which the motions are partially frozen, so that the relative loss of translational, rotational, and internal entropy in going to a transition state is minimized.[53]

Conclusion

Enzymes as we know them are the result of a long process of natural selection. Rapid advances in our understanding of enzyme evolution are taking place, and it seems pertinent to reexamine enzyme catalysis from this perspective. The reaction stereochemistry of an enzymic process is an important index of the organization of the active site and of details of mechanism. We have, therefore, tried to interpret part of the extensive literature on enzyme stereochemistry in terms of the selective pressures encountered in evolution.

Two extreme situations have been noted above: A single ancestral protein may give rise to a whole class of related enzymes that share a common stereochemistry because the complexity of the protein structure associated with substrate binding has survival value.

Alternatively, the stereochemistry of the reaction catalyzed may be independent of any contribution by the enzyme so that enzymes with the same reaction stereospecificity may have evolved separately. We believe, however, that the main power and novelty of our approach lie in its ability to identify mechanistic factors in enzyme catalysis whose survival value depends upon the subtle ways in which the catalytic groups at the active site are deployed and reused.

We have identified two general determinants of stereochemical uniformity in reaction classes: (a) the use of the minimal number of catalytic groups (often with the multiple use of a single base to permit proton recycling within the reaction sequence) and (b) the use of a maximal separation of catalytic groups (often upon opposite walls of a cleft in the enzyme). Undoubtedly these broad categories require further analysis or modification. It remains for the future to provide adequate structural, thermodynamic, or kinetic explanations for the preferential selection in a given reaction class according to one or the other determinant.

(52) The extent to which the energy barrier to bond formation depends upon orbital alignment has been debated; see, *e.g.*, A. Dafforn and D. E. Koshland, Jr., *Biochem. Biophys. Res. Commun.*, **52**, 779 (1973), and references therein.
(53) W. P. Jencks and M. I. Page (in "Enzymes Structure and Function"), *FEBS (Fed. Eur. Biochem. Soc.) Symp.*, **29**, 45 (1972).

The Return of Sulfenes

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This Account, though mainly an orthodox review of the chemistry of a class of useful reactive intermediates, is also a tale of the return of a simple chemical idea.

Sulfenes[1] are molecules of the formula $RR'C=SO_2$ and may be regarded either as the sulfonyl analogs of ketenes or as derivatives of sulfur trioxide formally obtained by replacement of one oxygen atom by a CRR' group. They are most often formed by the action of amines on alkanesulfonyl chlorides, as, for example, in the ordinary preparation of methanesulfonate esters and other "mesylate" derivatives by the reaction of methanesulfonyl chloride and pyridine with alcohols and the like. Paradoxically, sulfenes may very well be more often used but less well known than either ketenes or sulfur trioxide. One purpose of this review is to provide the information which may rectify this anomaly.

Historical Background

Wedekind and Schenk[2] proposed the name "sulfene" in 1911, and made the first planned attempt to synthesize one. Staudinger's discovery of the relative stability of diphenylketene,[3] taken with Wedekind's previous work on the formation of ketenes from acid chlorides, led them to hope that the reaction of a tertiary amine and diphenylmethanesulfonyl chloride might yield diphenylsulfene as a stable compound. After failing to obtain the starting chloride, however, they settled for the reaction of phenylmethanesulfonyl chloride with triethylamine, which led to the isolation of *trans*-stilbene and triethylammonium chloride. They suggested that these products arose as follows:

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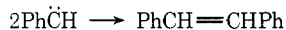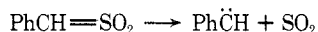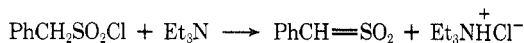
(1) G. Opitz' review (*Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967)) gives authoritative coverage of the literature to the latter part of 1966; this is extended to early 1970 by (a) a supplementary review by W. E. Truce and L. K. Liu (*Mech. React. Sulfur Compounds*, **4**, 145 (1969)) and (b) brief summaries in The Chemical Society Specialist Periodical Reports, "Organic Compounds of Sulphur, Selenium and Tellurium," D. H. Reid, Senior Reporter, Vol. 1, pp 199–201 and 290–296 (1970), Vol. 2, pp 85–86, 116–118, 225–228, and 317–320 (1973).
(2) E. Wedekind and D. Schenk, *Ber.*, **44**, 198 (1911).
(3) H. Staudinger, *Ber.*, **38**, 1735 (1905).

$$\text{PhCH}_2\text{SO}_2\text{Cl} + \text{Et}_3\text{N} \longrightarrow \text{PhCH}\!=\!\text{SO}_2 + \text{Et}_3\overset{+}{\text{N}}\text{HCl}^-$$

$$\text{PhCH}\!=\!\text{SO}_2 \longrightarrow \text{Ph}\overset{..}{\text{C}}\text{H} + \text{SO}_2$$

$$2\text{Ph}\overset{..}{\text{C}}\text{H} \longrightarrow \text{PhCH}\!=\!\text{CHPh}$$

Wedekind also explored the reaction of camphorsulfonyl chlorides (*e.g.*, **1**) with triethylamine in the

1   2
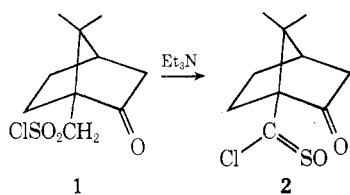
hope of isolating a stable sulfene or at least a sulfur-containing product. This work[4] gave the first examples of "sulfines" (*e.g.*, **2**) and also proved the location of the sulfonyl groups in two of the camphorsulfonic acids.

In 1916 Staudinger and Pfenninger,[5] having noted that diphenyldiazomethane evolves nitrogen on treatment with sulfur dioxide, investigated this reaction further, also in the express hope of isolating diphenylsulfene. They observed the following, which included the first observation of an episulfone.

$$\text{Ph}_2\text{CN}_2 + \text{SO}_2$$
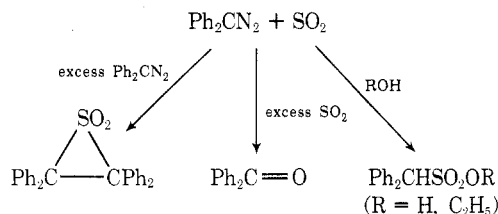
They postulated initial formation of $\text{Ph}_2\text{C}\!=\!\text{SO}_2$ and N_2 and explicitly referred to the expected analogy of sulfenes with ketenes. They did point out, however, that the formation of the sulfonic acid and ester could also be explained without invoking the sulfene.

Three other references to sulfene structures were made at roughly the same period, but their significance has been small. Zincke,[6] anticipating even the Wedekind work, suggested that "sulfoquinones" arise as transitory colored intermediates in the polymerization of certain *p*-hydroxybenzenesulfonyl chlorides by base; Schroeter[7] in 1919 suggested the formation of sulfene to explain some rather ill-defined reactions of methanedisulfonyl chloride (*e.g.*, that with ammonia); and Locher and Fierz[8] in 1927 reported that they had isolated a stable sulfene from 2-methylanthraquinone-1-sulfonyl chloride. Schroeter's suggestion does not appear to have been studied further, and the other two have been discredited: Recent investigations indicate that Zincke's colored intermediate is the phenoxide anion[9·] and that the Locher and Fierz claim is unfounded.[10]

The 'thirties and 'forties provided no new work on sulfenes. The Wedekind and Staudinger–Pfenninger

reactions were occasionally used, the former being applied to a few more terpene derivatives[11] and the latter to synthesize stilbestrol analogs,[12] but these papers do not mention sulfenes. About the only acknowledgment during this period that such species might exist is in Suter's book,[13] which points out that "a sulfone of the structure $\text{R}_2\text{C}\!=\!\text{SO}_2 \ldots$ has not been prepared" and refers to some of the above papers.[14]

The extent to which sulfenes were effectively banished from the thinking of the time is also shown by the lack of any mention of either sulfenes or the work of Wedekind and Staudinger in a number of papers in which these may now, with present knowledge, be seen to be relevant. The observation that certain hydroxyl groups are more readily converted to mesylates than to tosylates by the action of the sulfonyl chloride in pyridine was discussed on various occasions, always with the emphasis on the greater size of the tosyl group and no mention of any possibility that the sulfonylating agents in the two cases might be different types of molecules.[15] Other investigators,[19] examining the mechanism of solvolysis of alkanesulfonyl halides, noted the accelerating effect of base on this reaction, but none even raises the possibility of a sulfene process.

In a different context, Cope, as part of his classic study of thermal rearrangements, suggested[20] the possibility that heating allyl vinyl sulfone "would give C_3H_5—$\text{CH}_2\text{CH}\!=\!\text{SO}_2$," but "only decomposition and polymerization were observed when [allyl vinyl sulfone] was heated at 125, 150, and 175°." We have recently shown[21] that the original idea of Cope, *et al.*, is indeed correct. It is evident that their failure to demonstrate the expected rearrangement derived ultimately from an unfamiliarity with the early work on sulfenes.

In 1952, however, Backer and Kloosterziel and co-workers recalled the name sulfene to the chemical literature in a series of papers[22] extending and clarifying the experiments of Staudinger and Pfenninger. In 1957, Hesse and coworkers[23] further extended this

(4) E. Wedekind, D. Schenk, and R. Stüsser, *Ber.*, **56**, 633 (1923); E. Wedekind and R. Stüsser, *ibid.*, **56**, 1557 (1923); *cf.* E. Wedekind, *Z. Angew. Chem.*, **25**, 1186 (1912).

(5) H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916).

(6) T. Zincke and R. Brune, *Ber.*, **41**, 902 (1908); **44**, 185 (1911); see also T. Zincke and W. Glahn, *ibid.*, **40**, 3039 (1907).
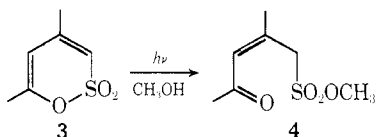
(7) G. Schroeter, *Justus Liebigs Ann. Chem.*, **418**, 161 (1919).

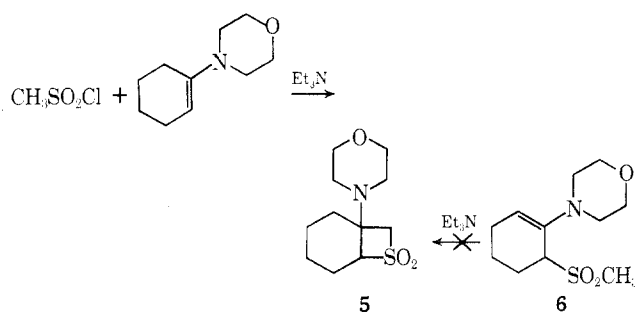(8) A. Locher and H. E. Fierz, *Helv. Chim. Acta*, **10**, 642 (1927).

(9) W. L. Hall, *J. Org. Chem.*, **31**, 2672 (1966).

(10) J. F. King, P. de Mayo, E. Morkved, A. B. M. A. Sattar, and A. Stoessl, *Can. J. Chem.*, **41**, 100 (1963).

(11) T. Hasselström, *Acta Acad. Sci. Fennicae*, A30, No. 12, 3 (1930); *cf.* H. Burgess and T. M. Lowry, *J. Chem. Soc.* **127**, 271 (1925).

(12) L. v. Vargha and E. Kovacs, *Ber.*, **75**, 794 (1942).

(13) C. M. Suter, "The Organic Chemistry of Sulfur," Wiley, New York, N. Y., 1944, p 659.

(14) At this point I should perhaps acknowledge my own debt, for it was this brief comment (read early in 1959) which initiated my interest in sulfenes.

(15) Helferich[16] referred to "the small mesyl group in contrast with the very much larger tosyl group." Roberts[17] was more explicit: "mesyl chloride ... might be expected to overcome some of the difficulties [of esterifying the hydroxyl groups in cellulose] since it is chemically similar to tosyl chloride but of smaller molecular size." Similar thinking is evident in reviews.[18]

(16) B. Helferich and A. Gnüchtel, *Ber.*, **71**, 712 (1938).

(17) R. W. Roberts, *J. Amer. Chem. Soc.*, **79**, 1175 (1957).

(18) R. S. Tipson, *Advan. Carbohyd. Chem.*, **8**, 107 (1953), especially p 132; D. H. Ball and F. W. Parrish, *ibid.*, **23**, 233 (1968).

(19) H. Böhme and W. Schürhoff, *Chem. Ber.*, **84**, 28 (1951); R. B. Scott, Jr., and R. E. Lutz, *J. Org. Chem.*, **19**, 830 (1954); G. Geiseler and F. Asinger, *Chem. Ber.*, **89**, 1100 (1956); H. K. Hall, *J. Amer. Chem. Soc.* **78**, 1450 (1956); R. Foon and A. N. Hambly, *Aust. J. Chem.* **15**, 668 (1962).

(20) A. C. Cope, D. E. Morrison and L. Field, *J. Amer. Chem. Soc.*, **72**, 59 (1950).

(21) J. F. King and D. R. K. Harding, *Chem. Commun.*, 959 (1971).

(22) H. Kloosterziel, M. H. Deinema, and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, **71**, 1228 (1952); H. Kloosterziel and H. J. Backer, *ibid.*, **71**, 1235 (1952); H. Kloosterziel, J. S. Boerema, and H. J. Backer, *ibid.*, **72**, 612 (1953).

(23) G. Hesse and E. Reichold, *Chem. Ber.*, **90**, 2101 (1957); G. Hesse, E. Reichold, and S. Majmudar, *ibid.*, **90**, 2106 (1957); G. Hesse and S. Majmudar, *ibid.*, **93**, 1129 (1960).

work, also making brief reference to sulfenes. Finally, in the early 1960's, some completely new sulfene chemistry appeared. First came a report by de Mayo and coworkers[24] that ultraviolet irradiation of six-membered-ring diene sultones (*e.g.*, **3**) gives products (*e.g.*, **4**) regarded as arising from the sulfene expected from the normal photochemical cycloreversion of cyclohexadienic systems. Early in 1962, wider interest was aroused by the almost simultaneous publication of papers by Stork and Borowitz[25] and by Opitz and Adolph[26] on the formation of sulfene-enamine cycloaddition products (*e.g.*, **5**). Shortly afterward related communications by Truce[27] and Fusco[28] and their respective coworkers appeared. This, then, was the first stage in the return of sulfenes, the detailed argument for which now follows.

Evidence for the Existence of Sulfenes

For the purpose of providing evidence for the existence of sulfenes, the above results fall into two categories. In one are the synthesis of episulfones,[5,23] olefins,[2,5] and sulfines,[4] reactions which are too complex to be of much use in making a case for or against sulfenes, at least without further investigation. In the other are reactions in which the putative sulfene reacts like a ketene, and which therefore contribute to a circumstantial case for the existence of sulfenes. The reaction of diphenyldiazomethane and sulfur dioxide in the presence of water or alcohol[5] (or thiols or amines[22]) was the earliest example of this category; this was followed much later by the photochemical ring opening of cyclic sultones[24] and the cycloadditions with enamines and ketene acetals.[25-28]

It was at this point that the first latter-day experiments to test for sulfenes were carried out. Among these was the demonstration that alkylsulfonyl enamines such as **6** do not cyclize under the conditions of the enamine cycloaddition reaction.[28,29] Since such a cyclization had been the most probable alter-native to a sulfene reaction, its exclusion made it more likely that the sulfene mechanism was correct.

A more direct approach was tried at roughly the same time by Truce, *et al.*,[30] and by us.[31] We reasoned that if the action of base on an alkanesulfonyl chloride were to proceed through a sulfene, then in the presence of D_2O (or a deuterated alcohol or amine, etc.) the product would contain one atom of deuterium per molecule. Writing the sulfonyl chloride as RCH_2SO_2Cl and the deuterated substrate as DZ, we may formulate this as follows:

$$RCH_2SO_2Cl + R'_3N \longrightarrow RCH{=}SO_2 + R'_3\overset{+}{N}HCl^-$$
$$RCH{=}SO_2 + DZ \longrightarrow RCHDSO_2Z$$
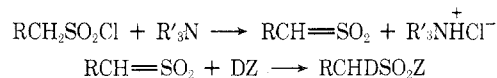
A direct substitution of halogen[32] by DZ or R'_3N would, of course, lead to RCH_2SO_2Z, and any random exchange of hydrogen for deuterium would give a mixture of CH_2, CHD, and CD_2 products. Experimentally, in the presence of base, with an array of sulfonyl chlorides, bases, and substrates, the product was more or less entirely $RCHDSO_2Z$ (provided the substrate DZ was present in substantial excess).[30,31]

Recently another form of reaction product study has yielded an entirely different kind of evidence for the intermediacy of a sulfene.[34] In the reaction of camphor-10-sulfonyl chloride (**1**) with menthylamine (**7**), we found that reaction of (+)-**1** with racemic **7**
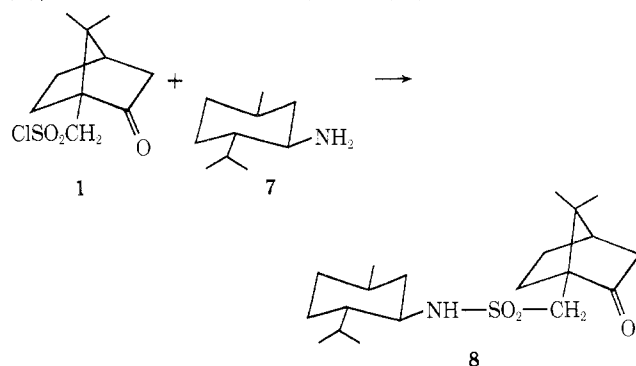
gave a mixture of the two diastereomers (**8**) in which one was about twice as abundant as the other. On the other hand, the product mixture from racemic **1** and (−)-**7** contained essentially the *same* amounts of the two diastereomers (**8**). This phenomenon, which we named[34] "nonreciprocal kinetic resolution," requires an intermediate that (a) is chiral, (b) is capable of yielding both diastereomers (depending on which enantiomer of the substrate it reacts with), and (c) undergoes this reaction rapidly. The sulfene obviously suffices.

We have also applied a kinetic test for the intermediacy of a sulfene. Since numerous attempts either to isolate a sulfene or to observe one as a transitory intermediate in solution had failed, it was prob-

(24) E. Henmo, P. de Mayo, A. B. M. A. Sattar, and A. Stoessl, *Proc. Chem. Soc., London*, 238 (1961).

(25) G. Stork and I. J. Borowitz, *J. Amer. Chem. Soc.*, 84, 313 (1962).

(26) G. Opitz and H. Adolph, *Angew. Chem., Int. Ed. Engl.*, 1, 113 (1962).

(27) W. E. Truce, J. J. Breiter, D. J. Abraham, and J. R. Norell, *J. Amer. Chem. Soc.*, 84, 3030 (1962).

(28) R. Fusco, S. Rossi, and S. Maiorana, *Chim. Ind. (Milan)*, 44, 873 (1962).

(29) I. J. Borowitz, *J. Amer. Chem. Soc.*, 86, 1146 (1964).

(30) W. E. Truce, R. W. Campbell, and J. R. Norell, *J. Amer. Chem. Soc.*, 86, 288 (1964); W. E. Truce and R. W. Campbell, *J. Amer. Chem. Soc.*, 88, 3599 (1966).

(31) J. F. King and T. Durst, *J. Amer. Chem. Soc.*, 86, 287 (1964); 87, 5684 (1965).

(32) This is evidently the mechanism of the reaction of arenesulfonyl chlorides: *cf.* O. Rogne, *J. Chem. Soc. B*, 1294 (1968), and papers cited therein.

(33) (a) J. F. King and T. W. S. Lee, *J. Amer. Chem. Soc.*, 91, 6524 (1969); (b) T. W. S. Lee, Ph.D. Thesis, University of Western Ontario, London, Ontario, Canada, 1969.

(34) J. F. King and S. K. Sim, *J. Amer. Chem. Soc.*, 95, 4448 (1973); J. F. King, S. K. Sim, and S. K. L. Li, *Can. J. Chem.*, 51, 3914 (1973).

able that the sulfene is consumed very rapidly, and hence the measured rate of reaction should be independent of the concentration of the sulfene trap. This was indeed found; the reaction, $CH_3SO_2Cl + Et_3N + ROH \rightarrow CH_3SO_2OR + Et_3NH^+Cl^-$, where R = propyl or isopropyl, was shown[33] to be first order in both CH_3SO_2Cl and Et_3N and *zero* order in ROH.

Simple isolation and characterization are normally the best way to prove that a class of compounds exists, but it is evident that isolation of sulfenes would require either special structures or unusual reaction conditions. It has been suggested that a sulfene might be made stable enough by either electron delocalization or steric protection,[35,36] but this has not yet been shown experimentally. Flash thermolysis,[39] however, has been more successful. We found[40] that chlorosulfonylacetic acid ($ClSO_2CH_2CO-OH$) at 640° and 1 μ gave products which, when trapped in methanol at −196° followed by warming, gave methyl mesylate in 40% yield; with HCl and DCl as the sulfene traps the products were respectively CH_3SO_2Cl and CH_2DSO_2Cl (>50% yields). When the thermolyzate was deposited on a NaCl plate at −196°, the infrared spectrum showed five characteristic bands (see below) ascribed to sulfene. When the sample was allowed to warm to −155° these bands began to disappear and were replaced by bands characteristic of CH_3SO_2Cl. In the presence of methanol above −155° the sulfene peaks were replaced by those of methyl mesylate. The same ir peaks were observed on flash thermolysis of methanesulfonic anhydride,[40] and recently additional confirmation of the origin of these bands was found by observing the same peaks on low-temperature photolysis of 3-thietanone 1,1-dioxide.[41]

The infrared spectrum of sulfene itself (at −196° in the presence of HCl and other thermolysis products) is the only physical property of sulfene as yet measured directly. We observed[40] bands of medium intensity at 3140 and 3040 cm^{-1} assigned to C–H stretching, strong bands at 1330 and 1230 cm^{-1} regarded as reasonable for S–O stretching, and a rather weak band at 950 cm^{-1}. A rough value of 35 ± 5 kcal/mol for the π-bond energy of sulfene (defined as $E_\pi(C{=}SO_2) = E(C{=}SO_2) - E(C{-}SO_2)$), has been estimated[42] in a rather roundabout way.

Generation of Sulfenes: the Methods and Their Scope and Mechanism

It is obvious from the foregoing that, if one is to assemble a list of "how to make sulfenes," one must have some criterion, however arbitrary, for deciding if a reaction goes by way of a sulfene or not. I have included in Table I those reactions which could be reasonably formulated as proceeding *via* a sulfene and which have at least one piece of corroborating data, usually the isolation of a simple, characteristic product that is known to be formed under the reaction conditions whenever a sulfene is present (see ref 2, 5, 10, 21–23, 40–57, and this Account). Possible sulfene reactions which lack such authentication are discussed in the next section.

Sulfene formation is evidently the major result when those alkanesulfonyl chlorides (and bromides and anhydrides) which bear at least one α hydrogen are treated with tertiary amines. Thus methanesulfonyl chloride with triethylamine,[30,31] pyridine,[33b] or tributylamine[58] in the presence of deuterated water or alcohols gives primarily the monodeuterated product. With the sterically least hindered tertiary amines (quinuclidine, trimethylamine, etc.) multiexchanged products are formed,[58] but the evidence indicates that the sulfene is nonetheless formed initially.

The reaction of phenylmethanesulfonyl chloride with amines or hydroxide proceeds through the sulfene,[31] but hydrolysis or methanolysis of $PhCD_2SO_2Cl$ in the *absence* of base gives the dideuterated product and hence must take place by a displacement mechanism.[32]

Since either elimination (sulfene formation) or displacement may thus occur with the same sulfonyl chloride, it would be useful to know what factors

(35) L. A. Paquette, J. P. Freeman, and R. W. Houser, *J. Org. Chem.*, 34, 2901 (1969). These authors focussed their attention on "delocalization of the partial negative charge on carbon."

(36) Our first essay into sulfene chemistry was an attempt to form a sulfene stabilized by an electron-*donating* substituent, but this was thwarted by difficulties in making starting materials: D. J. Peterson, B.Sc. Thesis, University of Western Ontario, 1961. "Thiourea dioxide" may be formally regarded[37] as an example of such stabilization: $^+NH_2{=}C(NH_2)SO_2^- \leftrightarrow NH_2C(NH_2){=}SO_2$, but X-ray data show the molecule to be adequately represented by the former canonical form.[38] It has recently been concluded from MO calculations that electron-donating substituents should stabilize sulfenes: J. P. Snyder, *J. Org. Chem.*, 37, 3965 (1973).

(37) *Cf.* W. Walter, *Justus Liebigs Ann. Chem.*, 633, 35 (1960).

(38) R. A. L. Sullivan and A. Hargreaves, *Acta Crystallogr.*, 15, 675 (1962).

(39) *Cf.* P. de Mayo, *Endeavour*, 31, 135 (1972), and references cited therein.

(40) J. F. King, P. de Mayo, and D. L. Verdun, *Can. J. Chem.*, 47, 4509 (1969); J. F. King, R. A. Marty, P. de Mayo, and D. L. Verdun, *J. Amer. Chem. Soc.*, 93, 6304 (1971).

(41) R. Langendries, F. C. De Schryver, P. de Mayo, R. A. Marty, and J. Schutyser, *J. Amer. Chem. Soc.*, 96, 2964 (1974).

(42) J. F. King and E. G. Lewars, *Can. J. Chem.*, 51, 3044 (1973); *J. Chem. Soc., Chem. Commun.*, 700 (1972).

(43) (a) Y. Shirota, T. Nagai, and N. Tokura, *Bull. Chem. Soc. Jap.*, 39, 405 (1966); *Tetrahedron*, 23, 639 (1967); *Tetrahedron Lett.*, 2343 (1968); *Tetrahedron* 25, 3193 (1969); (b) see also T. Nagai and N. Tokura, *Int. J. Sulfur Chem.*, 7B, 207 (1972).

(44) T. Durst, Ph.D. Thesis, University of Western Ontario, London, Ontario, Canada, 1963: (a) pp 45–46, 82–83, and 118–120; (b) 86–87 and 138–139; (c) 88–89 and 139–140.

(45) J. F. King and R. P. Beatson, Sixth International Symposium on Organic Sulphur Chemistry, July 1–5, 1974, Abstract B20; J. R. Singh, M.Sc. Thesis, University of Western Ontario, London, Ontario, Canada, 1971.

(46) J. F. King and J. R. du Manoir, to be published.

(47) For a review see N. H. Fischer, *Synthesis*, 393 (1970).

(48) J. F. King and R. P. Beatson, *Chem. Commun.*, 663 (1970); see also E. Dykman, *ibid.*, 1400 (1971), and T. Kempe and T. Norin, Fifth International Symposium on Organic Sulphur Chemistry, June 5–9, 1972, Abstract III.11.

(49) J. F. King, P. de Mayo, C. L. McIntosh, K. Piers, and D. J. H. Smith, *Can. J. Chem.*, 48, 3704 (1970).

(50) W. J. Mijs, J. B. Reesink, and U. E. Wiersum, *J. Chem. Soc., Chem. Commun.*, 412 (1972).

(51) M. S. Ao and E. M. Burgess, *J. Amer. Chem. Soc.*, 93, 5298 (1971).

(52) (a) J. L. Charlton and P. de Mayo, *Can. J. Chem.*, 46, 55 (1968); (b) S. T. Weintraub and B. F. Plummer, *J. Org. Chem.*, 36, 361 (1971); (c) T. Durst and J. F. King, *Can. J. Chem.*, 44, 1869 (1966); (d) J. F. King, E. G. Lewars, and D. R. K. Harding, to be published.

(53) R. J. Mulder, A. M. van Leusen, and J. Strating, *Tetrahedron Lett.*, 3057 (1967).

(54) R. F. T. Langendries and F. C. DeSchryver, *Tetrahedron Lett.*, 4781 (1972).

(55) L. I. Ragulin, P. P. Ropalo, G. A. Sokol'skii, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1045 (1971); G. A. Sokol'skii, L. I. Ragulin, G. P. Ovsyannikov, and I. L. Knunyants, *ibid.*, 1270 (1971); I. L. Knunyants and G. A. Sokolski, *Angew. Chem., Int. Ed. Engl.*, 11, 583 (1972).

(56) J. F. King, E. G. Lewars, and L. J. Danks, *Can. J. Chem.*, 50, 866 (1972).

(57) L. W. Christensen, *Synthesis*, 534 (1973).

(58) J. F. King, E. A. Luinstra, and D. R. K. Harding, *J. Chem. Soc., Chem. Commun.*, 1313 (1972).

Table I
Reactions Leading to Sulfenes

Reagents	Comments	References
Alkanesulfonic acid derivatives ($RR'CHSO_2X$) + base		
(a) X = Cl (Br, OSO_2R''); amines, RO^-, etc.	The traditional route to sulfenes; requires a basic medium.	2, also see text
(b) X = F; $R''Li$, OH^-		43, 44a, 55
(c) X = p-nitrobenzoate, 2,4-dinitrobenzoate		45 (also 56, 57)
(d) X = $^+NR''_3$	A promising new method: rapid reaction, mild conditions	46
Diazoalkanes and sulfur dioxide	An apparently general route but little used except for synthesis of episulfones (and olefins)	5, 22, 23, 43, 47
Fragmentation of α-haloalkanesulfinate anions		48
Thermolysis of		
(a) Sulfonyl halides and anhydrides	Requires high temperatures	21, 40
(b) Allyl vinyl sulfones (sulfo-Cope rearrangement)	Potentially useful in synthesis	21
(c) Dihydrothiopyran dioxides (reverse Diels–Alder)		42
(d) Thiete 1,1-dioxides and derivatives		49
(e) N-Alkylsulfonylphthalimides		50
(f) Benzothiazete 1,1-dioxides		51
Photolysis of		
(a) Cyclic unsaturated sultones, sultams, and sulfones		10, 24, 52
(b) α-Diazo sulfones (sulfo-Wolff rearrangement)	Minor reaction	53
(c) 3-Thietanone 1,1-dioxide		41, 54

govern the reaction course. No systematic study has been reported, but a few additional features are apparent from assorted data. Primary and secondary amines, for example, appear to react with saturated alkanesulfonyl chlorides by both mechanisms, direct displacement being favored with aromatic amines, and the sulfene process with aliphatic amines, particularly those with bulky alkyl groups.[59] Unsaturation in the sulfonyl chloride can alter things: $PhCD_2SO_2Cl$ reacts via phenylsulfene with both aniline and diethylamine,[31] while with 1-propenesulfonyl the result is more complex: triethylamine and D_2O lead to both direct displacement and 1,4 elimination to form vinylsulfene, but no 1,2 elimination to give the cumulated sulfene.[30] Aromatic sulfonyl chlorides with an ortho or para methyl group appear to react entirely by displacement and not via the quinonoid sulfene.[63]

Other reactions, besides direct displacement on sulfur, may also preclude sulfene formation when alkanesulfonyl chlorides or bromides are treated with basic reagents. "Soft" nucleophiles commonly reduce the chlorosulfonyl group, evidently by direct nucleophilic attack on halogen.[64] Phenylmethanesulfonyl

chloride gave mainly phenylmethanesulfinic acid with butyllithium[44a] or phenyllithium,[43] and with triphenylphosphine appeared to give only oxidation-reduction products.[56] Another, less common, "non-sulfene" reaction is the substitution–fragmentation process illustrated by the reaction of phenylmethanesulfonyl bromide and tetraethylammonium bromide to give benzyl bromide and sulfur dioxide,[65] via a direct substitution on the carbon bearing the sulfonyl group.

Sulfonyl derivatives other than chlorides, bromides, and anhydrides have been shown to yield sulfenes but have been little used as sulfene sources. Phenylmethanesulfonyl fluoride does not react with triethylamine under mild conditions,[66] but 1,2,2,2-tetrafluoroethanesulfonyl fluoride has been found by Knunyants and Sokol'skii and coworkers[55] to give the sulfene–pyridine zwitterionic adduct ($CF_3C^-FSO_2N^+C_5H_5$) on heating with pyridine; these authors also conclude[55] that sulfenes are produced by the action of aqueous base on sulfonyl fluorides bearing α-hydrogen atoms. Phenylmethanesulfonyl fluoride on treatment with butyllithium[44a] or phenyllithium[43] gives a mixture of trans-stilbene and other products, including the sulfone 9. In the pres-

$$PhCH_2SO_2CHSO_2R$$
$$|$$
$$Ph$$

9, R = $CH_2CH_2CH_2CH_3$ or Ph
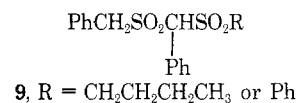
ence of a ketene acetal some of the sulfene cycloadduct was obtained.[43]

p-Nitrophenyl and 2,4-dinitrophenyl phenylmethanesulfonates and the like have been found to yield the sulfene with base;[45] the reaction has occasional synthetic use.[56,57]

(59) Cram and coworkers[60] found that amide formation from 2-octanesulfonyl-2-d chloride was accompanied by no deuterium loss with N-methylaniline, 8% deuterium loss with aniline, and 46% deuterium loss with dimethylamine. We have found that p-toluidine reacts with either CH_3SO_2Cl or camphor-10-sulfonyl-10-d_2 chloride (1-d_2) and gives mainly (~80%) unchanged amide.[61] The product from reaction of CH_3SO_2Cl with butylamine-d_2 indicated perhaps some (>10%) direct displacement.[62a] With 1-d_2 and menthylamine,[34] tert-butylamine,[61] and benzylamine,[61] the amounts of unexchanged product are respectively 8, 15, and 50%.

(60) D. J. Cram, R. D. Trepka, and P. S. Janiak, *J. Amer. Chem. Soc.*, **88**, 2749 (1966).

(61) J. F. King and S. K. Sim, to be published.

(62) E. A. Luinstra, Ph.D. Thesis, University of Western Ontario, London, Ontario, Canada, 1971: (a) pp 187, 188; (b) pp 8, 89, and 90.

(63) Hydrolysis of 2,5-dimethylbenzenesulfonyl chloride in the presence of D_2O and triethylamine gave a product which showed no sign of deuterium incorporation: R. W. Campbell, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1966, pp 25, 62, and 63.

(64) *Cf.* E. Buncel, A. Raoult, and L. A. Lancaster, *J. Amer. Chem. Soc.*, **95**, 5964 (1973).

(65) J. F. King and D. J. H. Smith, *J. Amer. Chem. Soc.*, **89**, 4803 (1967).

(66) J. F. King and T. Durst, *Can. J. Chem.*, **44**, 819 (1966).

Of more general practical value is our recent finding[46] that quaternary methylsulfonylammonium salts (e.g., $CH_3SO_2NMe_3^+FSO_3^-$ and $CH_3SO_2N-MeEt_2^+FSO_3^-$) very rapidly mesylate alcohols in the presence of a weak base such as pyridine or dimethylaminoacetonitrile. 5α-Cholestan-3β-ol, for example, may be quantitatively converted to the mesylate in about 1 min at $-70°$.

The reaction of diazoalkanes with sulfur dioxide[5,43b] appears to be a general route to sulfenes, but has found almost no application except in the formation of episulfones,[47] a reaction in which excess diazoalkane and the sulfene undergo cycloaddition and loss of N_2; the episulfones with varying degrees of ease undergo thermal loss of sulfur dioxide to form the olefin. As noted earlier, with diphenyldiazomethane and SO_2 the characteristic trapping products expected from ketene-like behavior have been obtained with water, ethanol, aliphatic amines, and mercaptans.[5,22] Diazomethane, however, reacts with SO_2 and alcohols to give, *not* the alkyl methanesulfonate, but the alkyl methyl sulfite.[23] Though this is not a sulfene reaction, sulfenes presumably are formed when hydroxylic reagents are absent, since diazomethane and SO_2 in inert solvents give ethylene episulfone.

Hesse and Majmudar[23] questioned Staudinger and Pfenninger's structures for the products from diphenyldiazomethane, but we have recently confirmed both sets of results.[67] We have also noted that the reaction of phenyldiazomethane and SO_2 in the presence of isopropyl alcohol gives only stilbene and *no ester* unless a base such as pyridine or triethylamine is present, in which case an excellent yield of the ester is obtained.[67] Moreover, notwithstanding a contrary report,[22] we find that aromatic amines (e.g., p-toluidine) react readily to form sulfonamides in this reaction.[67]

Of the remaining reactions in Table I, the sulfo-Cope rearrangement appears likely to be used in synthesis; it gives reasonably good yields at 120 to 200° in the liquid phase, and is not only a method of making a sulfene but of forming a carbon–carbon bond as well. The other reactions in Table I either have not been studied enough to show their utility or else are of restricted application because of exceptional reaction conditions or structural limitations.

The mechanism of formation of sulfenes by reaction of alkanesulfonyl derivatives with base has been studied enough to indicate that these reactions show some of the complexities already found in olefin-forming eliminations,[68] including a tendency for the mechanism to change with change in substrate or conditions. From a number of lines of evidence, including "axial:equatorial rate ratios,"[69] we concluded[33] that alkanesulfonyl chlorides probably react with tertiary amines *via* an "E1cb-like" or "paene-carbanion" E2 process;[68] an "irreversible" E1cb mechanism was regarded as much less likely but not wholly excluded. To gain information about the latter mechanism we sought—and found—both "revers-

ible" and "irreversible" E1cb mechanisms in the reactions of aryl arylmethanesulfonates ($ArCH_2-SO_2OAr'$) with triethylamine, the former mechanism appearing when $Ar' = p$-nitrophenyl and the latter when $Ar' = 2,4$-dinitrophenyl.[45]

Relatively little is known of the mechanisms of the other reactions listed in Table I. Flash photolysis experiments[52a] indicate that the sulfene from opening of cyclohexadienic sultones or sultams must be very short-lived (if formed at all), but this requirement is consistent with other work on sulfenes. The sulfo-Cope rearrangement and some of the other thermal reactions are evidently cyclic, concerted processes and not radical recombinations. The cyclic nature of the reactions is indicated by labeling experiments; e.g., 10 on heating with pyridine and ethanol-d gave[21] the product with the deuterium exclusively in the positions shown in 11.

10   11
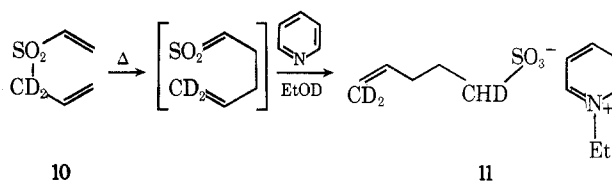
The fragmentation of α-chloroethanesulfinic acid in the presence of base is believed to be a simple loss of chloride ion from the sulfinate anion.[48] The reaction goes at the same rate at pH's in which the acid is essentially converted to the anion, and the remote possibility that the reaction proceeds by rearrangement to ethanesulfonyl chloride has been excluded by deuteration experiments.

"Possible Sulfene" and "Non-Sulfene" Reactions

Not all reactions which might be imagined to proceed *via* a sulfene have yielded the "corroborating data" needed for inclusion in Table I. For some, the intermediacy of a sulfene is reasonable but not adequately supported—as yet, at least; these I refer to as "possible sulfene" reactions.

In this category are both the thermolysis and chlorinolysis of 12, to give respectively 13a and 13b, perhaps as shown.[79]

12

13

a, X = H; b, X = Cl
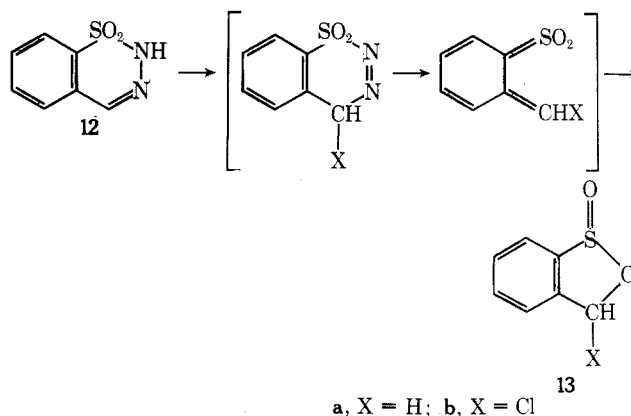
Further "possible sulfene" reactions include (a) certain reactions of sulfoacetic acid derivatives (e.g., $PhNHCOCH_2SO_2OPh + PhNH_2 \rightarrow PhNHCOCH_2-SO_2NHPh$), as suggested by Hoogenboom,[70] (b) some analogous reactions in the methanedisulfonic acid series (e.g.,[7] $CH_2(SO_2OPh)_2 + NH_3 \rightarrow$

(67) J. F. King, Y. I. Kang, and D. R. K. Harding, to be published.

(68) For reviews of the mechanism of elimination reactions, see J. F. Bunnett, *Surv. Progr. Chem.*, 5, 53 (1969), and F. G. Bordwell, *Accounts Chem. Res.*, 5, 374 (1972).

(69) J. F. King and M. J. Coppen, *Can. J. Chem.*, 49, 3714 (1971); J. F. King and T. W. S. Lee, *Can. J. Chem.*, 49, 3724 (1971).

Table II
Reactions of Sulfenes

Reaction	Illustrative example	Comments
(1) Sulfonylation of active hydrogen compounds[82]	$CH_3SO_2Cl + CH_3CH_2OH \xrightarrow{Et_3N} CH_3SO_2OCH_2CH_3$	The most generally useful reaction of sulfenes; substrates include alcohols,[5] amines,[22] mercaptans[22] (and also phenols,[83] phthalimide,[84] α- and β-diketones,[44b] etc)
(2) Cycloaddition onto a nucleophilic olefin[85]		Olefins include enamines, ynamines, ketene acetals and aminals, vinyl ethers; acyclic sulfonylenamines also formed; a conjugated sulfene or enamine also gives a six-membered ring
(3) Episulfone formation[47]	$PhCH_2SO_2Cl + CH_2N_2 \xrightarrow{Et_3N}$	Generation of the sulfene from the diazoalkane gives the symmetric episulfone; since episulfones readily lose SO_2 to form the olefin (stereospecifically), this reaction is part of a useful olefin synthesis; thiadiazole derivatives sometimes formed
(4) Cycloaddition with electrophilic ketones and aldehydes[86]	$CH_3SO_2Cl + Cl_3CCHO \xrightarrow{Et_3N}$	Substrates usually highly halogenated; with a hydrogen α to the carbonyl, a vinyl sulfonate results instead
(5) Desulfinylation[21,40,49]	$ClSO_2CH_2COOH \xrightarrow[\text{(flash)}]{940°} CH_2O + SO + CO_2 + HCl$	A general reaction of sulfenes on flash thermolysis above ~750°; also may occur photochemically[54]
(6) Chlorosulfine formation[4,66]	$PhCH_2SO_2Cl \xrightarrow{Et_3N}$	May yield both cis and trans isomers
(7) α-Keto sulfene cycloadditions[87]	$2PhCOCH_2SO_2Cl \xrightarrow{Et_3N}$	α-Keto sulfenes react similarly with $Ph_2C{=\!=}CO^{88}$ and anils and carbodiimides[89]

(8) Additional reactions of simple sulfenes with:
    (a) Nitrones $\longrightarrow$ cycloaddition followed by rearrangement[90,91]
    (b) Nitrile oxides $\longrightarrow$ α-chloro aldoxime sulfonates[91,92]
    (c) Triphenylphosphine $\longrightarrow$ alkyltriphenylphosphonium salts[56]
    (d) Tropone $\longrightarrow$ cycloadducts[93]
    (e) Ylides $\longrightarrow$ substituted ylides, episulfones, olefins[94]
    (f) Tertiary amines $\longrightarrow$ zwitterionic[55,58,95] ($RR'C^-SO_2NR''_3{}^+$) and oligomeric intermediates or products[87,96]
    (g) Tri- or tetraalkylammonium fluorides $\longrightarrow$ sulfonyl fluorides[62b]
    (h) Carboxylic acids $\longrightarrow$ carboxylic anhydrides or chlorides, probably *via* the mixed anhydride[44c]
    (i) *N*-Phenylhydroxylamine $\longrightarrow$ *o*-aminophenol derivative[90]
(9) Other reactions (possibly) proceeding *via* complex sulfenes lead to:
    (a) Pyrroles[52c]
    (b) Sultines[49,79]
    (c) Lactones (possibly *via* photochemical desulfinylation; see above)[97]
    (d) 1,4-Benzothiazine derivatives[51]

$CH_2(SO_2NH_2)_2$), including perhaps the one originally suggested by Schroeter in 1919,[7] and (c) the reaction of certain mesylates with NaOMe in DMSO leading to alcohols of retained configuration[71] or to methyl ethers,[72] as suggested by Durst.[73]

A "possible sulfene" may be at the root of some confusion about the partial hydrolysis of chlorosulfonylacetyl chloride ($ClSO_2CH_2COCl$). The product of this reaction on treatment with aniline was found to give 15 by Bodendorf and Senger,[74] who concluded that the partial hydrolysis product was sulfoacetyl chloride (HO_3SCH_2COCl). Subsequently, however, this product was shown[75,76] to be chlorosul-

(70) B. E. Hoogenboom, M. S. El-Faghi, S. C. Fink, E. D. Hoganson, S. E. Lindberg, T. J. Lindell, C. J. Linn, D. J. Nelson, J. O. Olson, L. Rennerfeldt, and K. A. Wellington, *J. Org. Chem.*, 34, 3414 (1969).

(71) F. C. Chang, *Tetrahedron Lett.*, 305 (1964); F. C. Chang and N. F. Wood, *Steroids*, 4, 55 (1964).

(72) D. H. Ball, E. D. M. Eades, and L. Long, Jr., *J. Amer. Chem. Soc.*, 86, 3579 (1964); E. D. M. Eades, D. H. Ball, and L. Long, Jr., *J. Org. Chem.*, 31, 1159 (1966).
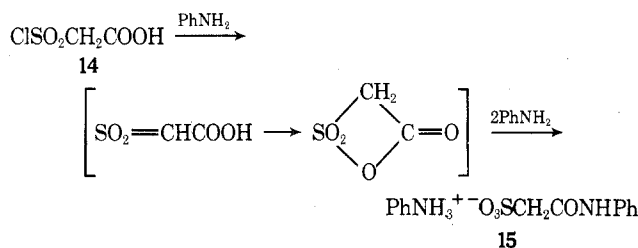
(73) T. Durst, *Advan. Org. Chem.*, 6, 285 (1969), especially pp 303-305.

(74) K. Bodendorf and N. Senger, *Ber.*, 72B, 571 (1939).

(75) R. Vieillefosse, *C. R. Acad. Sci.*, 208, 1406 (1939); R. L. Hinman and L. Locatell, *J. Amer. Chem. Soc.*, 81, 5655 (1959).

fonylacetic acid (14); this may be pictured as forming 15 *via* a sulfene and a mixed (perhaps cyclic) anhydride, *e.g.*

$$ClSO_2CH_2COOH \xrightarrow{PhNH_2}$$
14

$$\left[SO_2=CHCOOH \rightarrow SO_2 \left\langle \begin{array}{c} CH_2 \\ \\ O \end{array} \right\rangle C=O \right] \xrightarrow{2PhNH_2}$$

$$PhNH_3^+ \ ^-O_3SCH_2CONHPh$$
15

There are also "non-sulfene" processes, reactions in which sulfene intermediacy seemed reasonable until experiment showed otherwise. A number of these have been mentioned above in the discussion of the limits of sulfene formation from sulfonyl chlorides. We may also include as "non-sulfene" reactions (a) photolysis of β-keto sulfones, which, evidently, does not undergo Norrish type II cleavage to form the sulfene,[78] and (b) thermolysis of 3-butene-1-sulfonyl chloride,[21] 2-propene-1-sulfonyl chloride,[21] 2,1-benzoxathiin-3-one 1,1-dioxide,[79] *o*-toluenesulfonyl chloride,[80] and α-chloroethanesulfinic acid.[80]

Oxidation of >C=S or >C=SO groups has as yet shown no clear sign of sulfene formation.[81]

The Reactions of Sulfenes

Much of the importance of sulfenes lies in their usefulness in synthesis. Rather than give a full treatment here, I have simply presented a tabular summary of the reactions known to date (Table II; see ref 4, 5, 21, 22, 40, 44b,c, 47, 49, 51, 52, 54, 56, 58, 62b, 66, 79, 82–97), with references primarily intend-

ed to provide the reader with direct access to further data. The first reaction listed in Table II, namely the sulfonylation of alcohols and amines and so forth, is the most commonly used reaction of sulfenes. Of great potential synthetic application are the reactions leading to the three- and four-membered ring products, *i.e.*, the episulfone synthesis and the cycloadditions of enamines and the like.

One reaction conspicuously absent from Table II is thermal decomposition of a sulfene into a carbene and sulfur dioxide. It will be recalled that this was the second of the three steps in the mechanism that Wedekind first put forward[2] to account for formation of stilbene from phenylmethanesulfonyl chloride and triethylamine. Such a reaction has been looked for on a number of occasions by a number of people, in all cases without any positive indications whatever.[1,66] We have estimated[42] that the decomposition of sulfene into methylene and sulfur dioxide is endothermic by about 55–60 kcal/mol; the second step in Wedekind's proposal is probably incorrect.

But the basic idea of the first step of Wedekind's mechanism is both correct and fruitful, and the oblivion into which it fell unfortunate in its consequences. The work of the past dozen years, however, has established sulfene in its rightful place as a recognized intermediate in an array of useful and interesting reactions. Furthermore, there is need for continued work to complete the gamut of sulfene reactions, to learn more about the mechanism of sulfene formation, and to gain information about the mechanisms by which sulfenes undergo further reaction, this last a virtually unexplored field.

(76) We also have prepared this material and have found that its infrared spectrum is consistent only with structure 14. In addition, notwithstanding a contrary report,[77] (a) 14 is the major product of the partial hydrolysis (isolated yield >70%) and (b) 14 readily gives 15 in good yield on treatment with aniline. Unfortunately, the hydrogen atoms of the methylene group proved too labile to allow evidence for the sulfene to be obtained from a deuterium labeling experiment (J. F. King and G. R. MacDonald, unpublished).

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(78) C. L. McIntosh, P. de Mayo, and R. W. Yip, *Tetrahedron Lett.*, 37 (1967).

(79) J. F. King, B. L. Huston, A. Hawson, J. Komery, D. M. Deaken, and D. R. K. Harding, *Can. J. Chem.*, 49, 936 (1971); J. F. King, A. Hawson, B. L. Huston, L. J. Danks, and J. Komery, *ibid.*, 49, 943 (1971).

(80) J. F. King and D. R. K. Harding, unpublished.

(81) *Cf.* B. Zwanenburg, L. Thijs, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, 86, 577 (1967); B. Zwanenburg, A. Wagenaar, and J. Strating, *Tetrahedron Lett.*, 4683 (1970); W. Walter and K.-D. Bode, *Justus Liebigs Ann. Chem.*, 660, 74 (1962).

(82) For some useful procedures, see: R. K. Crossland and K. L. Servis, *J. Org. Chem.*, 35, 3195 (1970); R. K. Crossland, W. E. Wells, and V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, 93, 4217 (1971); D. S. Noyce, B. E. Johnston, and B. Weinstein, *J. Org. Chem.*, 34, 463 (1969); H. Böhme and P.-H. Meyer, *Synthesis*, 205 (1971); also ref 31.

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(84) M. S. Heller and A. M. Adelman, *Synthesis*, 545 (1970).

(85) For reviews with extensive compilations of data see: H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967, esp. Chapter 8; L. L. Müller and J. Hamer, "Synthesis of Heterocyclic Four-Membered Rings, Interscience, New York, N. Y., 1967, pp 212–240.

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(88) J. B. Stothers, L. J. Danks, and J. F. King, *Tetrahedron Lett.*, 2551 (1971); *cf.* T. Nagai, M. Tanaka, and N. Tokura, *ibid.*, 6293 (1968), and also *J. Org. Chem.*, 37, 4106 (1972).

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(91) F. Eloy and A. Van Overstraeten, *Bull. Soc. Chem. Belg.*, 76, 63 (1967).

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