

ether and acetone then removed by fractional distillation until a residue of approximately 0.2 cc. remained. Analytical gas-phase chromatography showed that this residue contained approximately 50% of methyl butyrate, the remainder being acetone and ether and only traces of substances having considerably longer retention times. Pure methyl butyrate was isolated from this mixture by preparative gas-phase chromatography (Wilkins Aerograph Instrument, Walnut Creek, Calif.) on a 20% silicone rubber column operating at 60°, the retention time of the ester being approximately 10 min. The absolute purity of the ester obtained in this manner was confirmed on an analytical instrument (Wilkins, Hy-F1 instrument).

Methyl 4-*d*₁-Butyrate (III).—A solution of the tosylate XI (1.58 g.) in ether (50 cc.) was added to a magnetically stirred suspension of lithium aluminum deuteride (420 mg.) in ether (150 cc.). After 30 min. the product (728 mg.) was isolated in the usual manner and gave, after distillation, 4-*d*₁-butanol 1-tetrahydropyranyl ether (II, 564 mg.). A portion of this material (250 mg.) was oxidized (using 7 cc. of 6 *N* Jones reagent²⁶) and methylated as described above and pure methyl 4-*d*₁-butyrate (II) isolated by preparative gas-phase chromatography.

Methyl 4,4-*d*₂-Butyrate (III).—A solution of the ester VII (800 mg.) in ether (40 cc.) was added to a magnetically stirred sus-

pension of lithium aluminum deuteride (400 mg.) in ether (150 cc.). After 1 hr., the product was isolated in the usual manner giving 1,1-*d*₂-tetramethylene-1,4-diol 4-tetrahydropyranyl ether (IX, 700 mg.). On treatment of this material with tosyl chloride (1.5 g.) in pyridine (5 cc.) for 1.5 hr., there was obtained, after the usual work-up, 1,1-*d*₂-tetramethylene-1,4-diol 4-tetrahydropyranyl ether 1-tosylate (XII, 1.3 g.). A solution of this tosylate in ether (25 cc.) was added to a magnetically stirred suspension of lithium aluminum hydride (300 mg.) in ether (150 cc.). After 15 min., the usual isolation procedure gave a colorless oil (560 mg.), which was purified by distillation giving 4,4-*d*₂-butanol tetrahydropyranyl ether (XV) (480 mg.). A portion of this material (280 mg.) was oxidized (using 8 cc. of Jones reagent²⁴) and methylated as previously described and pure methyl 4,4-*d*₂-butyrate (III) isolated in the above described manner.

Methyl 4,4,4-*d*₃-Butyrate (IV).—A solution of XII (1.4 g.) in ether (40 cc.) was reduced with lithium aluminum deuteride (300 mg.) in ether (180 cc.) in the usual manner. The resulting 4,4,4-*d*₃-butanol tetrahydropyranyl ether (XVI, 520 mg.) was oxidized and the derived butyric acid esterified with ethereal diazomethane to give methyl 4,4,4-*d*₃-butyrate (IV).

Acknowledgment.—Financial support was provided by the National Institutes of Health (Grant No. 5T4-CA5061 and AM-04257) of the U. S. Public Health Service.

(25) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

COMMUNICATIONS TO THE EDITOR

The Existence of Sulfenes

Sir:

The intermediacy of a sulfene (RR'C=SO₂) has been proposed to rationalize the course of three general reactions: (1) the reaction of sulfonyl halides of the type RR'CHSO₂Cl with tertiary amines,¹ (2) the reaction of diazoalkanes with sulfur dioxide,² and (3) the photolysis of unsaturated sulfones.³ Although the formation of sulfenes in these transformations is currently regarded^{3,3a,4} as highly probable, in no case has it been proved. We wish to describe our experiments which show that sulfenes are produced in reaction 1, above.

Benzylsulfonyl chloride, when treated with an alcohol in the presence of triethylamine, is quantitatively converted in less than 1 min. at room temperature into the corresponding ester. Two possible mechanisms for this reaction are: (a) a bimolecular nucleophilic substitution at the sulfur atom by the alcohol⁵ (or its conjugate base) or (b) initial formation of phenylsulfene by an elimination reaction, followed by addition of the alcohol. In an experiment to distinguish these possibilities, benzylsulfonyl chloride (1.9 mmoles) was treated with triethylamine in isopropyl alcohol-*d* (~13 mmoles, estimated deuterium content: 92 ± 2% of the active hydrogen). The following data show the constitution of the ester so obtained. (1) The melting point of a mixture with natural abundance

isopropyl benzylsulfonate is undepressed. (2) *Anal.* Calcd. for a mixture of 91% PhCHDSO₃CH(CH₃)₂ and 9% PhCH₂SO₃CH(CH₃)₂: 6.49 atom % excess D. Found: 6.48 atom % excess D. (3) The intensity of the band at 4.15 δ in the deuterated ester corresponded to the presence of ~90% PhCHDSO₃CH(CH₃)₂; the other bands in the spectrum were identical with those of the natural abundance ester. (4) The infrared spectrum of the deuterated material (0.6 *M* in CCl₄) was virtually identical with that of the natural abundance compound above 1450 cm.⁻¹; below that the spectra were basically similar⁶ but the deuterated sample showed additional bands at 1223 (m), 1188 (s), 1154 (s), and 940 cm.⁻¹ (s), and lacked the bands at 1410 (w), 1268 (m), 1204 (s), 1158 (w), and 1137 cm.⁻¹ (m) present in the natural abundance ester. (5) The peaks in the mass spectrum⁷ of the natural abundance ester at *m/e* 91 (61.2% of Σ₃₃) and *m/e* 107 (1.8% of Σ₃₃) were largely shifted in the spectrum of the deuterated material to *m/e* 92 and 108, the relative intensities in the latter spectrum corresponding well with the content of monodeuterated ester as estimated by the above methods. The intensities of the bands at *m/e* 93 and 109 in the mass spectrum of the deuterated material were such as to exclude the possibility of >2% PhCD₂SO₃CH(CH₃)₂.

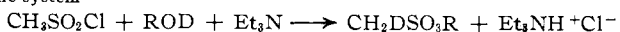
It is concluded from the above data that with the quantities and reactants given, the ester formed contains about 90% of the monodeuterated ester, PhCHDSO₃CH(CH₃)₂, the remainder being the nondeuterated ester with very little or none of the dideuterated compound, PhCD₂SO₃CH(CH₃)₂. The formation of such a product requires that the deuterium be incorporated in an irreversible step (and clearly excludes any significant incorporation of deuterium either by the sulfonyl chloride prior to reaction with the alcohol, or by the ester). We feel that mechanism b uniquely ful-

(1) E. Wedekind and D. Schenk, *Ber.*, **44**, 198 (1911).

(2) H. Staudinger and F. Pfenninger, *ibid.*, **49**, 1941 (1916).

(3) E. Henmo, P. de Mayo, A. B. M. A. Sattar, and A. Stoessl, *Proc. Chem. Soc.*, 238 (1961); J. F. King, P. de Mayo, E. Morkved, A. B. M. A. Sattar, and A. Stoessl, *Can. J. Chem.*, **41**, 100 (1963).

(3a) Like results and conclusions to those reported herein have been obtained by W. E. Truce, *et al.*, *J. Am. Chem. Soc.*, **86**, 288 (1964), as regards the system



(4) (a) G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **84**, 313 (1962);

(b) G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962); (c) W. E. Truce, J. J. Breiter, D. J. Abraham, and J. R. Norell, *J. Am. Chem. Soc.*, **84**, 3030 (1962); W. E. Truce, and J. R. Norell, *ibid.*, **85**, 3231 (1963); (d) J. F. King and T. Durst, *Tetrahedron Letters*, 585 (1963); (e) R. H. Hasek, P. G. Gott, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **28**, 2496 (1963).

(5) Such a mechanism has been proposed for the uncatalyzed alcoholyses of aryl- and alkylsulfonyl chlorides: E. Tommila and P. Hirsjärvi, *Acta Chem. Scand.*, **5**, 659 (1951); P. Hirsjärvi and E. Tommila, *ibid.*, **5**, 1097 (1951); R. B. Scott, Jr., and R. E. Lutz, *J. Org. Chem.*, **19**, 830 (1954).

(6) The other significant peaks below 1450 cm.⁻¹ for the deuterated material are at 1388 (m), 1365 (vs), 1345 (vs), 1175 (s), 1096 (s), 1077 (w), 1030 (w), 920 (vs), 883 (vs), 825 (w), 695 cm.⁻¹ (s), and for the natural abundance ester are at 1387 (m), 1365 (vs), 1345 (vs), 1173 (vs), 1095 (s), 1073 (w), 1030 (w), 920 (vs), 887 (vs), 825 (w), 697 cm.⁻¹ (s).

(7) We wish to express our thanks to Dr. W. A. Ayer (University of Alberta), through whose courtesy this mass spectrum was obtained.

fills the requirements for at least the major portion⁸ of the product.

In additional experiments triethylamine has been added to each of the following solutions: benzylsulfonyl chloride in D₂O and dioxane, benzylsulfonyl chloride in CH₃OD, benzylsulfonyl chloride in (CH₃)₂CO, methanesulfonyl chloride in D₂O and dioxane, and ethanesulfonyl chloride in D₂O and dioxane. Also pyridine and a solution of sodium deuterioxide in D₂O were added, respectively, to benzylsulfonyl chloride in a mixture of dioxane and D₂O, and finally diethylamine was added to a solution of PhCD₂SO₂Cl 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,¹ *cis*-1,2-diphenylethylene sulfone,⁹ and the oxythiobenzoyl chlorides¹⁰ 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,^{1a-b} ketene acetals,^{4c} and some related reagents.^{4e} 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.¹¹ This provides circumstantial evidence, at least, that these reactions all proceed through a common intermediate, that is, the sulfene.

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(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,^{2,3} esters,^{2,3} or amides.^{2,12} In the absence of further reagents reactions 1^{1,9} and 2^{2,9,12-15} 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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RECEIVED NOVEMBER 6, 1963

Sulfene, an Intermediate in the Alcoholysis of Methanesulfonyl Chloride¹

Sir:

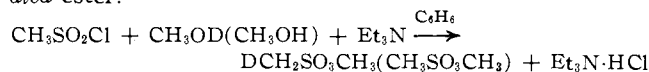
Recently² the background and evidence for the sulfene intermediate, particularly as regards formation of cycloadducts from α -hydrogen-containing sulfonyl chlorides and both ketene acetals and enamines, was reviewed and discussed. Now we should like to pre-

(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 (CH₂SO₂), 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*, DCH₂SO₂CH₃, 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.

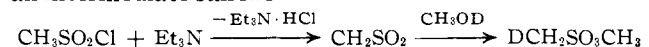


The mass spectrum contains peaks of strong intensity at *m/e* 15 (CH₃), 16 (CH₂D), 78, 79, and 80, with no detectable response at 17 (CHD₂) and 81 (CHD₂SO₂). Less intense parent peaks were found at *m/e* 110 and 111. The n.m.r. spectrum consisted of two singlets at 3.02 and 3.85 δ which coupled with 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.¹ A Tetracyclic Common Intermediate

Sir:

We have recently reported a convenient method for the preparation of the [3.2.1]bicyclooctane system.¹ We have now succeeded in applying this method to syntheses of diterpenes^{2a} and diterpene alkaloids.^{2b} 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).