in a similar manner, but using 30% H₂O₂ in acetic acid instead of KMnO₄.

Irradiation of III under the same conditions as before, gave a product mixture shown in Table I. The presence of the vinyl sulphonate in the mixture excluded the Norrish Type II mechanism since III has no γ hydrogen atoms available for abstraction.

TABLE I
Yield (%; Isolated)

RSO ₂ CH ₂ COR'	R.SO ₂ H	R-R	RCH ₂ COR'	CH ₃ COR'	RSO ₂ C $\begin{matrix} \diagup \text{CH}_2 \\ \diagdown \text{R}' \end{matrix}$
R=C ₆ H ₅ CH ₂ R'=Me	44 ^a	22	13	59 ^b	6 ^e
R=C ₆ H ₅ CH ₂ R'=C ₆ H ₅	22 ^c	24		78	-
R=(CH ₃) ₃ C R'=Me(f)	28	(d)		56	16 ^g

(a) Identified as acid and methyl ester; (b) estimated by gas-liquid chromatography and identified as the 2,4-dinitrophenylhydrazone; (c) characterised as the methyl ester; (d) 16% of the sulphonic ester was obtained; (e) N.M.R.: ν 1.87 (s, 3H), 4.34 (s, 2H), 4.74 (2H) doublet of doublets, $J_{AB} = 2.0$, $\nu_B - \nu_A = 7.8$ c.p.s., 7.40 (s, 5H); ν_{\max} 1670, 1365, 1167, 953 cm⁻¹; $\epsilon_{200} = 3,000$; (f) N.M.R.: ν 1.36 (s, 9H), 2.38 (s, 3H), 3.96 (s, 2H); ν_{\max} 1720, 1713, 1112 cm⁻¹; $\epsilon_{200} = 2,000$; 2,4-dinitrophenylhydrazone; m.p. 171-172°, N.M.R.: ν 1.46 (s, 9H), 2.02 (s, 3H), 4.80 (2H) doublet of doublets $J_{AB} = 2.0$, $\nu_B - \nu_A = 10.7$ c.p.s.; ν_{\max} 1668, 1345, 1149, 951 cm⁻¹; $\epsilon_{200} = 2,400$.

The process of formation of the vinyl sulphonates appeared, superficially, to be related to that of a family of reactions involving the interconversions of β -diketones, enolic esters, and lactones¹⁰⁻¹⁴ for which a radical pathway had been suggested¹⁵. However, a third, intramolecular, pathway rejected for these reactions¹⁵, remained to be considered for the formation of the vinyl sulphonates.

In Table II, the results of the effects of attempts to penetrate or modify any solvent cage are shown. Under a variety of conditions, including an excess of oxygen, the yield of ester estimated from N.M.R. spectra remains essentially constant. The proportions of other components are, in contrast, seriously affected. In benzene, for instance, no sulphonic acid

is formed (no hydrogen easily available for extraction) whilst in the presence of oxygen all the benzyl radicals are trapped before dimerisation, or ketone formation.

It thus appears that the process leading to the formation of the vinyl sulphonates, if it occurs in a solvent cage, is independent of the nature of the molecules constituting that cage, and that external agents such as oxygen cannot intervene. Yet, nonetheless, a constant fraction of the sulphonyl radicals do escape to undergo other transformations.

This evidence renders radical combination a less engaging rationalisation¹⁶ whilst that of an intramolecular four-centre process, involving expansion of the sulphur shell, need not now be deemed a wild surmise.

TABLE II
Product composition from the irradiation of I at 0°

Solvent	Additive	(ϕ CH ₂) ₂	ϕ CH ₂ SO ₂ H	ϕ CH ₂ SO ₃ C ₃ H ₅	ϕ CH ₂ CH ₂ COCH ₃
MeOH ^a	-	31		11	12
MeOH ^a	C ₄ H ₈ (10% ^{w/v})	9	None	11	5
MeOH ^a	O ₂	None	8 ^a	13	Trace
C ₆ H ₆ ^{a, b.}	-	40	None	10	32
MeOH ^c	-	22	44	6	13
Diisopropyl- ether	-			6	
EtOH(95%) ^c	-			7	

(a) Estimated yields from N.M.R. (b) 10° (c) Isolated yields (d) Sulphonic ester.

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