

Unusual Effect of a Remote SO₂ Group on the Reactivity of the Double Bond in Unsaturated Cyclic Sulphones towards Ethoxycarbonylnitrene

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Except in a two-phase system and contrary to expectation, ethoxycarbonylnitrene when generated from Lwowski's reagent by α -elimination does not add to the unsaturated cyclic sulphones (1)—(10) owing to the presence of orbital interactions (through bonds and through space) between the SO₂ group and the double bond, as evidenced by u.v.-photoelectron spectroscopy.

Cyclic olefins,¹ especially strained systems,² normally react readily with nitrenes to form aziridines. To our surprise we have found that the presence of a remote SO₂ group in a series of unsaturated cyclic sulphones (1)—(10) drastically diminishes the susceptibility of the double bond to attack by ethoxycarbonylnitrene, albeit in an organic phase under homogeneous conditions. From results provided by u.v.-photoelectron spectroscopy (u.v.-p.e.s.), we attribute this effect to the presence of orbital interactions through bonds and/or through space³ between the SO₂ group and the double bond, making the latter remarkably electron deficient. Chemical repercussions of this type of interaction are scarce,⁴ and to our knowledge there are no previously reported examples of a sulphone group having a marked influence on the reactivity of a remotely located functionality.

Although singlet ethoxycarbonylnitrene, when generated by the reaction of ethyl *p*-nitrophenylsulphonyloxycarbamate (Lwowski's reagent) (11) with Et₃N in CH₂Cl₂, successfully adds to cyclohexene to the extent of 57%,⁵ no reaction occurred with the annelated sulphone (7) under the same conditions. This unprecedented lack of reactivity was not the result of any instability of the expected aziridine product (12) since the latter could be obtained in 40% yield[†] by irradiation of (7) in neat ethyl azidoformate.‡ Similar unreactive behavi-

[†] All new compounds were fully characterised by ¹H- and ¹³C-n.m.r., i.r., and mass spectral and microanalytical data.

‡ *A priori*, this reaction does not involve a nitrene, but proceeds by addition of electronically excited azide⁶ and subsequent loss of nitrogen from the resulting triazoline.

Table 1. Formation of aziridines from unsaturated sulphones (% yields).

Compound	Reaction conditions			
	EtO ₂ CN ₃ <i>hν</i> ^a	EtO ₂ CN ₃ Heat ^b	EtO ₂ CN:	
			Homo- geneous ^c	Phase transfer ^d
(1)	N.r. ^g	N.r.	N.r.	N.r.
(2)	41 ^h	N.r.	N.r.	16
(3)	31	21	N.r.	43
(4)	40	—	N.r.	17
(5) ^e	12	—	N.r.	54
(6) ^e	N.r.	N.r.	N.r.	N.r.
(7)	40	N.r.	N.r.	40
(8) ^e	75	38	N.r.	30
(9) ^e	22	8	N.r.	20
(10) ^f	N.r.	N.r.	N.r.	N.r.

^a Irradiation of *ca.* 3 mmol of sulphone in 10-fold excess of neat azide through quartz with a 400 W medium-pressure Hg lamp. ^b Boiling under reflux in dry CCl₄. ^c According to the method described in ref. 5. ^d The same procedure as in ref. 8 was employed using benzyltriethylammonium chloride as catalyst. ^e *endo*-Configuration. ^f *exo*-Configuration. ^g N.r. = no aziridine formed; only nitrene by-products were isolated. ^h A. I. Meyers and T. Takaya, *Tetrahedron Lett.*, 1971, 2609.

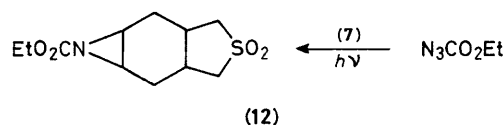
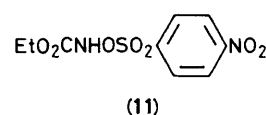
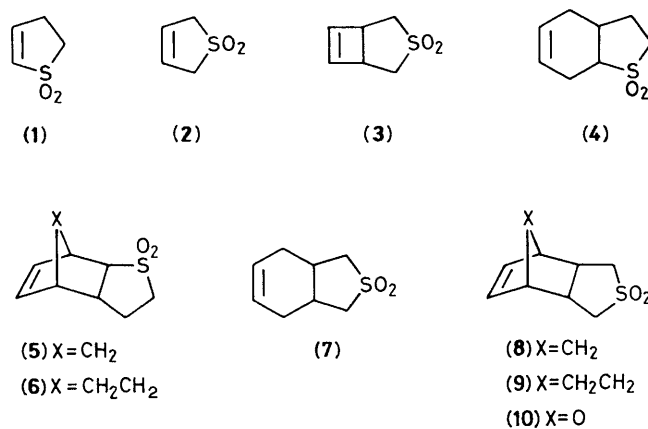
Table 2. Vertical ionisation potentials (eV)^a for unsaturated sulphones (1–10) and comparison olefins.

Compound	πI_p	Compound	πI_p
(1)	10.28	Cyclopentene	9.18 ^b
(2)	10.35	2,4-Dihydrothiophen	9.86 ^c
(3)	10.25	Cyclobutene	9.43 ^b
(4)	9.59	Cyclohexene	9.12 ^b
(7)	9.69		
(5)	9.55	Norbornene	8.97 ^d
(8)	9.60		
(6)	9.80	Bicyclo[2.2.2]oct-2-ene	9.05 ^d
(9)	9.75		
(10)	9.83	7-Oxabicyclo[2.2.1]hept-2-ene	9.44 ^e

^a All photoelectron spectra were determined with a Perkin-Elmer PS16 spectrometer, modified by the incorporation of a Helectros hollow cathode lamp (He I, 21.2 eV) and a Varian C 1024 signal averager. ^b P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, 1970, 53, 1677; D. C. Clary, A. A. Lewis, D. Morland, J. N. Murrell, and E. Heilbronner, *J. Chem. Soc., Faraday Trans. 2*, 1974, 70, 1889. ^c H. Schmidt and A. Schweig, *Tetrahedron Lett.*, 1973, 1437. ^d P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, 1969, 52, 1745. ^e A. D. Bain, J. C. Bünzli, D. C. Frost, and L. Weiler, *J. Am. Chem. Soc.*, 1973, 95, 291.

our towards ethoxycarbonylnitrene was observed with other unsaturated sulphones (Table 1), some of which also showed a marked reluctance to react thermally and photochemically with ethyl azidoformate. In each case the sulphone was recovered unchanged, the reagent (11) consumed, and only nitrene by-products were isolated.

The failure of the sulphone (2) to react with ethoxycarbonylnitrene presumably reflects a decrease in electron availability at the double bond due to interaction with the SO₂ group through bonds. While this proximity effect can also be used to explain the inertness of the unsaturated sulphone (1) and possibly (3)–(6), its importance is likely to be less in compounds (7)–(10) where the substituent is separated from



the double bond by four σ -bonds.[§] For these compounds we attribute the extraordinary effect of the remote SO₂ group on the reactivity of the double bond to orbital interactions not only through bonds, but also through space. An alternative explanation whereby the SO₂ group itself forms a weak but diverting interaction with the nitrene was excluded by the finding that aziridine formation with cyclohexene (*vide supra*) proceeds normally in the presence of an unsaturated sulphone, *e.g.* (7).[¶]

Our claims are also substantiated by the unusually high ionisation potentials (πI_p) found for the unsaturated sulphones by u.v.-p.e.s. (Table 2).^{**} From a comparison of these values with those given for hydrocarbon analogues, it is evident that there is a net mixing (through bonds and through space) of the $n(\text{SO}_2)$ molecular orbital with the π molecular orbital, which results in a lowering of the energy level of the latter orbital. It follows that the ability of the double bond to add a nitrene should be diminished. This is in accord with

[§] Although four σ -bonds intervene between the SO₂ group and the double bond in these molecules, Dreiding models show that they can take up favourable conformations in which the substituents are spatially very close [*e.g.* *ca.* 1.8 Å in (7)].

[¶] Besides the SO₂ group, we have found that other equally remote groups for which complexation with the nitrene is less likely also prevent aziridine formation as evidenced by the inertness of *endo*-norbornylene 2,3-dicarboxylic anhydride and 2-oxabicyclo[2.2.0]hexan-3-one (W. H. Pirkle and L. H. McKendry, *J. Am. Chem. Soc.*, 1969, 91, 1179).

^{**} The assignments are supported by *ab initio* molecular orbital (configuration interaction) methods for key members of the series (ref. 7).

experimental observation, but apparently only for homogeneous reactions between the reactants in an organic phase. As shown in Table 1, most of the unsaturated sulphones do in fact afford low yields of addition products with ethoxycarbonylnitrene when the corresponding reactions are conducted under phase-transfer catalysis conditions. This is the first report of ethoxycarbonylnitrene so produced⁸ being more reactive than its conventionally generated counterpart. The reasons for this divergent chemical behaviour are not certain, but it is most likely that the generation of ethoxycarbonylnitrene by phase-transfer catalysis⁹ ensures an environment at, or close to, the aqueous-organic phase boundary where the only possible acceptor is the substrate double bond, and even though this may be deactivated, the opportunity for repeated collisions (in effect an overwhelming concentration of nitrene) eventually brings about reaction. For the substrates in question, the possibility also exists that in the two-phase system the SO₂ group, because of its hydrophilic nature, penetrates the aqueous phase. As a result its electronic influence will be dampened, thus exalting the ability of the nitrene to add to the (lipophilic) double bonds as observed.

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