Basic Catalysis in the Trapping of Sulphenes

By JAMES F. KING and YONG IK KANG

(*Department of Chemistry, University of Western Ontario, London, Ontario, Canada* N6A 3K7)

Summary The trapping of phenylsulphene with alcohols or aromatic amines is catalysed by amines; in the reaction of phenylsulphene with a mixture of propan-2-ol and *p*-toluidine, changing the catalyst from a strong to a weak tertiary amine changes the chief component of the product from the sulphonamide to the ester.

THE most commonly used reaction of sulphenes is that with alcohols and amines, to form esters and sulphonamides *etc.* We describe evidence showing that at least some simple examples of this process have two related and previously unrecognised features, *viz.* (a) they are catalysed by bases, and (b) the product composition in trapping competition reactions is highly sensitive to the nature of this catalyst.

Reaction of a diazoalkane (*e.g.* **1**) and SO_2 (**2**) is believed to give the sulphene,[1] which in the absence of other sulphene traps usually reacts with more diazoalkane to give the episulphone or its desulphonylation product, the olefin.[2] The picture is less clear for the reaction in the presence of protic sulphene traps. Diazomethane and (**2**) in the presence of alcohols undergo a quite different reaction to give the methyl alkyl sulphite,[3] but diazobutane and (**2**) with piperidine are reported to give no characterised products;[4] diphenyldiazomethane and (**2**) in the presence of alcohol or water give the sulphonic ester or acid,[2a] whereas phenyldiazomethane (**1**) and SO_2 in water yield the same mixture of stilbene and episulphone found in the absence of water.[5] We found that (**1**) and (**2**) in propan-2-ol–CH_2Cl_2 also yield the stilbene–episulphone mixture,† but in the presence of sufficient base (*e.g.* pyridine) the isopropyl ester (**4a**) is produced in high yield. Weak tertiary amines such as pyridine or dimethylaminoacetonitrile (DMAA) appear to catalyse formation of (**4a**) more efficiently than stronger amines such as triethylamine or 1,5-diazabicyclo[5,4,0]undec-5-ene (DBU); with the latter bases, however, the concentration of free amine may be small owing to more extensive complex formation with (**2**).[6] 2,6-Di-t-butylpyridine, di-isopropylethylamine, and *p*-toluidine catalyse formation of (**4a**), though the first two are less effective than their less hindered homologues and

TABLE. Competition experiments in the trapping of phenylsulphene (**3**) with *p*-toluidine and propan-2-ol[a] (in CH_2Cl_2 at room temperature)

Sulphene source	Other reagents[b]	Yields (%) of products[c] Stilbene[d]	Amide (**4b**)	Ester (**4a**)
(**1**) and (**2**)	Et_3N (1), Et_2O ..	23	31	10
”	Et_3N (14)	~3	85	10
”	DBU (1), Et_2O ..	27	38	10
”	Pr^i_2EtN (1), Et_2O ..	31	27	11
”	Pyridine (14)	26	13	61
”	DMAA (14)	51	8	41
”	Et_3N (14), $Et_4N^+Cl^-$ (6)	0	61	8
”	Pyridine (14), $Et_4N^+Cl^-$ (6)	~3	53	29
”	DMAA (14), $Et_4N^+Cl^-$ (6)	15	50	9
(**5**)	Et_3N (14)	—	58	29
”	Pyridine 14)	—	46	45
”	DMAA (14)	—	15	79
”	Pyridine (14), Et_4N^+-Cl^- (6)	—	56	16
”	DMAA (14), $Et_4N^+Cl^-$ (6)	—	80	16
”	Pyridine (14), $Et_4N^+Cl^-$ (6), SO_2 (6)	—	37	30

[a] In CH_2Cl_2 at room temperature with *p*-toluidine and propan-2-ol each present in three-fold initial excess. [b] Numbers in parentheses refer to the initial molar ratio of that compound relative to (**2**) or (**5**). [c] Totals of percentage yields from (**5**) are roughly ±3, those from (**1**) about ±10, with the relative yields of (**4a**) and (**4b**) more accurate (ratio ±10% or better). [d] See footnote†.

---

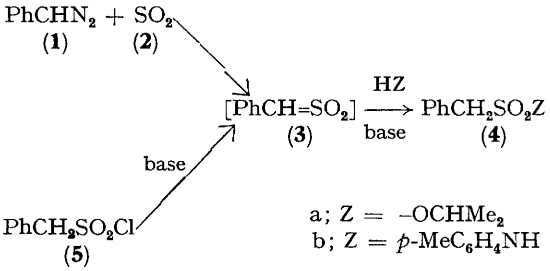
† With careful workup the product is primarily a mixture of *trans*-stilbene and *cis*-1,2-diphenylethylene sulphone. In most of the experiments described here, the workup was such as to convert the episulphone into *cis*-stilbene, and the mixture of *cis*- and *trans*-stilbene so obtained is referred to in the Table.

the last also yields the sulphonamide (**4b**); these observations point strongly to base catalysis rather than nucleophilic catalysis.

The reaction of *p*-toluidine with (**1**) and (**2**) to form (**4b**) is also catalysed by amines, but in this case the stronger bases (*e.g.* triethylamine) are the more effective. This difference in the catalytic effect of the bases leads to a striking result in competition experiments using *p*-toluidine and propan-2-ol as the sulphene traps (Table). With triethylamine the amide (**4b**) is the major product, whereas with pyridine or DMAA the ester (**4a**) predominates over the amide (**4b**).

As expected, this product composition switch is also found when the sulphene (**3**) is generated by the action of tertiary amines on the sulphonyl chloride (**5**). With (**5**) and triethylamine, the major product in the competition is again the amide (**4b**), whereas with DMAA the ester (**4a**) predominates. With pyridine, however, roughly the same amounts of (**4a**) and (**4b**) were obtained; since the hydrochloride had not precipitated from the medium (unlike the DMAA experiment), this suggested catalysis by chloride ion.[7] Added $Et_4N^+Cl^-$ appears to have an effect similar to that of triethylamine, favouring amide (**4b**) formation to the extent of completely reversing the product ratios with DMAA. Addition of SO_2 seems to increase ester (**4a**) formation, but the tendency for (**2**) to form complexes with alcohols[8] and amines [6,9] complicates interpretation of these observations.

In contrast with the above base-catalysed nucleophilic additions to a sulphene, a direct nucleophilic substitution at a sulphonyl chloride shows quite different behaviour, even when base catalysed; toluene-*p*-sulphonyl chloride under the above conditions yields only the sulphonamide, no ester at all being detectable by n.m.r. spectroscopy.



A change in product composition in trapping experiments should therefore be expected to accompany a change from an elimination–addition (sulphene) process to a direct substitution. This was found with methanesulphonyl chloride, which with triethylamine gave a mixture of the sulphonyl-*p*-toluidide and isopropyl ester, but with pyridine gave only the sulphonamide. With deuteriated sulphene traps the amide and ester from the Et_3N reactions were monodeuteriated as required for a sulphene process, but the amide obtained using pyridine was undeuteriated in agreement with a direct displacement mechanism.

(*Received*, 11*th November* 1974; *Com*. 1373.)

---

[1] G. Opitz, *Angew Chem. Internat. Edn.*, 1967, **6**, 107.

[2] (a) H. Staudinger and F. Pfenninger, *Ber.*, 1916, **49**, 1941; (b) for a review see N. H. Fischer, *Synthesis*, 1970, **393**.

[3] G. Hesse and S. Majmudar, *Chem. Ber.*, 1960, **93**, 1129.

[4] S. T. Purrington and P. Wilder, *J. Org. Chem.*, 1966, **30**, 2070.

[5] N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, 1965, **31**, 349.

[6] J. A. Moede and C. Curran, *J. Amer. Chem. Soc.*, 1949, **71**, 852.

[7] *Cf.* S. D. Ross, M. Finkelstein, and F. S. Dunkl, *J. Org. Chem.*, 1974, **39**, 134.

[8] P. A. D. de Maine, *J. Chem. Phys.*, 1957, **26**, 1036, 1042.

[9] A. E. Hill, *J. Amer. Chem. Soc.*, 1931, **53**, 2598; A. E. Hill and T. B. Fitzgerald, *J. Amer. Chem. Soc.*, 1935, **57**, 250.