Heating of a mixture of 11.0 g (0.1 mole) of benzenethiol and 12.1 g (0.1 mole) of allyl bromide in the dark under nitrogen for 16 hr induced 8% reaction (based on nmr) yielding the same products.

Synthesis of 2-Bromopropyl Phenyl Sulfide.—Gaseous hydrogen bromide was slowly passed into 30.4 g (0.2 mole) of allyl pheny sulfide in flask wrapped securely in metal foil. After 13.4 g (0.17 mole) was absorbed, the reaction mixture was distilled to yield 13.3 g (33%) of product, bp 84–90° (0.35 mm). An infrared spectrum exhibited bands at 3.26, 3.37, 3.42, 6.29, 6.75, 6.92, 7.28, 8.52, 9.72, 11.15, 12.00, 13.43, and 14.45 μ.

Anal. Calcd for $C_9H_{11}BrS$: C, 46.76; H, 4.80; Br, 34.57; S, 13.87. Found: C, 46.69; H, 4.92; Br, 34.39; S, 13.8.

Reaction of Benzenethiol with Allyl Bromide in the Presence of β-Methallyl Sulfide.—A mixture of 6.7 g (0.06 mole) of benzenethiol, 7.4 g (0.06 mole) of allyl bromide, and 6.2 g (0.06 mole) of β-methallyl sulfide in a quartz tube was irradiated for 20 hr. Distillation of the reaction mixture provided two major fractions weighing 7.6 g (67%) and 4.6 g (50%), bp 56–68° (11 mm) and 86–88° (11 mm), respectively. Nmr and infrared spectra of the first fraction were virtually identical with those of 2-bromo-2-methylpropyl methyl sulfide and those of the second fraction of those of allyl phenyl sulfide. Ultraviolet irradiation of a mixture of 5.1 g (0.05 mole) of β-methallyl methyl sulfide and 11.6 g (0.05 mole) of 2-bromo-1-(phenylthio)propane for 20 hr produced absolutely no change in the mixture's nmr spectrum.

Synthesis of 2-Bromo-2-methylpropyl Methyl Sulfide.—Gaseous hydrogen bromide was slowly passed into 20.4 g (0.2 mole) of β-methallyl methyl sulfide in a foil-wrapped flask. During the reaction the 18.4 g (0.23 mole) of gas was absorbed and the solution temperature rose to 50°. The red reaction mixture was distilled to give 28.4 g (76%) of product, bp 52–54° (10 mm). An infrared spectrum showed major bands at 3.39, 3.44, 6.85,

6.95, 7.24, 7.31, 8.13, 8.30, 8.68, 9.10, 10.20, 10.45, 11.70, 12.38, and 13.58 μ.

Anal. Calcd for $C_5H_{11}BrS$: C, 32.79; H, 6.05; Br, 43.64; S, 17.51. Found: C, 32.90; H, 6.07; Br, 43.71; S, 17.95.

Competitive Hydrochlorination of β-Methallyl Chloride and β-Methallyl Methyl Sulfide.—A mixture of 15.3 g (0.15 mole) of β-methallyl methyl sulfide and 13.7 g (0.15 mole) of β-methallyl chloride was treated with gaseous hydrogen chloride until 4.6 g (0.13 mole) was absorbed. Nmr analyses of the reaction mixture showed that more than 90 mole % of the sulfide had reacted to form the 2-chloropropyl sulfide, while only a trace of 1,2-dichloro-2-methylpropane was formed.

Attempted Methanethiol Displacement of Chloride from 3-Chloro-2-methylpropyl Phenyl Sulfide.—A stirred mixture of 20.0 g (0.1 mole) of the chloropropyl phenyl sulfide and 5.0 g (0.12 mole) of methanethiol was sealed in a quartz tube and subjected to ultraviolet irradiation for 24 hr. The tube was then opened and nitrogen was drawn through the reaction mixture at room temperature under moderate vacuum. Nmr analysis of the residue showed only a small amount (7%) of signal from a (methylthio) moiety (at δ 2.27).

The Structures of the Camphene Sultones[1]

JOSEPH WOLINSKY, DONALD R. DIMMEL,[2b] AND THOMAS W. GIBSON[2a]

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The sulfonation of camphene with sulfuric acid in acetic anhydride gave, initially, 10-isobornyl sultone (3) and, after work-up, a 4:1 inseparable mixture of sultones 4 and 16. Neutralization of the initially formed reaction mixture with sodium carbonate afforded the acetoxysulfonate 35. Camphene and dioxane–sulfur trioxide gave sultone 3 and the unsaturated sulfonate 30. Upon heating sultone 3 rearranges to give pure sultone 4. The structures of 3, 4, 16, and 35 were established by lithium aluminum hydride reduction to isoborneol, camphene hydrate, 3,3,4-trimethyl-2-exo-norbornanol, and isoborneol, respectively. The structures of 3 and 35 were further verified by conversion into a derivative of 10-camphorsulfonic acid. The exo,cis ring juncture in sultone 4 was shown by conversion into 3-endo-methyl-3-exo-propyl-2-norbornanone (26), a compound synthesized by another stereospecific route.

While attempting to acylate camphene with acetic anhydride in the presence of sulfur trioxide, Lipp[3] observed the production of a crystalline, 1:1 adduct of camphene and sulfur trioxide, mp 133°. Acidification of the hydroxy sulfonate salt 1, obtained by the sodium–alcohol reduction of camphor sulfonic acid (2), also gave the same adduct and led Lipp to conclude that the structure of "camphene sultone" was represented by formula 3.

In 1938, Asahina[4] showed that basic hydrolysis of camphene sultone gave an unsaturated sulfonate salt 5 and proposed that the double bond was produced by dehydration of a tertiary alcohol, and the original sultone was best represented by gross structure 4.

Asahina also demonstrated that facile rearrangement of the bornyl ring system must occur since acidification of optically active sodium 10- and 9-(2-hydroxy)bornanesulfonates (1 and 6) gave rise to the same optically inactive sultone 4, mp 133°.

1   2   3   4

5   6   7
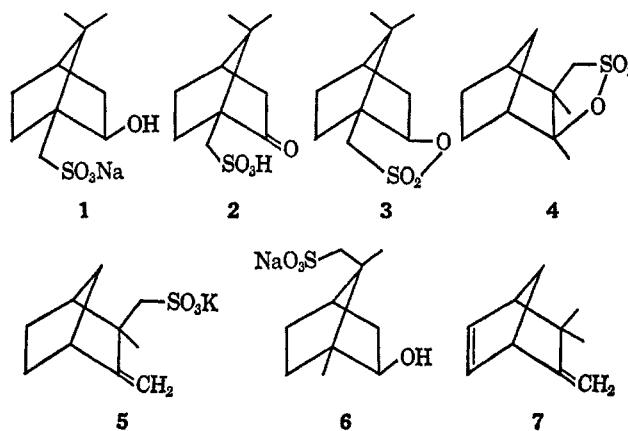
(1) Abstracted from part of the thesis submitted by D. R. D. in partial fulfillment of the requirements for the Ph.D. degree, Purdue University, Aug 1966.

(2) (a) National Institutes of Health Predoctoral Fellow, 1961–1963; (b) 1964–1966.

(3) P. Lipp and M. Holl, *Chem. Ber.*, **62**, 499 (1929).

(4) Y. Asahina, T. Sano, and T. Mayekawa, *ibid.*, **71**, 312 (1938).

More recently, Triebs[5] has shown that the sultone can be prepared from isobornyl acetate and that its pyrolysis affords camphenene 7.

Our interest in using camphene sultone in projected syntheses of sesquiterpenes, particularly β-santalene, led us to reinvestigate and carefully define its structure and stereochemistry.

Camphene sultone was prepared according to the procedure described by Asahina[4] (see Scheme I for a rough outline and the Experimental Section for exact details). Repeated recrystallization from methanol did not alter its melting point of 133°.

SCHEME I

Our investigation began with a spectral examination. The infrared spectrum of camphene sultone displayed strong SO_2 absorption at 7.5 and 8.6 μ. The nmr spectrum exhibited a singlet at δ 3.05 characteristic of a CH_2SO_2 group,[6] and two singlet methyl resonances, overlapping methylene and methine signals, at 1.30 and 1.52. Minor peaks at 4.0, 1.3, and 1.0 ppm were attributed to an impurity which could not be removed by recrystallization.

The mass spectrum of camphene sultone showed abundant ions at m/e 148, 67 (base), and 43 (base), which correlate[7] with a breakdown pattern of

m/e 67   m/e 148   m/e 43

Taken together, the spectral data establish the gross structure originally proposed by Asahina.

It was anticipated that the simplest approach to the stereochemistry of the sultone would be desulfurization to the corresponding bicyclic alcohol. Raney nickel desulfurization of the sultone was tried, but proved to be ineffective. Lithium aluminum hydride has been employed to reduce sultones to mercapto

alcohols;[8] consequently, its action on camphene sultone was investigated. There was obtained a 15% yield of a neutral fraction[9] which was subsequently shown to be a 4:1 mixture of camphene hydrate (8) and 3,3,4-trimethyl-2-exo-norbornanol (9). Acidification of the aluminum salts gave a poorly defined mixture of sulfur-containing alcohols which was desulfurized with nickel boride[10] to the same 4:1 mixture of alcohols as obtained directly by the hydride reduction.

8   9

Camphene hydrate was identified by comparison of its physical properties and vpc retention time with those of an authentic sample.[11] In a control experiment it was established that the endo isomer, 2-methyl-camphenilol, is stable to the conditions of the hydride reduction; therefore, camphene hydrate must form directly from the sultone and not by a rearrangement process.

The minor alcohol, 3,3,4-trimethyl-2-exo-norbornanol (9), obtained in the hydride reduction was identified by spectral analysis[7] and by oxidation to 4-methyl-camphenilone (10). An authentic sample of 10 was prepared from fenchone as outlined in Scheme II. The alcohol 13 was dehydrated with thionyl chloride rather than potassium bisulfate,[12] since the latter reagent gave approximately the same complex mixture of terminal olefins and tricyclenes (see the Experimental Section for the characterization of these hydrocarbons)

SCHEME II

(5) W. Triebs and I. Lorenz, *Chem. Ber.*, **84**, 666 (1951).
(6) R. W. Ohline, A. L. Allred, and F. G. Bordwell, *J. Am. Chem. Soc.*, **86**, 4641 (1964).
(7) D. R. Dimmel and J. Wolinsky, *J. Org. Chem.*, in press.
(8) A. Mustafa in "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, pp 183–197.
(9) *Cf.* E. L. Eliel, E. W. Della, and M. M. Rogič, *J. Org. Chem.*, **27**, 4712 (1962), for an example of the hydrogenolysis of RR′NCH₂CH₂SH with lithium aluminum hydride.
(10) W. E. Truce and F. M. Perry, *J. Org. Chem.*, **30**, 1316 (1965).
(11) Kindly supplied by Mr. J. Kawakami and Dr. H. C. Brown.
(12) S. S. Nametkin, *Ann.*, **432**, 230 (1923); **459**, 153 (1927).

from either alcohol 11 or 13. The 4-methylcampheni-lone (10)[13] prepared in this manner was identical in all respects with the ketone obtained by oxidation of the minor alcohol from the hydride reduction of camphene sultone.

The minor alcohol 9 obtained by the hydride reduction of the camphene sultone mixture displayed a singlet C*H*OH resonance signal in its nmr spectrum. Examination of molecular models indicates that the dihedral angle between the proton at bridgehead C-1 and the *exo* proton at C-2 is approximately 45°, whereas the dihedral angle between the proton at C-1 and the *endo* proton at C-2 is 90°. It has been observed experimentally that the coupling constant $J_{1\text{-}2\text{-}exo}$ is of the order of magnitude of 4–5 cps, whereas $J_{1\text{-}2\text{-}endo}$ is approximately 0.[14-16] On this basis the alcohol group in 9 is assigned an *exo* configuration.

Lithium aluminum hydride reduction of 4-methyl-camphenilone (10) affords a 9:1 mixture[17] of *endo*- and *exo*-4-methyl camphenilols 15 and 9. The alcohol mixture resulting from this reduction was only partially separated by vpc. The minor *exo* alcohol 9 appeared as a shoulder in front of the main peak due to alcohol 15 when a 150-ft quadrol capillary column was employed. Enriching the mixture with a sample of alcohol 9 obtained from the sultone reduction increased the relative intensity of the shoulder. The nmr spectrum of the alcohol mixture exhibited a doublet ($J = 4.5$ cps) C*H*OH signal which further strengthened the argument that the major alcohol from LiAlH$_4$ reduction of 4-methylcamphenilone was the *endo* isomer and indirectly insured the *exo* configuration for the other isomer.

Returning to the hydride desulfurization, we were led to conclude that the two alcohols 8 and 9 were derived from two sultones, 4 and 16, which form a sharp-melting, inseparable mixture. Examination of the nmr spectrum of the sultone shows the presence of *ca.* 20% of an isomer with signals at δ 4.0, 1.3, and 1.0 which can be attributed to sultone 16.[18]

While the chemical and spectral evidence so far presented are fully in accord with structure 4, the β-sultone 17 can not be unambiguously excluded. In order to provide a definitive basis for a choice between 4 and 17, the sultone mixture was reduced with lithium aluminum deuteride to yield camphene hydrate-d_1 (18). The location of the deuterium atom in a methyl group at C-3 in the reduction product was determined on the basis of its nmr and mass spectra. The resonance signal at δ 1.13 which corresponds to the methyl group at C-2 was unaltered, whereas the relative intensity of one of the methyl groups at C-3 was reduced by a factor of $^1/_3$. High-resolution mass spectra showed that the m/e 41.0391 ion, to which the *gem*-dimethyl group at C-3 in camphene hydrate contributes was substantially shifted to 42.045 in the monodeuterio de-

rivative, while the m/e 43.0284 ion which corresponds to the acylium ion and arises from C-2 is equally intense in both isomers. These observations exclude the possibility that camphene sultone is represented by the β-sultone 17.

17   18
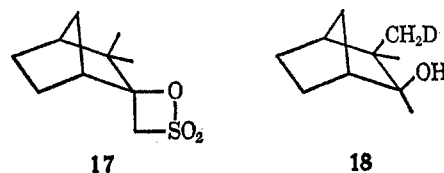
We turn next to the configuration of the CH$_2$SO$_3$ group in camphene sultone which was demonstrated by the sequence of transformations outlined in Schemes III and IV. Treatment of the sultone mixture with phenyllithium gave a mixture of hydroxy sulfones 19 and 20. Distillation of this mixture at 200° or mild treatment with thionyl chloride–pyridine transformed hydroxy sulfone 19 into 9-(phenylsulfonyl)camphene (21). The structure of 21 was established by spectral analysis and by ozonolysis to the ketosulfone 22 and subsequent desulfurization with Raney nickel to camphenilone 23.

SCHEME III

SCHEME IV
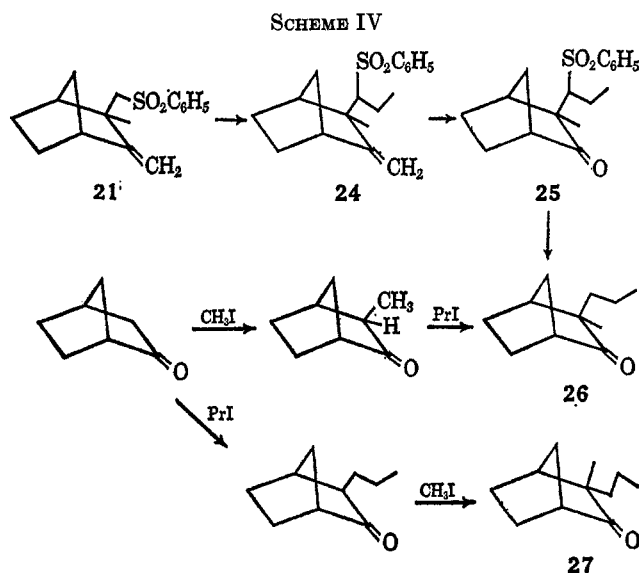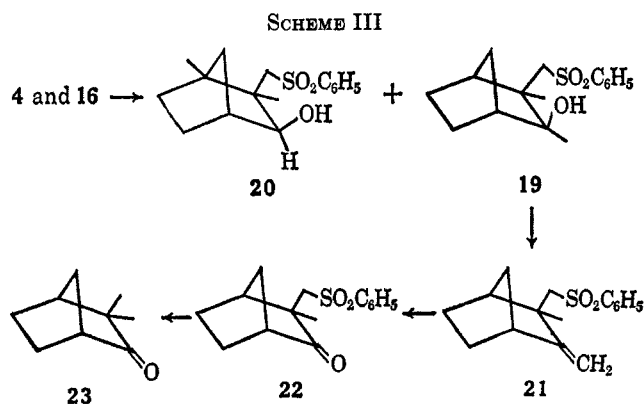
The unsaturated sulfone 21 was alkylated with ethyl iodide using either sodium amide in liquid ammonia or tritylsodium in ether. Ozonolysis of the resulting 9-phenylsulfonyl-9-ethylcamphene 24 afforded the keto-sulfone 25, which was desulfurized with Raney nickel

(13) G. Komppa and G. A. Nyman, *Ber.*, **69**, 334 (1936); W. Z. Antkow-iak, *Bull. Acad. Polon. Sci.*, **14**, 1 (1966); *Chem. Abstr.*, **64**, 19685 (1966).

(14) N. S. Bhacca and D. H. Williams, "Application of NMR Spectroscopy in Organic Chemistry," Holden Day, Inc., San Francisco, Calif., 1964, pp 49, 50.

(15) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(16) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).

(17) *Cf.* S. Beckman and R. Mezger, *Chem. Ber.*, **89**, 2738 (1956); P. Hirsjarvi, *Ann. Acad. Sci. Fenicae. Ser. A, II*, No. 81, 16 pp (1957); No. 84, 15 pp (1957).

(18) Hitherto the name "camphene sultone" will refer to compound 4 and the camphene sultone mixture to the mixture of 4 and 16.

to 3-*endo*-methyl-3-*exo*-propyl-2-norbornanone (**26**). The structure of ketone **26** was established by comparison with authentic samples of 3-*endo*-methyl-3-*exo*-propyl-2-norbornanone (**26**) and 3-*exo*-methyl-3-*endo*-propyl-2-norbornanone (**27**) prepared by stereospecific stepwise alkylation of norbornanone with methyl iodide–propyl iodide and propyl iodide–methyl iodide, respectively, according to a procedure described by Corey.[19] These two isomers were readily distinguished by infrared and nmr spectroscopy, as well as by vpc. The ketone isolated from Raney nickel reduction of **25** proved to be identical in all respects with ketone **26**. This observation established the presence of an *exo*-CHSO$_2$ group in **25**, **24**, and **21**, and, in turn, confirms the presence of an *exo,cis*-sultone ring fusion in camphene sulfone **4**.

The minor sultone **16** in the camphene sultone mixture is also assigned an *exo,cis* ring juncture. The nmr resonance signal for the CH$_2$SO$_2$ protons in hydroxy sulfone **20** appear as a widely spaced AB-type quartet (J = 13.8 cps). The same type of AB quartet is observed in the hydroxy sulfone **19**, whereas with sulfones **21** and **22** the CH$_2$SO$_2$ protons appear as a singlet. An interaction between *cis*-SO$_2$ and -OH groups evidently accentuates the nonequivalence of the CH$_2$SO$_2$ protons in the former cases.

We now turn back to the sulfonation of camphene. If the diluted reaction mixture is extracted with ether there is obtained a mixture of isobornyl acetate and a third sultone (see Scheme I). This sultone is relatively insoluble in isobornyl acetate and generally crystallizes on standing. Lithium aluminum hydride reduction of this sultone affords isoborneol **28** and thereby requires its structure to be represented by 10-isobornyl sultone **3** or 8-isobornyl sultone **29**.

Hydrolysis of the sultone with sodium hydroxide gave only a small amount of a hydroxy sulfonate. The main product proved to be the α,β-unsaturated salt **30** which can arise from **3** by removal of an active α proton, followed by a reverse Wagner–Meerwein-type elimination of sulfonate ion.

Treatment of the sultone with N-lithio-N-methyl-anilide afforded N-methyl-10-(2-*exo*-hydroxy)bornane-sulfonanilide (**31**). The alcohol **31** was oxidized with chromium trioxide according to the Jones procedure[20] and gave the ketosulfonamide **32** which was identical in all respects with a sample of N-methyl-10-camphor-sulfonanilide **32** prepared from 10-camphorsulfonyl chloride and N-methylaniline. On the basis of this conversion the third sultone must have the constitution represented by 10-isobornyl sultone (**3**).

Two alternate routes to sultone **3** were found. Reduction of 10-camphorsulfonic acid with sodium and alcohol gave a mixture of sodium 10-(2-*exo*-hydroxy)- and 10-(2-*endo*-hydroxy)bornanesulfonates **1** and **33**. The action of *p*-toluenesulfonyl chloride in pyridine on this mixture gave 10-isobornyl sultone **3** in about 20% yield; the corresponding *endo* isomer, 10-bornyl sultone, was not found.

The sulfonation of camphene with dioxane–sulfur trioxide also gave a 20% yield of 10-isobornyl sultone **3**. The principal product in this reaction was the unsatu-

rated sulfonic acid which was isolated as the sodium salt **30**. The salt **30** was characterized by the preparation of the N-methylsulfonanilide **34**. No reaction was observed between camphene and pyridine–sulfur trioxide complex. At elevated temperature, Dombrovskii[21] reported that the unsaturated sulfonate **30** was formed.
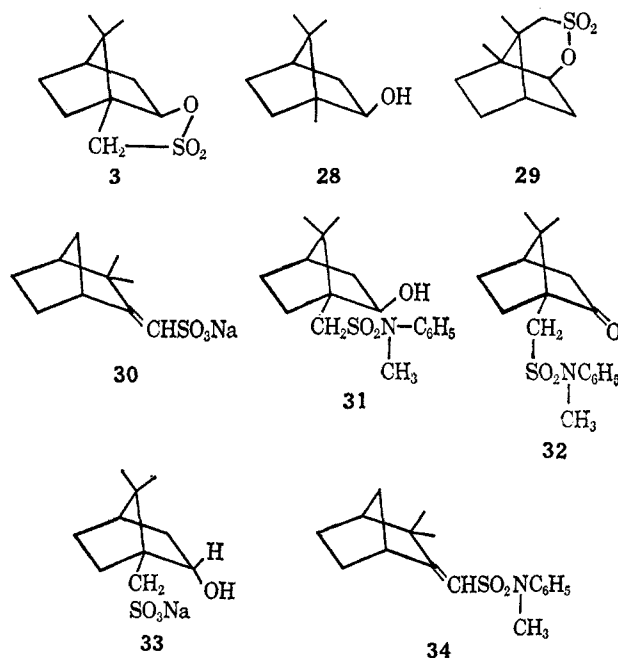
While standing in a desiccator for 4 months, one sample of 10-isobornyl sultone **3** was transformed completely to camphene sultone **4**. This remarkable transformation can be brought about by heating **3** at 145° for 5 min or at 200° for 90 sec. The rearrangement is quantitative and affords camphene sultone **4**, mp 133–135°, free of sultone **16**.

An investigation of the intermediates formed when camphene is treated with sulfuric acid was next undertaken. If the cold reaction mixture of camphene, sulfuric acid, and acetic anhydride is carefully neutralized with solid sodium carbonate and the solvents are removed, there is left a sticky, solid mass. Extraction with ether affords isobornyl acetate and 10-isobornyl sultone **3**. Extraction with chloroform affords a mixture of sodium acetate and the acetoxysulfonate **35**.

The structure of intermediate **35** was established as outlined in Scheme V. Treatment of the mixture of salts with phosphorus pentachloride gave a mixture of sulfonyl chlorides **36** and **37**. Reductive desulfurization of this mixture with excess lithium aluminum hydride yielded isoborneol (**28**) contaminated with camphene and established the fact that the sulfonate salt **35** has an *exo*-acetoxy group.

The sulfonyl chloride mixture was treated with N-methylaniline to give sulfonanilides **38** and **34** which were separated by preparative thin layer chromatography. One of these sulfonanilides was identical with the unsaturated sulfonanilide **34** described earlier. Acetoxy sulfonanilide **38** was hydrolyzed with sodium hydroxide and the resulting hydroxysulfonanilide **31** was oxidized to the known N-methyl-10-camphorsul-fonanilide **32**, thereby establishing the structure of the intermediate in the camphene sulfonation as sodium

(19) E. J. Corey, R. Hartmann, and P. A. Vatakencherry, *J. Am. Chem. Soc.*, **84**, 2611 (1962).
(20) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(21) A. V. Dombrovskii, *Ukr. Khim. Zh.*, **16**, 539 (1956).

SCHEME V
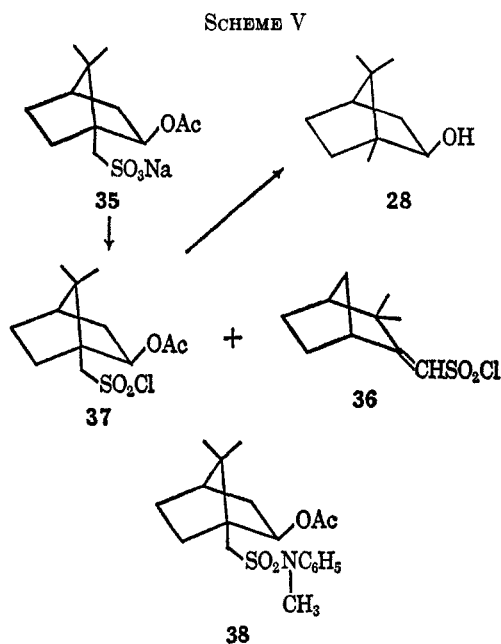
10-(2-*exo*-acetoxy)bornanesulfonate (35). Finally, 35 was converted into the camphene sultone mixture by treatment with base followed by treatment with hydrochloric acid.

Reasonable pathways for the formation of the camphene sultones are outlined in Scheme VI. The sequence 39 → 40 → 40' → 39' → is demanded by the formation of optically inactive camphene sultone from all optically active precursors tested to date. Whereas the route 41 → 42 → 43 → 44 → 4 is less direct than 39 → 44 → 4, it is preferred in view of the exclusive *exo* shifts[22] which have been found in analogous systems. In the absence of results with specifically labeled camphene or sulfonate 1, a rigorous choice between these alternatives cannot presently be made.

Experimental Section[23]

Camphene Sultones.—Concentrated sulfuric acid (75 g) was added slowly to an ice-cooled flask containing 250 g of distilled acetic anhydride. To the resulting cooled solution was added, with stirring, 100 g of camphene at such a rate that the temperature did not rise above 15°. The mixture was kept at 0° for 4 days and was then poured onto ice, diluted with water, and extracted several times with ether.

The combined ether extracts were washed with sodium bicarbonate solution and dried with magnesium sulfate. The ether was evaporated leaving a light brown solid. Recrystallization from methanol gave 2.5 g (1.5%) of colorless crystals, mp 117–119°. The infrared spectrum of sultone 3 displayed strong bands at 7.47, 8.50 (SO_2) and 11.52, 11.90, 12.30, and 13.55 μ. The nmr spectrum of 3 exhibited a doublet of doublets for the CHO proton at 4.40, a singlet CH_2SO_2 resonance at 3.25, and two singlet methyl resonances at 0.97 and 1.13 ppm. The solid did not absorb in the ultraviolet above 200 mμ. The mass spectrum

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of 3 did not show a parent ion, but had abundant ions at m/e 135, 109, 108 (base), 93, 91, 79, 67, and 41.

Anal. Calcd for $C_{10}H_{16}O_8S$: C, 55.52; H, 7.46; S, 14.83. Found: C, 55.58; H, 7.25; S, 14.63.

The aqueous, acidic solution was made alkaline with potassium hydroxide pellets. The alkaline solution was concentrated to near dryness on a steam bath. The resulting, crystalline mass was collected by filtration and was suspended in 200 ml of concentrated hydrochloric acid. The resulting solution was heated on a steam bath and allowed to evaporate slowly. After cooling, solid was removed by filtration and washed thoroughly with water to remove inorganic salts. The solid was recrystallized twice from methanol to give 20–60 g (12–36%) of camphene sultone, mp 133–134° (lit.[3-5] mp 133°). The infrared spectrum (Nujol mull) showed strong absorption at 7.48, 8.58, 11.18, 11.36, 11.75, and 12.03 μ.

Attempted Raney Nickel Desulfurization of the Camphene Sultone Mixture.—A mixture of 20–25 g of W-2 Raney nickel[24] and 3.4 g of the camphene sultone mixture (mp 133°) in 100 ml of absolute alcohol was stirred at room temperature and then at the reflux temperature of the solvent for 13 hr. The Raney nickel and solvent were removed and the solid residue was washed with cold acetone to remove a small amount of unaltered camphene sultone. Recrystallization of the insoluble portion from hot acetone gave a colorless solid, mp ca. 275°. This solid gave a positive test for nickel with dimethylglyoxime and afforded a benzylthiouronium derivative, mp 164–168°, indicating that the product was a nickel salt of a sulfonic acid (infrared peaks at 8.5 and 9.6 μ). This material was not further characterized.

Lithium Aluminum Hydride Reduction of the Camphene Sultone Mixture.—To a vigorously stirred suspension of 3.5 g (93.6 mmoles) of lithium aluminum hydride in anhydrous ether was added an ether solution of 5.0 g (23.4 mmoles) of the camphene sultone mixture. The mixture was stirred at room temperature for 24 hr and then quenched with aqueous sodium sulfate solution. The salts and solvent were removed to leave a cream-colored solid, which upon sublimation gave 0.56 g (16%) of a colorless solid. Vapor phase chromatography of the solid using a 150-ft poly UC oil LB 550X capillary column showed it was a 4:1 mixture of two components, the minor component showing the longer retention time. These two components were separated using a 15-ft quadrol column at 100°.

The major component showed mp 148–150° and characteristic hydroxyl absorption bands in the infrared. The nmr spectrum (CCl_4) exhibited three singlet methyl resonances at 0.87, 0.93, and 1.11 ppm. The properties of this alcohol were identical in all respects (infrared, nmr and vpc retention time) with an authentic sample of camphene hydrate 8 prepared from camphene hydrate hydrochloride.[25]

The minor component 9 (mp 172–173.5°) displayed infrared peaks at 2.86, 7.20, 7.31, and 9.60 μ. The nmr spectrum (CCl_4) showed a singlet at 3.27 (CHO), a singlet at 2.09 which was temperature dependent (OH), and three singlet methyl resonances at 0.84, 0.89, and 0.95 ppm. A mass spectrum exhibited a parent ion of 154 and abundant ions at m/e 93, 84, 81, 57, 55, 43, and 41 (100% relative abundance).

The aluminum salts resulting from the above hydride reduction were dissolved in 10% hydrochloric acid and the aqueous solution was extracted with ether. The ether was removed to give 3.2 g of light yellow solid, mp 135–143°. The infrared spectrum of the solid displayed hydroxyl absorption at 3.0 μ and the nmr spectrum seemed to indicate two singlet methyl signals at 1.04 and 1.23 and a widely spaced AB quartet centered at 3.07 which was attributed to the CH_2S protons. Desulfurization of this solid with nickel boride[10] gave the same 4:1 mixture of camphene hydrate and 3,3,4-trimethyl-2-*exo*-norbornanol described above.

Lithium Aluminum Deuteride Reduction of the Camphene Sultone Mixture.—To a stirred suspension of 0.5 g (12 mmoles) of lithium aluminum deuteride in anhydrous ether was added 0.5 g (2.3 mmoles) of the camphene sultone mixture. After stirring overnight, aqueous sodium sulfate solution was added and the insoluble salts were removed. The ether was evaporated and sublimation afforded 110 mg (31%) of a colorless solid, mp 147–149°, whose nmr spectrum showed the usual camphene hydrate signals except for reduction in intensity of the peak at 0.65 ppm.

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(22) J. A. Berson, R. G. Bergman, J. H. Hammons, A. W. McRowe, A. Remanic, and D. Houston, *J. Am. Chem. Soc.*, **87**, 3246 (1965); A. M. T. Finch and W. R. Vaughan, *ibid.*, **87**, 5520 (1965).

(23) All boiling and melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer, Model 137-B. Nmr spectra were determined at 60 Mc on a Varian Associates A-60 spectrometer by the Purdue University Spectral Service Department. Chemical shifts are recorded in parts per million (ppm) with reference to tetramethylsilane as an internal standard. Mass spectra were recorded on Hitachi RMU-6A and RMU-6D (resolution of 4000) instruments using a heated inlet system, ionization energy of 75 ev, inlet temperature of about 185°, and a source temperature of about 160°. Microanalyses were performed by Dr. C. S. Yeh and associates.

(24) R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 181.

(25) We wish to express our appreciation to Mr. James Kawakami for a sample of camphene hydrate.

SCHEME VI
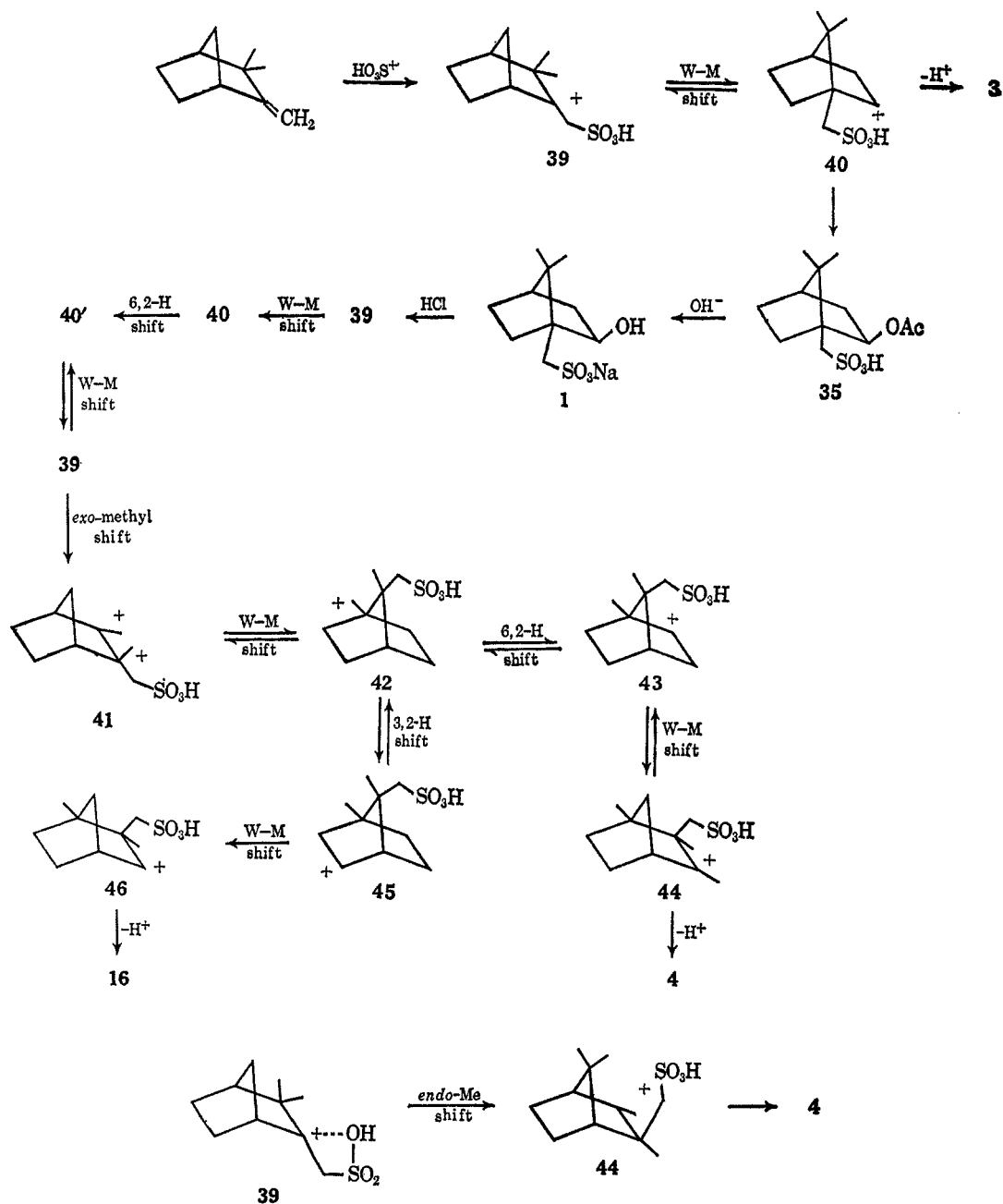
4-Methylcamphenilone (10).   **A.**   **Oxidation of 3,3,4-Trimethyl-2-*exo*-norbornanol (9).**—A solution of 16 mg (0.1 mmole) of 9, obtained from the hydride reduction of the camphene sultone mixture, in 1 ml of ether was stirred for 6 hr with 1 ml (1 mmole) of chromic acid solution.[26] The ether was separated and washed with aqueous sodium bicarbonate solution and water, dried with magnesium sulfate, and evaporated to yield 10 mg of colorless solid. Purification by vpc gave a solid whose retention time and infrared spectrum (carbonyl absorption at 5.75 μ) were identical with those of authentic 4-methylcamphenilone (10).

B. From Fenchone. 1,2,3,3-Tetramethyl-2-*endo*-norbornanol (11).—To an ethereal solution of methylmagnesium iodide, prepared from 225 g (1.7 moles) of methyl iodide and 47 g (1.95 g-atoms) of magnesium, was added 200 g (1.3 moles) of fenchone in ether. The mixture was refluxed for 2.5 hr and 150 ml of a saturated solution of ammonium chloride was slowly added. The insoluble salts were separated by filtration and washed several times with ether. The ether was removed leaving *ca.* 200 g of orange liquid whose infrared spectrum indicated the presence of fenchone (5.73 μ) and the desired alcohol (2.80 μ). This mixture was used directly in the next step.

Dehydration of 1,2,3,3-Tetramethyl-2-*endo*-norbornanol (11).—The alcohol–ketone mixture obtained above was heated at 160° for 4 hr with 400 g of potassium bisulfate.[12] The mixture was poured onto ice and extracted with ether. The ether extracts were washed with aqueous sodium bicarbonate solution and dried, and the ether was removed. The residue was distilled through a Todd fractionating column to give 64 g of colorless liquid, bp 164–166°, whose infrared spectrum showed strong terminal olefin absorption at 6.04 and 11.43 μ and a weak carbonyl peak at 5.73 μ. Higher boiling fractions showed increasing amounts of ketone and were not employed in subsequent reactions.

Analysis of the olefin by vpc using a 15-ft Carbowax column at 100° showed four peaks. These peaks were collected and infrared spectroscopy demonstrated that the two fastest eluting peaks were tricyclenes (CH stretching vibration at 3.30 μ[27] and absence of vinyl methyl and olefinic proton resonances in their nmr spectra) while the two with longest retention times were terminal olefins. A solution of 1.0 g of this mixture in 15 ml of methanol

(26) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

(27) H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959); E. J. Corey, S. W. Chow, and R. A. Scherrer, *J. Am. Chem. Soc.*, **79**, 5773 (1957); J. D. Roberts, E. R. Trumbull, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950).

was treated at −50° with a stream of 3% ozone until the solution turned blue. The excess ozone was removed by flushing with oxygen and the solution was added to 8 ml of methanol, 3 ml of acetic acid, and 4 g of potassium iodide at −20°.[28] After standing at −20°, the solution was treated with aqueous sodium thiosulfate and extracted with ether. The ether was removed and the residual solid displayed five peaks on vpc analysis using a Carbowax column at 100°. The peaks were collected and identified on the basis of their retention times and infrared spectra. The first two peaks were tricyclenes, the last three were fenchone, 4-methylcamphenilone 10 and camphor. The original dehydration product is a mixture of two isomeric methyltricyclenes, 2-methylene-1,3,3-trimethylnorbornane (12), 2-methylene-1,7,7-trimethylnorbornane, and β-methylcamphene (14).

4-Methylisobornyl Acetate.—A mixture of 64 g of the tricyclene–olefin mixture obtained above, 160 ml of glacial acetic acid, and 6 ml of sulfuric acid was heated at 60° for 12 hr. The solution was poured into 1.5 l. of water and extracted with ether. The ether extracts were washed with aqueous sodium bicarbonate solution, dried, and distilled to give 50 g of a colorless liquid, bp 126–128° (28 mm), which displayed strong acetate absorption at 5.77 and 8.06 μ.

4-Methylisoborneol (13).—A mixture of 48 g (0.23 mole) of 4-methylisobornyl acetate, 56 g (1.0 mole) of potassium hydroxide, 100 ml of water, and 100 ml of methanol was stirred and refluxed for 16 hr.[12] The solution was cooled and ether and 600 ml of water were added. The ether phase was separated, washed with water, dried, and evaporated to leave 38 g of 4-methylisoborneol which showed a strong peak at 2.95 μ (OH) and was void of carbonyl and olefinic absorption. A sublimed sample (mp 183–185°) proved to be 95% pure by vpc using a 15-Carbowax column at 150° (lit.[12] mp 183–184°). The nmr spectrum (CCl₄) showed a one-proton multiplet at 3.53 and four singlet methyl resonances at 0.89 ppm. The mass spectrum exhibited a parent ion of m/e 168 and a very intense ion at m/e 109 which suggests the four methyl groups are at C-1, -4, and -7.[7]

Dehydration of 18 g of 4-methylisoborneol by heating with 44 g of potassium bisulfate at 160° for 3 hr afforded 15.3 g (93%) of crude hydrocarbon. Recrystallization from methanol gave a colorless solid, mp 54–60°. Vapor phase chromatographic analysis of this solid showed four peaks in a ratio of 15:20:25:40 which were identical with the tricyclenes and terminal olefins obtained by dehydration of 1,2,3,3-tetramethyl-2-endo-norbornanol. Ozonolysis of this mixture employing the procedure described above gave a mixture containing two isomeric tricyclenes, fenchone, 4-methylcamphenilone, and camphor.

β-Methylcamphene (14).—Following a modified procedure of Corey,[19] 5.5 g (33 mmoles) of 4-methylisoborneol was dissolved in 8 ml (100 mmoles) of pyridine and 3 ml (42 mmoles) of thionyl chloride was added slowly with stirring. The resulting mixture was stirred for 3 hr and water and ether were added. The ether layer was separated and washed successively with 5% hydrochloric acid, sodium bicarbonate solution, and water. After drying, the ether was carefully removed. Sublimation of the residue at 90° (30 mm) gave 1.75 g (36%) of a colorless solid (mp 102.5–104°) whose infrared spectrum showed strong terminal methylene absorption at 6.04 and 11.40 μ (lit.[12] mp 100–101°). Vapor phase chromatographic analysis using a Carbowax column demonstrated the presence of ca. 10% of several olefinic impurities. Continued sublimation at a lower pressure gave 0.64 g of solid whose infrared spectrum indicated the presence of a mixture of olefin and starting alcohol.

4-Methylcamphenilone (10) from β-Methylcamphene (14).—A suspension of 1.70 g of β-methylcamphene in 15 ml of methanol was treated at −50° with ozone for 1 hr. The cold mixture was transferred to a solution of 7 g of sodium iodide in 15 ml of methanol and 4 ml of glacial acetic acid at −20°. After standing at −20° for 90 min, the dark solution was treated with aqueous sodium thiosulfate to destroy the iodine which had formed. The mixture was extracted with ether. The ether was removed and the residue was sublimed to afford 1.0 g (60%) of a colorless solid (mp 139–141°) whose infrared spectrum showed a strong carbonyl band at 5.78 μ (lit.[13] mp 135–137°). The nmr spectrum of 10 displayed a broadened, one-proton doublet centered at 2.45 which was assigned to the bridgehead proton at C-1, a singlet methyl resonance at 1.10, and a sharp singlet at 0.90 ppm, which accounted for two methyl groups. Analysis by vpc using a sili-

cone column at 180° showed the presence of fenchone and camphor as minor impurities.

3,3,4-Trimethyl-3-endo-norbornanol (15).—To a stirred suspension of 0.50 g (13.2 mmoles) of lithium aluminum hydride in anhydrous ether was added 0.50 g (3.3 mmoles) of 4-methylcamphenilone in ether. After heating for 1 hr, water was carefully added, and the salts were removed by filtration. The ether was removed and the residue was sublimed to give 0.36 g (72%) of a colorless solid, mp 163–167.5°, whose nmr spectrum exhibited a doublet at 3.57 for the CHOH proton, a singlet at 2.27 for the OH proton, and three singlets below 1.0 ppm for the three methyl groups. The mass spectrum showed a parent ion at m/e 154 and abundant ion at m/e 93, 84, 83, 81, 57, 55, 43, and 41 (base).

Vapor phase chromatography of this solid using a 150-ft capillary quadrol column showed a small shoulder on the main peak, in addition to minor amounts of borneol, isoborneol, and the fenchyl alcohols. Enriching the product with a small amount of 4-methylcamphenolol obtained from the hydride reduction of the camphene sultone mixture increased the intensity of the shoulder.

Hydrolysis of the Camphene Sultone Mixture.—A mixture of 20 g (93 mmoles) of the camphene sultone mixture and 3.7 g (93 mmoles) of sodium hydroxide in 40 ml of water was heated on a steam bath and allowed to slowly concentrate for 1 day. On cooling there was obtained 24.5 g (100%) of a colorless solid whose infrared spectrum displayed bands at 2.9 (OH), 6.02 and 11.04 (C=CH₂), and 8.0–9.9 μ (SO₃Na). The nmr spectrum (D₂O) showed peaks at 4.90 and 4.68 which flanked the water signal at ca. 4.7 ppm.

Camphene Sultone Mixture and N-Lithiopiperidine.—The camphene sultone mixture was recovered from treatment with sodium amide in liquid ammonia, sodium in dioxane, or N-lithio-N-methylaniline, and with tritylsodium in ether it was converted into a colorless, ether- and dioxane-insoluble solid which showed hydroxyl absorption and characteristic sulfonate peaks at 8.0–9.0 and 9.5 μ in the infrared.

To a solution of phenyllithium, prepared from 5.5 g of bromobenzene and 0.5 g of lithium, was added 3.0 g of piperidine and after 10 min, 3.0 g of camphene sultone in ether was also added. After heating for 36 hr, water was added and the ether layer was separated. The ether was removed and the partially crystalline residue was chromatographed on alumina. Elution with pentane and sublimation gave 1.2 g of sulfonamide: mp 87–88°; λₘₐₓ 2.83, 7.59, and 8.78 μ; nmr signals at 1.17, 1.23 (2-CH₃C), 1.63, 1.95 (CH₂, CH), an AB-type quartet centered at 3.00 (CH₂SO₂), 3.13 (CH₂N), and 3.23 (OH) ppm.

Anal. Calcd for C₁₅H₂₇NO₃S: C, 59.76; H, 9.03. Found: C, 60.04; H, 9.17.

9-(Phenylsulfonyl)camphene (21).—To an ether solution of phenyllithium, prepared from 2.1 g of lithium and 15.7 g (0.1 mole) of bromobenzene, was added an ether solution of 7.0 g (0.033 mole) of camphene sultone. The mixture was stirred at room temperature for 11 hr and then was poured into water. The ether layer was separated and the aqueous phase was extracted with ether. The combined ether solutions were washed with water and dried, and the ether was removed to give 9.2 g of a yellow oil, which showed infrared peaks at 2.70 (OH), 7.60, 8.70 (SO₂), and 6.25, 6.70, and 12.7 μ (aromatic). About 8 g of the oil was evaporatively distilled in vacuo using a bath temperature of 200°. A portion (3.0 g) of the resulting 6.8 g of distillate was chromatographed on 100 g of alumina. Elution with hexane gave 2.0 g of solid after recrystallization from hexane: mp 97.5–99°; λₘₐₓ 6.05, 11.0 (C=CH₂) 7.70, 8.70 (SO₂), 6.33, 12.7–14.5 μ (aromatic). The nmr spectrum (CDCl₃) showed five aromatic protons, two sharp singlet olefinic protons at 4.83 and 4.55, a complicated pattern between 2.4 and 3.4 accounting for four protons, and a singlet methyl group at 1.41 ppm.

Anal. Calcd for C₁₆H₂₀O₂S: C, 69.52; H, 7.29; S, 11.60. Found: C, 69.30; H, 7.20; S, 11.41.

Elution with 75% chloroform–benzene gave 0.5 g of an oil and then 0.3 g of solid. The oil crystallized from benzene–hexane to yield colorless crystals of 19 (mp 85–86°) showing hydroxyl, sulfone, and aromatic peaks in its infrared spectrum. The nmr spectrum (CDCl₃) displayed five aromatic protons, two singlet methyl groups at 1.33 and 1.39, a hydroxyl proton at 3.60, and CH₂SO₂ protons, comprising an AB pattern, at 3.01 and 3.89 (J = 13.8 cps).

Anal. Calcd for C₁₆H₂₂O₃S: C, 65.27; H, 7.53. Found: C, 65.21; H, 7.75.

(28) P. S. Bailey, *Chem. Ber.*, **88**, 795 (1955).

The third compound obtained by chromatography was recrystallized from benzene–hexane to give **20** as colorless crystals (mp 150–152°) whose infrared spectrum showed hydroxyl, sulfone, and aromatic peaks. The nmr spectrum (CDCl₃) indicated the presence of five aromatic protons, two singlet methyl groups at 0.84 and 1.18, a CHOH group with multiplets at 2.51 and 3.59, and a CH₂SO₂ group displaying an AB-type pattern at 2.81 and 4.28 (J = 13.8 cps).

Anal. Calcd for C₁₆H₂₂O₃S: C, 65.27; H, 7.53; S, 10.89. Found: C, 65.11; H, 7.61; S, 10.74.

In another experiment involving the reaction of phenyllithium with camphene sultone, the crude product was treated with thionyl chloride in pyridine. After stirring for 12 hr at room temperature, the mixture was added to aqueous sodium bicarbonate solution. The aqueous solution was extracted with ether, which in turn, was washed with water, dried, and evaporated. The resulting oil was recrystallized several times from hexane to give colorless crystals, mp 96.5–98.5°, whose melting point was not depressed on admixture with a sample of 9-(phenylsulfonyl)-camphene (**21**) obtained as described above.

9-(Phenylsulfonyl)camphenilone (22).—A solution of 620 mg of 9-(phenylsulfonyl)camphene (**21**) in 5 ml of methanol was treated at −50° with a stream of 3% ozone until the solution turned blue (20 min). The excess ozone was flushed with oxygen and the solution was added to a −20° cooled mixture of 7 ml of methanol, 2 ml of acetic acid, and 3 g of potassium iodide. After standing at −20° for 5 hr, the solution was treated with aqueous sodium thiosulfate solution until the iodine color disappeared. The mixture was extracted with ether. The ether solution was dried and the ether was removed leaving 720 mg of oil which crystallized on standing. Recrystallization from benzene–hexane gave colorless crystals: mp 102–102.5°; λmax 5.73, 6.60, 8.73, 6.32, and 12.8–14.7 μ. The nmr spectrum (CDCl₃) showed a singlet for the CH₂SO₂ protons at 3.10, the C-1 proton as a multiplet at 3.27, and five aromatic protons.

Anal. Calcd for C₁₅H₁₈O₃S: C, 64.72; H, 6.52. Found: C, 64.86; H, 6.25.

Desulfurization of 9-(Phenylsulfonyl)camphenilone (22).—A mixture of 223 mg (0.78 mmole) of 9-(phenylsulfonyl)camphenilone (**22**), 1.5 g of Raney nickel, and 30 ml of absolute ethanol was refluxed for 18 hr. After cooling, the catalyst was removed and the filtrate was diluted with water. The aqueous solution was extracted with ether. The ether extracts were washed with water and dried, and the ether was removed to leave a light yellow oil showing hydroxyl and carbonyl bands at 2.85 and 5.73 μ.

The oil was dissolved in acetone and was treated with 8 N CrO₃ in sulfuric acid–water until the solution remained orange. Isopropyl alcohol was added to destroy the excess oxidant and the salts were removed by filtration. The filtrate was diluted with water and extracted with ether. The ether was washed with water and dried and the ether was removed. Vapor phase chromatography on a silicone column gave one peak with the same retention time as camphenilone. This peak was collected and showed an infrared spectrum identical with that of camphenilone. The 2,4-dinitrophenylhydrazone derivative of the collected ketone showed mp 160–161° and the melting point was undepressed on admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of camphenilone.

9-Ethyl-9-(phenylsulfonyl)camphene (24).—To a solution of a few crystals of Fe(NO₃)₃·9H₂O in 100 ml of liquid ammonia was added 180 mg (8.0 mg-atoms) of sodium. The mixture was stirred for 30 min and 630 mg (2.3 mmoles) of 9-(phenylsulfonyl)-camphene (**21**) in dry ether was added. After stirring for 30 min, 390 mg (2.5 mmoles) of ethyl iodide was added. The ammonia was allowed to evaporate and ether and water were added. The ether layer was separated and the aqueous phase was extracted with ether. The combined ether phases were washed with 2% hydrochloric acid and water and dried, and the ether was removed to give 645 mg of colorless oil. Recrystallization from hexane gave 150 mg of 9-(phenylsulfonyl)camphene (**21**) as shown by a mixture melting point determination and infrared comparison. The hexane was removed from the mother liquor and the residue was recrystallized from methanol to give a solid. Two more recrystallizations from methanol gave 120 mg of colorless solid: mp 80.5–82°; λmax 6.07, 11.10 (C═CH₂), 7.70, 8.70 (SO₂) and 6.30, and 12.8–15.0 μ (aromatic). The nmr spectrum of this solid exhibited five aromatic protons, two singlet olefinic protons at 4.88 and 4.68, an allylic proton as a multiplet at 3.30, a one-proton multiplet at 2.66, a one-proton triplet signal for CHSO₂ at 2.80, a singlet methyl at 1.40, and a triplet methyl

at 0.47 ppm. Molecular models show that the methyl group of the 9-ethyl substituent is situated over the phenyl ring and, thus, explains why its nmr resonance is shifted upfield.

Anal. Calcd for C₁₈H₂₄O₂S: C, 71.03; H, 7.95. Found: C, 70.97; H, 8.04.

Similar results were observed when tritylsodium was used as a base.

9-Ethyl-9-(phenylsulfonyl)camphenilone (25).—A solution of 475 mg of 9-ethyl-9-(phenylsulfonyl)camphene (**24**) in methanol was ozonized at −50° according to the procedure described earlier to afford 530 mg of a colorless oil. Recrystallization from hexane–benzene gave colorless crystals (mp 86–87°) whose infrared spectrum displayed absorption at 5.80 (C═O), 7.72, 8.72 (SO₂), and 6.35, 12.8–15.0 μ (aromatic). An nmr spectrum (CDCl₃) showed five aromatic protons, the C-1 proton as a multiplet at 3.54, a one-proton triplet for the CHSO₂ group at 3.00, another one-proton multiplet at 2.59, a singlet methyl resonance at 1.35, a triplet methyl at 0.43, and nine other protons in the range between 1.15 and 2.50 ppm.

Anal. Calcd for C₁₇H₂₂O₃S: C, 66.63; H, 7.24; S, 10.46. Found: C, 66.62; H, 7.02; S, 10.37.

Desulfurization of 9-Ethyl-9 (phenylsulfonyl)camphenilone (25). —A mixture of 270 mg (0.9 mmole) of 9-ethyl-9(phenylsulfonyl)-camphenilone (**25**), 2 g of Raney nickel, and 30 ml of absolute ethanol was stirred and refluxed for 17 hr. The catalyst was removed by filtration and the filtrate was diluted with water and extracted with ether. The ether extracts were washed with water and dried and the ether was evaporated leaving 150 mg of light yellow liquid, whose infrared spectrum displayed strong carbonyl absorption and relatively weak hydroxyl and sulfonyl peaks. The liquid was analyzed by vpc using an apiezon column at 150° and showed four peaks in a ratio of 8:2:80:10. The major product was collected by preparative vpc and exhibited infrared, nmr, and mass spectra identical with the spectra of authentic 3-*endo*-methyl-3-*exo*-propyl-2-norbornanone (**26**). Insufficient amounts of the minor products were obtained and they were not characterized.

A mixture of the desulfurization product and authentic 3-*endo*-methyl-3-*exo*-propyl-2-norbornanone **26** showed a single peak with retention time of 15 min using a 150-ft capillary poly(propylene glycol) UC oil LB 550-X column, a nitrogen pressure of 30 mm, and a temperature program of 100° (2 min)–140° (10°/min). A mixture of the desulfurization product and authentic 3-*exo*-methyl-3-*endo*-propyl-2-norbornanone (**27**) gave two sharp peaks with retention times of 15.0 and 15.7 min.

3-*exo*-Methyl-2-norbornanone.—A solution of tritylsodium, prepared from triphenylchloromethane[29] according to the procedure described by Renfrow and Hauser,[30] was added rapidly to a vigorously stirred solution of 8.0 g (7.3 mmoles) of norcamphor in 45 ml of anhydrous dioxane until the red color persisted. Methyl iodide (65 g, 0.45 mole) was added in one batch and the mixture was stirred for 18 hr at room temperature. Most of the ether was removed by distillation and water was added. The organic layer was separated, washed with water, dried, and distilled to give 8.5 g (85%) of 3-*exo*-methyl-2-norbornanone: bp 67–72° (13 mm), 5.73 μ [lit.[19] bp 67° (14 mm)]. The nmr spectrum (CCl₄) displayed a doublet methyl resonance at 0.98, seven protons between 1.15 and 2.15, and two protons α to the carbonyl group as multiplets at 2.27 and 2.40 ppm.

3-*exo*-Propyl-2-norbornanone.—To a vigorously stirred solution of 6.5 g (5.9 mmoles) of norcamphor in 50 ml of anhydrous ethyl ether was added an ether solution of tritylsodium until the red color persisted. Propyl iodide (71 g, 0.5 mole) was added and the mixture was stirred for 18 hr at room temperature. The reaction was worked up in the usual fashion to give 5.2 g (60%) of 3-*exo*-propyl-2-norbornanone, bp 55–70° (2–5 mm). The product showed a single peak on vpc analysis and a strong carbonyl band at 5.73 μ in the infrared. The mass spectrum had a parent ion of m/e 152 and abundant ions at m/e 110, 82, 67, 55, and 41.

3-*endo*-Methyl-3-*exo*-propyl-2-norbornanone (26).—To a stirred solution of 4.3 g (0.0347 mole) or 3-*exo*-methyl-2-norbornanone in 30 ml of anhydrous ether was added an ether solution of trityl-sodium until the red color persisted. Propyl iodide (40 g, 0.24 mole) was added at once and the mixture was stirred at room temperature for 18 hr. Work-up of the reaction mixture in the usual manner gave 1.8 g of 3-methyl-2-norbornanone, bp 58–80° (4 mm), and 1.5 g (26%) of 3-*endo*-methyl-3-*exo*-propyl-

(29) W. E. Bachman, *Org. Syn.*, **23**, 100 (1943).

(30) W. B. Renfrow and C. R. Hauser, *ibid.*, **19**, 100 (1939).

2-norbornanone (26), bp 80–84° (4 mm), 5.73 μ. The purity of this ketone was checked by vpc and was determined to be about 98%. The mass spectrum showed a parent ion at m/e 166 and abundant ions at m/e 124, 97, 67, 55 (base), and 41. The nmr spectrum (CCl₄) displayed a two-proton multiplet at 2.38, a singlet methyl resonance superimposed upon a methylene resonance at 0.92, and what appears to be the propyl methyl group at 1.28 ppm.

Anal. Calcd for C₁₁H₁₈O: C, 79.47; H, 10.91. Found: C, 79.20; H, 11.14.

3-*exo*-Methyl-3-*endo*-propyl-2-norbornanone (27).—To a stirred solution of 4.3 g (28.5 mmoles) of 3-*exo*-propyl-2-norbornanone in 30 ml of anhydrous dioxane was added an ether solution of tritylsodium until the red color remained. Methyl iodide (50 g, 0.35 mole) was added and the mixture was stirred at room temperature for 30 hr. Addition of water, ether extraction, and distillation of the ether extracts afforded 3.6 g of liquid [bp 74–84°· (3 mm)] which was shown to be a 50:50 mixture of 3-propyl-2-norbornanone and 3-*exo*-methyl-2-*endo*-propyl-2-norbornanone (27) by vpc analysis. The latter compound was collected by preparative vpc and showed strong carbonyl absorption at 5.73 μ. A mass spectrum had a parent ion at m/e 166 and abundant ions at m/e 124, 97, 67, 55 (base), and 41. The nmr spectrum (CCl₄) showed a one-proton multiplet at 2.42 and another at 2.25, a singlet methyl group superimposed over a methylene group at 0.86 and the methyl of the propyl group at 1.29 ppm.

Lithium Aluminum Hydride Reduction of 10-Isobornyl Sultone (3).—To a stirred suspension of 220 mg (5.8 mmoles) of lithium aluminum hydride in anhydrous ether was added an ether solution of 227 mg (1.0 mmole) of 10-isobornyl sultone. The mixture was heated to reflux for 3 hr and kept at room temperature overnight. After cooling to 0°, 1 ml of saturated sodium sulfate solution was added and the insoluble salts were removed by filtration. The ether filtrate was dried and the ether was removed to leave an oil which afforded 20 mg of colorless solid on sublimation. Vapor phase chromatographic analysis using a 150-ft poly UC oil LB 550-X capillary column indicated the presence of a minor component (12%) with a retention time of 30 min compared with the 39-min retention time for the major component. The retention times for isoborneol, borneol, epiborneol, and epiisoborneol[31] were 39.1, 44.7, 46.6, and 50.3 min, respectively. The infrared spectrum of the major component, collected by preparative vpc, was identical with the infrared spectrum of isoborneol.

The aluminum salts isolated from the hydride reduction were dissolved in 10% hydrochloric acid and extracted with ether. Analysis of the solid obtained after evaporation of the ether indicated the presence of at least six different compounds, which were not further investigated.

Hydrolysis of 10-Isobornyl Sultone (3).—An aqueous solution of 2.2 g (10 mmoles) of 10-isobornyl sultone (3) and 0.4 g (10 mmoles) of sodium hydroxide was stirred with slight warming for 18 hr. The water was evaporated and the residue was dried at 105° to give 1.9 g of solid. The infrared spectrum (Nujol mull) showed the presence of hydroxyl absorption at 2.85 and a carbon–carbon double bond at 6.15 μ. From the relative integrated areas of the CHSO₃Na proton (5.94 ppm) and methyl protons, in the nmr spectrum (D₂O) of the salt, it was established that it was primarily composed of the unsaturated sulfonate salt **30** contaminated with some hydroxy sulfonate salt **1**.

N-Methyl-10-(2-*exo*-hydroxy)bornanesulfonanilide (31).—To a solution of N-methylaniline in 50 ml of dry ether was added 6.0 ml of a 1.5 N solution of butyllithium in hexane. After stirring for 20 min, 1.0 g (4.6 mmoles) of 10-isobornyl sultone **3** in ether was added. The mixture was stirred at room temperature for 30 min, water was added, and the ether layer was separated and washed with dilute acid and water. The ether was removed leaving 1.9 g of light yellow oil which soon solidified. Recrystallization from hexane gave 1.1 g (75%) of cream-colored solid, mp 104–104.5°. The melting point was not depressed on admixture with a sample of N-methyl-10-(2-*exo*-hydroxy)bornanesulfonanilide (31) obtained by hydrolysis of the acetate derivative **38**. The infrared and nmr spectra of these two samples were also identical.

N-Methyl-10-camphorsulfonanilide (32). A. From 31.—To a solution of 97 mg (0.3 mmole) of N-methyl-10-(2-*exo*-hydroxy)bornanesulfonanilide (31) in 5 ml of acetone was added 0.15 ml of 8 N CrO₃ in sulfuric acid–water. The excess oxidant was

destroyed with isopropyl alcohol. The solution was decanted from the chromium salts, diluted with water, and extracted with methylene chloride. The methylene chloride extracts were washed with sodium bicarbonate solution and water, dried, and evaporated to give 92 mg (95%) of an oily solid. Recrystallization from absolute ethanol gave colorless crystals which showed mp 85–86°; λmax 5.72, 6.25, 6.70, 7.43, 8.74, 13.00, and 14.45 μ. The nmr spectrum exhibited five aromatic protons at 7.39, a widely spaced, AB-type quartet for the CH₂SO₂ group centered at 3.18, and three singlet methyl groups at 0.83, 1.09, and 3.37 ppm. The melting point of this derivative was not depressed when mixed with a sample of N-methyl-10-camphorsulfonanilide (32) prepared from camphorsulfonyl chloride as described below.

Anal. Calcd for C₁₇H₂₃O₃S: C, 63.55; H, 7.17; N, 4.36. Found: C, 64.04; H, 7.29; N, 4.39.

B. From 10-Camphorsulfonyl Chloride.—A solution of 1.0 g (4.0 mmoles) of 10-camphorsulfonyl chloride[32] in 2 ml of pyridine was added to a solution of 1.0 g (9.3 mmoles) of N-methylaniline in 1 ml of pyridine. The reaction mixture was worked up in the usual manner to give a light yellow oil which crystallized on standing. Two recrystallizations from absolute ethanol gave crystals, mp 84.5–86°.

Sodium–Ethanol Reduction of 10-Camphorsulfonic Acid.—To a stirred solution of 30 g of 10-camphorsulfonic acid (2) in 600 ml of freshly dried and distilled absolute ethanol was added, in small pieces, 60 g of sodium. A precipitate formed, but dissolved again with heating. The solvent was removed under diminished pressure leaving a solid which was neutralized to pH 9 with 20% aqueous hydrochloric acid and then to pH 7 with carbon dioxide. Water was removed by vacuum distillation and the residue was dried at 110°. The brown solid was placed in a Soxhlet extractor and extracted for 2 days with two separate portions of absolute ethanol. At the end of this period the Soxhlet thimble contained only sodium chloride. The ethanol extract was evaporated to dryness affording a solid which gave a negative silver nitrate test. Recrystallization from dilute sodium hydroxide solution gave a first crop of 6.0 g, a second crop of 7.0 g, and a residue of 14.0 g. The infrared spectrum of the crystalline salt showed strong hydroxyl and sulfonate absorption. The nmr spectrum (D₂O) indicated the presence of three singlet methyl groups and two different CH₂SO₂ groups. On the basis of the integrated ratios of these two CH₂SO₂ signals it was determined that a 2:3 mixture of sodium 10-(2-*endo*-hydroxy)- and 10-(2-*exo*-hydroxy)-bornanesulfonates was present. The *endo* isomer **33** had a singlet CH₂SO₃ resonance and a singlet at 0.92 ppm for its two methyl groups. The more abundant *exo* isomer **1** showed a widely spaced AB-type quartet for the CH₂SO₃-type protons and singlets at 0.88 and 1.02 ppm for its two methyl groups.

Acetylation of Sodium Sulfonates 1 and 33.—A mixture of 290 mg of the reduction product from 10-camphorsulfonic acid, 8 ml of pyridine, and 8 ml of acetic anhydride was stirred at room temperature for 20 hr. The excess volatile reagents were removed under diminished pressure and the solid residue was washed thoroughly with ether. A solid settled out of the ether solution. The infrared spectra of the two solids showed acetoxy absorption at 5.8 and 7.9, in addition to sulfonate peaks at 8.3 and 9.4 μ. The nmr spectra of the two solids were different, but showed that each had some of the other component in it. The ether insoluble solid was tentatively assigned as sodium 10-(2-*endo*-acetoxy)bornanesulfonate and showed a multiplet of doublets at 5.20 for the CHO proton, a singlet at 2.98 for the CH₂SO₃ protons, a singlet acetoxy methyl resonance at 2.09, and a singlet at 0.94 for the *gem*-dimethyl groups. The nmr spectrum of the ether-soluble solid, assigned as the corresponding *exo* isomer **35**, displayed a one-proton multiplet at 4.85, a widely spaced AB quartet centered at 3.03 for the CH₂SO₃ protons, a singlet acetoxy methyl at 2.06, and two singlet methyl groups at 0.87 and 0.98 ppm.

10-Isobornyl Sultone from the 10-Borneol Sulfonate Mixture 1 and 33.—To a stirred suspension of 2.0 g (7.8 mmoles) of a mixture of sodium sulfonates 1 and 33 in 10 ml of pyridine was added, over a 10-min period, 1.5 g (8.0 mmoles) of *p*-toluenesulfonyl chloride. Heat was liberated and the salts gradually dissolved. The solution was kept at room temperature overnight, water was added, and the mixture was extracted with ether. The ether was removed and the residue was crystallized from methanol to give 200 mg of 10-isobornyl sultone (3), mp 115–117° whose infrared spectrum was identical with that of 10-isobornyl sultone isolated

(31) We wish to thank Mr. James Kawakami and Dr. H. C. Brown for supplying authentic samples of the epiborneols.

(32) M. A. Reychler, *Bull. Soc. Chim. France*, **19**, 120 (1898).

directly from the sulfonation of camphene with sulfuric acid or by sulfonation with the dioxane–sulfur trioxide complex as described below.

Sulfonation of Camphene with the Dioxane–Sulfur Trioxide Complex.—To a cooled solution of 29.0 g (0.36 mole) of sulfur trioxide in 80 ml of trichloroethylene was added slowly 31.2 g (0.36 mole) of anhydrous dioxane. The SO_3–dioxane complex promptly precipitated. To this stirred suspension was added slowly a solution of 45.0 g (0.33 mole) of camphene in trichloroethylene. The mixture was allowed to warm to room temperature and was kept for 4 hr and then poured slowly into aqueous sodium bicarbonate solution. The organic layer was separated and the aqueous phase was extracted with methylene chloride. The combined organic phases were concentrated under diminished pressure to afford a viscous, brown oil. The residue was dissolved in ether and 250 mg of an intractable, white solid was removed. The ether was removed and the residue was crystallized from methanol to yield 15.0 g (21%) of 10-isobornyl sultone, mp 116–118°.

Evaporation of the aqueous phase obtained above left 35 g of light brown solid whose infrared spectrum showed sulfonate peaks at 8.5 and 9.5 μ and whose nmr spectrum featured a singlet olefinic proton at 5.96 ppm. A 15-g portion of the dried solid was mixed with 15 g of phosphorus pentachloride at 0° and after standing for 1 hr the mixture was added to sodium bicarbonate solution and extracted with ether. The ether solution was dried and concentrated to give 9.1 g of a dark odoriferous liquid whose infrared spectrum showed strong bands at 7.30, 8.57 (SO_2), and 6.19 μ (C=C).

The crude sulfonyl chloride was dissolved in pyridine and added to a solution of 4.4 g of N-methylaniline in pyridine. After standing for 2 hr, the mixture was poured into dilute acid and extracted with ether. The dried ether solution was evaporated to leave 6.0 g of brown solid. Two recrystallizations from methanol gave the pure, unsaturated sulfonanilide **34**: mp 121–123°, λ_{max} 6.16, 6.31, 6.72, 7.45, 8.76, and 12.31 μ. The nmr spectrum of **34** showed five aromatic protons at 7.38, a singlet olefinic proton at 5.77, a multiplet for an allylic proton at 3.45, a singlet methyl at 3.27, and a singlet at 1.03 ppm accounting for six protons.

Anal. Calcd for $C_{17}H_{23}NO_2S$: C, 66.84; H, 7.59; S, 10.50. Found: C, 67.06; H, 7.63; S, 10.21.

Sulfonation of optically active camphene, $[\alpha]^{26}D + 39.2°$ ($CHCl_3$), with dioxane–sulfur trioxide, using the same conditions described above, gave optically inactive 10-isobornyl sultone (**3**).

Thermal Rearrangement of 10-Isobornyl Sultone (3).—10-Isobornyl sultone (**31**, 1.0 g, mp 117–119°) was heated at 145° for 5 min. Upon cooling the liquid solidified and showed an infrared spectrum essentially identical with that of camphene sultone **4**. The crude solid was heated with hexane and the clear solution was decanted. This procedure was repeated several times, the combined hexane extracts were evaporated, and the residue was crystallized from methanol to give 0.4 g of pure camphene sultone **4** (mp 133–135°) whose nmr spectrum indicated the absence of sultone **16**.

Camphene Sultone Intermediate 35.—To an ice-cold, stirred solution of 38 g of concentrated sulfuric acid in 125 g of acetic anhydride was gradually added 50 g of camphene. After standing at 0° for 1 day, solid sodium carbonate was carefully added until the mixture was completely neutralized. The liquid was carefully decanted from the solid which had precipitated. The liquid phase was concentrated under diminished pressure and the residue was extracted with chloroform. The solid obtained above was also washed thoroughly and the combined chloroform solutions were evaporated to dryness. The resulting solid was pulverized and triturated with ether in order to remove a small amount of isobornyl acetate. The infrared spectrum of the dried solid showed peaks at 2.90, 5.77, 6.3, 7.94, 8.4, and 9.5 μ. The nmr spectrum (D_2O) showed an acetoxy methyl resonance at 2.09, two singlet methyl signals at 1.02 and 0.90, a one-proton multiplet at 4.84, a widely spaced AB-type resonance for the CH_2SO_3 protons centered at 3.08, and a broadened singlet at 1.79 ppm for the methyl of sodium acetate. By comparison of integrated areas it was established that the solid was a mixture of 40% sodium acetate and 60% sulfonate **35**. Various attempts to separate this mixture were unsuccessful.

Hydrolysis of the Sultone Intermediate 35 and Conversion into Camphene Sultone.—A solution of 1.0 g of the mixture of **35** and sodium acetate and 0.3 g of sodium hydroxide in 4 ml of water was warmed for 16 hr. The solution was acidified with dilute

hydrochloric acid until it was only slightly basic. Evaporation to near dryness gave a colorless solid whose infrared spectrum displayed broad peaks at 3.0 (OH), 6.3 (NaOAc), 8.6, and 9.5 μ (SO_3Na). The nmr spectrum of the solid showed a one-proton multiplet centered at 4.08, an AB-type quartet centered at 3.07 (CH_2SO_3), two singlet methyl groups at 0.85 and 1.03, and a singlet at 1.92 ppm for the methyl group of sodium acetate.

A solution of 320 mg of the mixture of salts obtained above and 3 ml of concentrated hydrochloric acid was allowed to stand at room temperature overnight. The mixture was diluted with water and extracted with ether. The ether extracts were washed with bicarbonate solution and water, dried, and evaporated to give 30 mg of solid whose infrared spectrum was identical with that of camphene sultone.

In another experiment, 3.0 g of the sultone intermediate in 30 ml of 33% sulfuric acid was kept at room temperature. The solution was extracted with ether after 30 min, 1 day, and 3 days, respectively. In each instance approximately 200 mg of camphene sultone mixture was obtained from the ether extracts.

Desulfurization of the Camphene Sultone Intermediate.—Phosphorus pentachloride (6.5 g) was slowly added with stirring to 6.0 g of the dry mixture of **35** and sodium acetate. After 1 hr, the dark liquid was added to aqueous sodium bicarbonate solution and extracted with methylene chloride. The methylene chloride was removed and the residue was dissolved in dry ether and added to a stirred suspension of 2.0 g of lithium aluminum hydride in ether. The mixture was stirred for 18 hr and then aqueous sodium sulfate solution was carefully added. The salts were filtered and washed with ether. The filtrate was dried and the solvent was evaporated leaving 1.0 g of an oil which showed strong hydroxyl absorption and no carbonyl peak in its infrared spectrum. A mixture of this oil and 8.0 g of nickel chloride hexahydrate in 30 ml of methanol was treated at 0° with a solution of 3.7 g of sodium borohydride in water. The resulting mixture was stirred at room temperature overnight and then at reflux for 3 hr. After cooling, the catalyst was removed and the filtrate was diluted with water. The ether layer was separated, washed with water, dried, and evaporated to leave a solid. Sublimation *in vacuo* gave 300 mg of solid whose infrared spectrum and retention time on a 15-ft Carbowax column at 200° were identical with those of authentic isoborneol.

Conversion of the Sultone Intermediate 35 to Sulfonanilide 38.—To 4.0 g (14.5 mmoles) of **35** was added slowly, with stirring and cooling, 4.0 g (16.0 mmoles) of phosphorus pentachloride. After stirring at room temperature for 1 hr, the dark liquid was poured into aqueous sodium bicarbonate solution and extracted with ether. Evaporation of the dried ether extracts gave 1.7 g of light yellow oil whose infrared spectrum showed strong absorption at 5.80, 8.10 (acetoxy), 6.27 (conjugated olefin) and 7.37, 8.60 μ (sulfonyl chloride). The crude sulfonyl chloride was mixed with 1.3 g of N-methylaniline in pyridine and left at room temperature for 1 hr. The mixture was poured into dilute hydrochloric acid and extracted with ether. The ether extracts were washed with dilute hydrochloric acid, sodium bicarbonate solution, and water. The ether solution was dried and the ether was removed to leave a brown solid. A portion of this solid was subjected to preparative thin layer chromatography using large glass plates coated with 1 mm of silica gel G and chloroform as the solvent. Brief contact with iodine pointed out the position of two bands which were scraped from the plates and extracted with ether.

The fast-moving band was recrystallized from methanol to give 180 mg of the unsaturated sulfonanilide **34**, mp 124°.

The slower moving band was recrystallized from methanol to give 65 mg of N-methyl-10-(2-*exo*-acetoxy)bornanesulfonanilide (**38**, mp 116–117°) whose infrared spectrum displayed peaks at 5.82, 6.31, 6.73, 7.45, 8.03, 8.71, and 12.7 μ. The nmr spectrum ($CDCl_3$) showed five aromatic protons at 7.38, a multiplet at 4.88 for the CHO proton, a widely spaced AB-type quartet centered at 3.06 for the CH_2SO_2 protons, and four singlet methyl resonances at 3.31, 1.68, 0.96, and 0.86 ppm. The large shift upfield for the acetoxy methyl proton (1.68) is probably due to its proximity to the aromatic ring.

Anal. Calcd for $C_{19}H_{27}NO_4S$: C, 62.43; H, 7.45; N, 3.83; S, 8.77. Found: C, 62.53; H, 7.41; N, 3.82; S, 8.54.

Hydrolysis of 38.—A solution of 290 mg (0.8 mmole) of N-methyl-10-(2-*exo*-acetoxy)bornanesulfonanilide (**38**) and 160 mg (2.4 mmoles) of potassium hydroxide in 5 ml of methanol was heated for 18 hr. The solution was diluted with water and ex-

tracted with ether. The ether was washed with water, dried, and removed to afford 283 mg of an oil which crystallized on standing. Recrystallization from hexane gave needles: mp 102–103°; λ_{max} 2.80 (OH), 7.43, 8.76 (SO$_2$), and 6.25, 6.70, and 12.5 μ (aromatic). The nmr spectrum showed the presence of five aromatic protons at 7.39, three singlet methyl groups at 0.80, 1.05, and 3.37, a widely spaced AB-type quartet centered at 3.10 for the CH$_2$SO$_2$, a multiplet at 4.10 for the CHOH proton, and the hydroxyl proton at 3.07 ppm (disappears upon addition of trifluoroacetic acid).

Anal. Calcd for C$_{17}$H$_{25}$NO$_3$S: C, 63.15; H, 7.74; S, 9.91. Found: C, 63.03; H, 7.57; S, 9.67.

"Aprotic" Solvolysis of p-Toluenesulfinic Esters[1]

JAMES W. WILT, ROBERT G. STEIN, AND WILLIAM J. WAGNER

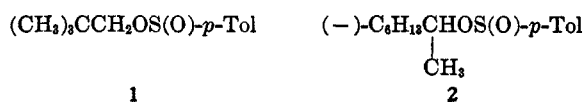*Department of Chemistry, Loyola University, Chicago, Illinois 60626*

Alkyl p-toluenesulfinates undergo cleavage to unrearranged alcohols when heated in various aprotic, nucleophilic amide solvents. Particularly effective is N-methyl-2-pyrrolidone (NMP). The yields are good in this solvent and the process is first order in ester. Studies with the neopentyl ester 1 and the (−)-2-octyl ester 2 in NMP indicate that the cleavage is probably an S$_N$ solvolysis where the solvent plays the roles both of attacking nucleophile and proton source, initiating cleavage by attack of the amide carbonyl on the sulfinate sulfur atom. Displaced alkoxide ion then, perhaps nearly concertedly, abstracts a proton from the α position of the amide leading to unrearranged alcohol product (when pertinent, with retention of configuration and optical purity). The cleavage is characterized by an extremely favorable activation enthalpy but a decidedly unfavorable activation entropy, reminiscent of B$_{Ac}$2 saponifications. Minor additional products observed from 1 in NMP are p-tolyl p-toluenethiolsulfonate (3) and the unusual salt N-methyl-2-pyrrolidonium tosylate (4). A side reaction involving dissociation of 1 is suggested as the source of these substances.

p-Toluenesulfinic esters are formed in the reaction of certain aldehyde tosylhydrazones with sodium methoxide in N-methyl-2-pyrrolidone (NMP) at 180°.[2] Such "aprotic" Bamford–Stevens reactions[3] ultimately lead to alcohols, and it was discovered that these esters were cleaved to alcohols without rearrangement by NMP under these reaction conditions. The present investigation was aimed at the elucidation of the mechanism of this cleavage.

Results

A number of p-toluenesulfinate esters were prepared in this study (see the Experimental Section), but the neopentyl ester 1 and the optically active (−)-2-octyl ester 2 were utilized most because of their obvious

$$(CH_3)_3CCH_2OS(O)\text{-}p\text{-Tol} \qquad (-)\text{-}C_6H_{13}CHOS(O)\text{-}p\text{-Tol}$$
$$\underset{1}{} \qquad \qquad \underset{2}{\overset{\displaystyle |}{\underset{\displaystyle CH_3}{}}}$$

mechanistic significance. Each ester was easily prepared by interaction of p-toluenesulfinyl chloride and the corresponding alcohol in ether–pyridine.[4] It was in the course of preparing and characterizing the sulfinic esters that the interesting nmr feature of magnetic nonequivalence of the methylene protons in the functionality CH$_2$OS(O) was noticed and reported.[5]

(1) Taken from the M.S. Thesis of R. G. S., Loyola University, 1966, and from a portion of the Ph.D. dissertation of W. J. W., Loyola University, 1967.

(2) J. W. Wilt, C. A. Schneider, H. F. Dabek, Jr., J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, **31**, 1543 (1966).

(3) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

(4) H. Phillips and J. Kenyon, *ibid.*, 2271 (1925).

(5) J. W. Wilt and W. J. Wagner, *Chem. Ind.* (London), 1389 (1964). Others had noted this earlier: J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961); M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **35**, 1428 (1962). We thank Professors Cotton and Iwamura for drawing our attention to their work.

It was quickly established that the use of hexadecane, another solvent often employed in aprotic Bamford–Stevens reactions, did not afford alcohols from sulfinic esters at 180°; thus the cleavage was not just a thermal process independent of solvent. Examination of a number of other aprotic solvents was then carried out. Neopentyl p-toluenesulfinate 1 was used as the test ester with the results given in Table I.

TABLE I
EFFECT OF SOLVENT ON CLEAVAGE
OF NEOPENTYL p-TOLUENESULFINATE (1)[a]

Solvent	Neopentyl alcohol, %[b]
N-Methyl-2-pyrrolidone	84
N-Methyl-ε-caprolactam	52
N-Methyl-2-piperidone	27
N,N-Dimethylacetamide	31
N,N-Dimethylformamide	5
N,N-Dimethylpivalamide	5
γ-Butyrolactone	59[c]
Diethyl malonate	6.5
Cumene	0
Hexadecane	0

[a] At 180° normally for 15 min, except for the low conversion reactions which were heated for as long as 3 hr. [b] No t-amyl alcohol was found by glpc except in the case of γ-butyrolactone. The values represent the highest percentage in several experiments. [c] t-Amyl alcohol was also formed (11%).

The data indicated that tertiary amide solvents were effective, but only those in which the carbonyl group was flanked by a methyl or a methylene group (*i.e.*, "enolizable" amides). γ-Butyrolactone also cleaved the ester but here some rearranged alcohol was also produced. The involvement of the α position of the amide solvent was substantiated through use of 3,3-