fills the requirements for at least the major portion[8] of the product.

In additional experiments triethylamine has been added to each of the following solutions: benzylsulfonyl chloride in D_2O and dioxane, benzylsulfonyl chloride in CH_3OD, benzylsulfonyl chloride in $(CH_3)_3COD$, methanesulfonyl chloride in D_2O and dioxane, and ethanesulfonyl chloride in D_2O and dioxane. Also pyridine and a solution of sodium deuteroxide in D_2O were added, respectively, to benzylsulfonyl chloride in a mixture of dioxane and D_2O, and finally diethylamine was added to a solution of $PhCD_2SO_2Cl$ 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 chlorides[10] 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,[4a-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.

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,[2,3] esters,[2,3] or amides.[3,12] 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 Chloride[1]

Sir:

Recently[2] 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 present more conclusive data for the intermediacy of sulfene (CH_2SO_2), particularly in the methanolysis of methanesulfonyl chloride in the presence of triethylamine.

(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).

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*, $DCH_2SO_3CH_3$, 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.

$$CH_3SO_2Cl + CH_3OD(CH_3OH) + Et_3N \xrightarrow{C_6H_6} DCH_2SO_3CH_3(CH_3SO_3CH_3) + Et_3N{\cdot}HCl$$

The mass spectrum contains peaks of strong intensity at *m/e* 15 (CH_3), 16 (CH_2D), 78, 79, and 80, with no detectable response at 17 (CHD_2) and 81 (CHD_2SO_2). 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

$$CH_3SO_2X + B: \rightleftharpoons {}^-CH_2SO_2X + BH^+ \rightleftharpoons \text{etc.}$$

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

$$CH_3SO_2Cl + Et_3N \xrightarrow{-Et_3N\cdot HCl} CH_2SO_2 \xrightarrow{CH_3OD} DCH_2SO_3CH_3$$

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.

Acknowledgment.—The authors gratefully acknowledge support of this work by the National Institutes of Health under grant No. CY-4536 and by a Purdue Research Foundation fellowship.

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RECEIVED NOVEMBER 22, 1963

Total Syntheses of Diterpenes and Diterpene Alkaloids. II.[1] A Tetracyclic Common Intermediate

Sir:

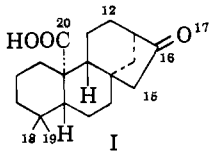
We have recently reported a convenient method for the preparation of the [3.2.1]bicyclooctane system.[1] We have now succeeded in applying this method to syntheses of diterpenes[2a] and diterpene alkaloids.[2b] This paper reports the synthesis of *dl*-16-keto-10-

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

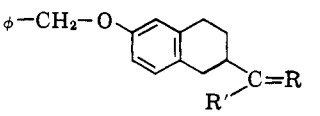
(2) For the chemistry of these compounds, see: (a) L. H. Briggs, *et al.*, *J. Chem. Soc.*, 1345 (1963); B. E. Cross, *et al.*, *ibid.*, 2944 (1963), and preceding papers of these references; F. Dolder, *et al.*, *J. Am. Chem. Soc.*, **82**, 246 (1960); A. I. Scott, *et al.*, *ibid.*, **84**, 3197 (1962), 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).

carboxy-17,20-bisnorkaurane (I)[3] which can be converted to the above two groups of natural products.

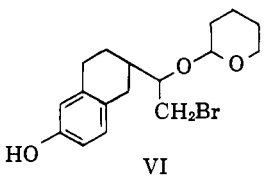
6-Benzyloxy-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (II), m.p. 149–150°, prepared from the corresponding phenol,[4] was treated successively with



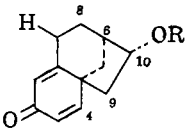
I



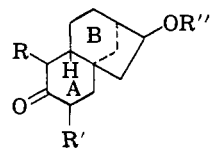
II, R = O; R′ = OH
III, R = O; R′ = CH_2Br
IV, R = OH, H; R′ = CH_2Br
V, R = OTHP, H; R′ = CH_2Br



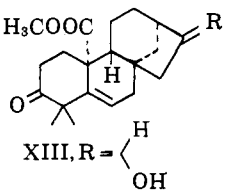
VI



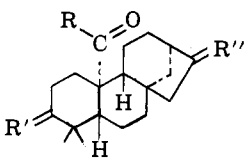
VII, R = THP
VIII, R = H



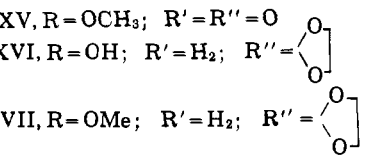
IXa, R = R′ = H; R″ = Bz
X, R = COOMe; R′ = H; R″ = Bz
XI, R = R″ = H; R′ = COOMe



XIII, R =



XIV, R = O



XV, R = OCH_3; R′ = R″ = O
XVI, R = OH; R′ = H_2; R″ =

XVII, R = OMe; R′ = H_2; R″ =

oxalyl chloride, diazomethane, and hydrobromic acid to afford a bromoketone (III), m.p. 64–65°. The sodium borohydride reduction of III provided a mixture of epimeric bromohydrins (IV), which was converted to the tetrahydropyranyl ethers (V). Hydrogenolysis of V with palladium on carbon gave the corresponding phenols (VI). The base treatment of VI under similar conditions to those used previously[1] effected the cyclization of only one isomer of VI to give the tetrahydropyranyl ether of a hydroxy dienone (VII). The corresponding hydroxy compound (VIII) melted at 115–116° (λ_{max}^{MeOH} 245 mμ (1.8 × 10^4), λ_{max}^{Chl} 3.0, 6.04, 6.18, 6.25 μ). The over-all yield of VIII from II is approximately 30%. The stereochemistry of the hydroxyl group of VIII is assigned as shown in VIII, based on the stereochemical course of cyclization.[5] A model shows that the ethereal oxygen atom of the *uncyclized* phenol in the transition state interacts severely with a hydrogen atom at position 8.

(3) All formulas shown in this paper are taken to represent racemates.

(4) J. Jacques and A. Horeau, *Bull. soc. chim. France*, 512 (1950). The ether cleavage of 6-methoxy-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid was effected with HBr–acetic acid.

(5) Attempts to cyclize 6-hydroxy-1,2,3,4-tetrahydronaphthalenes substituted in the 2 position with the following groups failed: an oxidethyl group, an α-keto-β-bromoethyl group, and the ethylene glycol ketal of α-keto-β-bromoethyl. This clearly defines the steric course of cyclization and presents excellent evidence to support the mechanism proposed for the S_N2 reaction of haloketones. See E. L. Eliel, "Steric Effects in Organic Chemistry," M. Newman, Ed., Chapman and Hall, New York, N. Y., 1956, p. 103.

Catalytic hydrogenation of the benzoate, m.p. 116–117°, of VIII with palladium–calcium carbonate afforded two isomeric tetrahydro compounds (IXa, m.p. 103–104°, and IXb), m.p. 105–106°, in a 7:3 ratio. Conversion of IXa to known *cis*-decalin-9-acetic acid[6] and further to the *cis*-decalin-9-carboxylic acid[6,7] shows that the A and B rings of IXa are *cis* fused.

Carbomethoxylation of IXa with triphenylmethyl sodium and carbon dioxide and methylation afforded a β-keto ester (X), m.p. 150–152°.[8] Alternatively, X was obtained by a similar carbomethoxylation of the benzoate of VIII (m.p. of the product, 108–109°) followed by hydrogenation. Therefore the carbomethoxy group of X must be located at position 1.

Ring A was constructed by a conventional method. Addition of ethyl vinyl ketone followed by cyclization provided a tetracyclic unsaturated ketone (XII), m.p. 126–127°. Exhaustive methylation of the tetrahydropyranyl ether of XII and then removal of the protective group afforded a dimethyl compound (XIII), m.p. 154–155°, which was oxidized with the Jones reagent to give an amorphous diketone (XIV). Catalytic hydrogenation of XIV resulted in only one saturated compound (XV), m.p. 130–131°, in approximately 60% yield. The Wolff–Kishner reduction on the monoketal of XV removed the ketone and provided an acid (XVI),[9] m.p. 205–207°, and an acid hydrazide. The corresponding ketal methyl ester (XVII) and keto acid (I) melted at 96–97.5° and 249–250°, respectively.

We have succeeded in converting veatchine azomethine acetate to the corresponding levorotatory enantiomers of XVI, XVII, and I. Infrared spectra of these compounds were completely superimposable, respectively. These results confirm that the assignments of structures and stereochemistry of all synthetic intermediates are correct. The conversion of veatchine into the synthetic intermediate (I) and the syntheses of a diterpene and diterpene alkaloids are described in accompanying papers.[10,11]

Acknowledgment.—The author is very grateful to Mr. N. T. Castellucci for preparing synthetic intermediates used in this investigation.

(6) R. D. Haworth and A. F. Turner, *J. Chem. Soc.*, 1240 (1958).

(7) The Wolff–Kishner reduction converted IXa to 10-hydroxy-4a,6-ethanodecalin, m.p. 45–46° (for numbering, see VIII), which was oxidized to the corresponding ketone. The Baeyer–Villeger reaction on this ketone gave a liquid lactone, which after alkaline hydrolysis, methylation, and oxidation afforded methyl 2-keto-decalin-9-acetate. The Clemensen reduction on this keto ester proceeded smoothly to afford *cis*-decalin-9-acetic acid, m.p. 117° (m.p. of its anilide, 158°). Application of the Barbier–Wieland degradation to this 9-acetic acid led to *cis*-decalin-9-carboxylic acid as reported.[6]

(8) Carbomethoxylation of IXa with dimethyl carbonate took a different course. The product (XI), m.p. 135–137°, is highly enolic, in contrast to X, and is represented by XI. Although the C-1 enolate anion is more stable than the C-3 anion due to the *cis* fusion of the rings, a bulky dimethyl carbonate molecular prefers the less hindered site: G. Stork and R. H. Hill, *J. Am. Chem. Soc.*, **79**, 495 (1957).

(9) The resolution of this acid was only partially successful due to the limited amount of material available. The highest rotation observed was $[\alpha]^{20}D = -16$. The pure (−) enantiomer had $[\alpha]^{27}D = -30$; see paper III of this series.

(10) Satisfactory analyses and spectra (infrared, ultraviolet, n.m.r.) were obtained for all new compounds described herein.

(11) This investigation was supported by a grant (GM 10369) from the National Institutes of Health, Public Health Service.

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RECEIVED OCTOBER 9, 1963

Total Syntheses of Diterpenes and Diterpene Alkaloids. III.[1] Kaurene

Sir:

We wish to report the degradation of veatchine, a major alkaloid of Garrya Lauriforia, to (−)-16-keto-

(1) Part II: S. Masamune, *J. Am. Chem. Soc.*, **86**, 288 (1964).