

fills the requirements for at least the major portion<sup>8</sup> of the product.

In additional experiments triethylamine has been added to each of the following solutions: benzylsulfonyl chloride in D<sub>2</sub>O and dioxane, benzylsulfonyl chloride in CH<sub>3</sub>OD, benzylsulfonyl chloride in (CH<sub>3</sub>)<sub>3</sub>COD, methanesulfonyl chloride in D<sub>2</sub>O and dioxane, and ethanesulfonyl chloride in D<sub>2</sub>O and dioxane. Also pyridine and a solution of sodium deuterioxide in D<sub>2</sub>O were added, respectively, to benzylsulfonyl chloride in a mixture of dioxane and D<sub>2</sub>O, and finally diethylamine was added to a solution of PhCD<sub>2</sub>SO<sub>2</sub>Cl in methylene chloride. In all of these experiments the product was shown by n.m.r. and infrared spectroscopy to contain the monodeuterated material in about the same proportion as that found with isopropyl benzylsulfonate, clearly showing sulfene formation to be a general process.

In view of this generality we feel that sulfenes must now be regarded as intermediates in some related transformations; these are, in particular, the formation of *trans*-stilbene,<sup>1</sup> *cis*-1,2-diphenylethylene sulfone,<sup>9</sup> and the oxythiobenzoyl chlorides<sup>10</sup> by the action of triethylamine on benzylsulfonyl chloride in nonpolar solvents, and also the synthesis of 1,1-dioxythietane derivatives from methanesulfonyl chloride and triethylamine in the presence of enamines,<sup>1a-b</sup> ketene acetals,<sup>4c</sup> and some related reagents.<sup>4e</sup> In reactions 2 and 3 above, sulfene formation cannot be tested by the deuteration experiment as readily as it can in reaction 1. However, though the comparison is somewhat limited, reactions 1, 2, and 3 apparently yield similar products under similar conditions.<sup>11</sup> This provides circumstantial evidence, at least, that these reactions all proceed through a common intermediate, that is, the sulfene.

**Acknowledgment.**—This work was supported by the National Research Council of Canada.

(8) The deuterium content of the ester is apparently slightly lower than the initial deuterium content of the alcohol. If this is real, it might arise from a portion of the ester being formed by mechanism a, or from an isotope effect ( $k_H/k_D < 2$ ) in the addition step, or as a result of the change in the deuterium content of the active hydrogen in the mixture as more and more hydrogen is released from the benzylsulfonyl chloride. The present evidence is not sufficient for the cause of the apparent lowering in deuterium content to be assigned, but, on the other hand the data do not require that the ester be formed by any process in addition to mechanism b.

(9) J. F. King and T. Durst, unpublished observations.

(10) J. F. King and T. Durst, *J. Am. Chem. Soc.*, **85**, 2676 (1963).

(11) Reactions 1, 2, and 3 in the presence of water, alcohols, or amines produce, respectively, the sulfonic acid,<sup>2,3</sup> esters,<sup>2,3</sup> or amides.<sup>3,12</sup> In the absence of further reagents reactions 1<sup>1,9</sup> and 2<sup>2,9,12-16</sup> give substituted ethylenes and ethylene sulfones.

(12) H. Kloosterziel, M. H. Deinema, and H. J. Backer, *Rec. trav. chim.*, **71**, 1228 (1952).

(13) L. von Vargha and E. Kovács, *Ber.*, **75**, 794 (1942).

(14) G. Hesse, E. Reichold, and S. Majmudar, *ibid.*, **90**, 2106 (1957).

(15) N. P. Neurieter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963).

(16) Holder of National Research Council of Canada Scholarships, 1961-1964.

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### Sulfene, an Intermediate in the Alcoholysis of Methanesulfonyl Chloride<sup>1</sup>

Sir:

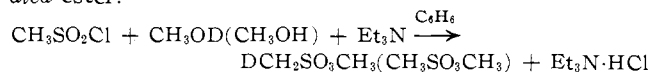
Recently<sup>2</sup> the background and evidence for the sulfene intermediate, particularly as regards formation of cycloadducts from  $\alpha$ -hydrogen-containing sulfonyl chlorides and both ketene acetals and enamines, was reviewed and discussed. Now we should like to pre-

(1) Related results and conclusions have been obtained and developed independently by J. F. King and T. Durst [*J. Am. Chem. Soc.*, **86**, 287 (1964)].

(2) W. E. Truce and J. R. Norell, *ibid.*, **85**, 3231 (1963).

sent more conclusive data for the intermediacy of sulfene (CH<sub>2</sub>SO<sub>2</sub>), particularly in the methanolysis of methanesulfonyl chloride in the presence of triethylamine.

Treatment of a solution of methanol-*d* (predominantly, but mixed with ordinary methanol) and triethylamine in dry benzene with methanesulfonyl chloride caused immediate precipitation of triethylamine hydrochloride. Filtration followed by evaporation of the solvent from the filtrate and subsequent distillation yielded methyl methanesulfonate (b.p. 78-80° at 11 mm.). Mass spectral and n.m.r. data for the ester showed it to be a mixture of *monodeuterated*, DCH<sub>2</sub>SO<sub>2</sub>CH<sub>3</sub>, and *undeuterated* ester (corresponding approximately to the deuterium content of the starting alcohol) with *no* evidence for the presence of either *di-* or *trideuterated* ester.

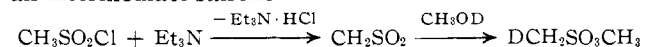


The mass spectrum contains peaks of strong intensity at *m/e* 15 (CH<sub>3</sub>), 16 (CH<sub>2</sub>D), 78, 79, and 80, with no detectable response at 17 (CHD<sub>2</sub>) and 81 (CHD<sub>2</sub>SO<sub>2</sub>). Less intense parent peaks were found at *m/e* 110 and 111. The n.m.r. spectrum consisted of two singlets at 3.02 and 3.85  $\delta$  which coupled with the mass spectral data were used to calculate the relative proportion of the two esters.

Incorporation of deuterium into the ester could be accounted for in the following two ways: (1) proton-deuterium exchange *via* the carbanion of the sulfonyl chloride and/or the sulfonate ester



(2) an elimination-addition sequence of steps involving an intermediate sulfene



Formation of the monodeuterated ester is consistent with path 2 while the absence of di- and trideuterated ester precludes path 1. In further support of this mechanism is the fact that with the weaker base, pyridine, practically no reaction occurred under comparable conditions.

The broad implications of these results are apparent and further work is being pursued as regards the possible intermediacy of sulfenes in various solvolyses of sulfonyl halides and related compounds.

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### Total Syntheses of Diterpenes and Diterpene Alkaloids.

#### II.<sup>1</sup> A Tetracyclic Common Intermediate

Sir:

We have recently reported a convenient method for the preparation of the [3.2.1]bicyclooctane system.<sup>1</sup> We have now succeeded in applying this method to syntheses of diterpenes<sup>2a</sup> and diterpene alkaloids.<sup>2b</sup> This paper reports the synthesis of *dl*-16-keto-10-

(1) Part I: S. Masamune, *J. Am. Chem. Soc.*, **83**, 1009 (1961).

(2) For the chemistry of these compounds, see: (a) L. H. Briggs, *et al.*, *J. Chem. Soc.*, 1345 (1963); B. E. Cross, *et al.*, *ibid.*, 2944 (1963), and preceding papers of these references; F. Dolder, *et al.*, *J. Am. Chem. Soc.*, **82**, 246 (1960); A. I. Scott, *et al.*, *ibid.*, **84**, 3197 (1962), and references therein; (b) S. W. Pelletier, *Tetrahedron*, **14**, 76 (1961); K. Wiesner and Z. Valenta, "Progress in the Chemistry of Organic Natural Products," Vol. XVI, Springer-Verlag, Vienna, 1958, p. 26; H. Vorbrueggen and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 2990 (1962).