

## Sultone Rearrangements. I. 10-Isobornyl and 4-Methyl-10-isobornyl Sultones

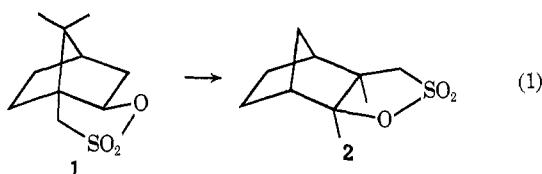
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Thermal rearrangement of 10-isobornyl sultone (1) affords *exo*-camphene sultone (2). In the early stages of the rearrangement *endo*-camphene sultone (8) can be isolated. The stability order for the sultones appears to be  $2 > 8 > 1$ . Two mechanisms are postulated to explain the transformation. One involves an *endo*-3,2-methyl shift and the other involves a circuitous route of an *exo*-3,2-methyl shift and several Wagner-Meerwein and 6,2-hydride shifts. A preparation of 4-methyl-10-isobornyl sultone (18) from either camphor or fenchone is described. Sultone 18 rearranges to an *endo* sultone (29) at moderate temperatures, but the only product found at higher temperatures is an aromatic hydrocarbon, 3,4-dimethylcumene (35). Mechanisms are proposed to account for the aromatization reaction.

A few years ago we discovered a unique thermal rearrangement of a sultone.<sup>1</sup> Upon being heated to its melting point, 10-isobornyl sultone (1) rearranges to *exo*-camphene sultone (2). It was subsequently



found that solid 1 can be transformed to solid 2 at temperatures below the melting point of 1.

Two mechanisms can be envisioned to explain the transformation: (A) an *exo*-3,2-methyl shift involving several steps or (B) an *endo*-3,2-methyl shift involving only a couple of simple steps. These mechanisms are shown in Scheme I. It is generally believed<sup>2</sup> that *exo*-3,2 shifts are lower in energy than *endo*-3,2 shifts, and on this basis mechanism A should be preferred to mechanism B. There have been, however, some reported cases of *endo*-3,2 shifts.<sup>3</sup>

Although ionic intermediates are shown in Scheme I, the reactions may be concerted. For example,  $1 \rightarrow 5$  and  $5 \rightarrow 2$  could proceed by a simultaneous movement of the sulfonate ion across one face of the molecule and an alkyl group across the other face, in an opposite direction. It is not easy to visualize a completely concerted process for pathway A. This paper and the subsequent one describe our attempts to distinguish the two proposed mechanisms, A and B.

## Results and Discussion

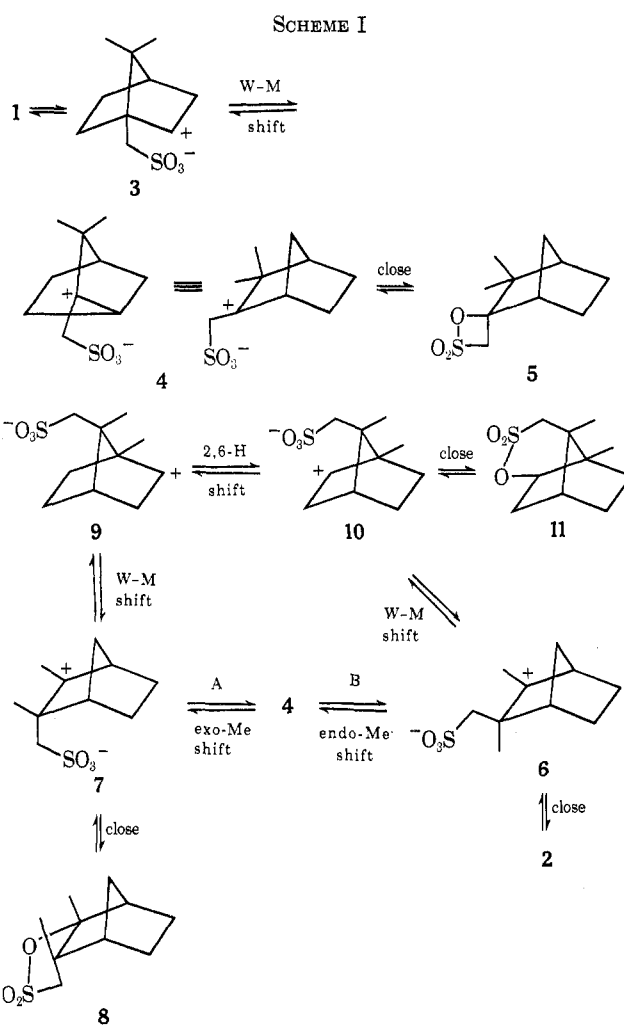
In reexamining the thermal rearrangement of 10-isobornyl sultone, a new sultone was observed in the initial stages of the reaction. Isolation of this new sultone was accomplished by heating 1 for 3–5 min at about 125° (just to a melt) and performing a quick column chromatography of the crude product through basic alumina. Unreacted starting material and sultone 2 were retained on the column, probably due to a rapid hydrolysis of the exposed sultone grouping.

Based on elemental analysis, mass spectrum, and in-

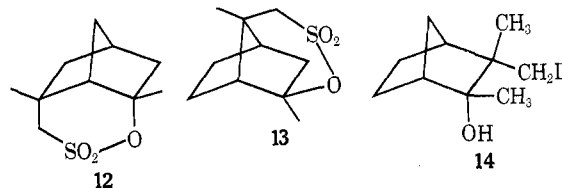
(1) J. Wolinsky, D. R. Dimmel, and T. W. Gibson, *J. Org. Chem.*, **32**, 2087 (1967).

(2) J. Berson, in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 3.

(3) (a) *Endo*-3,2-methyl shift: S. Rengaraju and K. D. Berlin, *Tetrahedron*, **27**, 2399 (1971); C. W. David, B. W. Everling, R. T. Killian, J. B. Stothers, and W. R. Vaughan, *J. Amer. Chem. Soc.*, **95**, 1265 (1973). (b) *Endo*-3,2-hydride shift: A. W. Bushwell and P. Wilder, Jr., *ibid.*, **89**, 5721 (1967). (c) Possible *endo*-3,2-chlorine shift: R. N. McDonald and R. N. Steppel, *ibid.*, **91**, 782 (1969).



frared spectrum, the new compound proved to be an isomer of the starting material. An nmr spectrum displayed singlet methyl groups at  $\delta$  1.34 and 1.52, an AB pattern for the  $-\text{CH}_2\text{SO}_2-$ , one doublet at 2.83 ( $J = 14$  Hz) and the other at 3.38 ( $J = 14$  Hz), and the remaining ring protons spread between 1.55 and 2.45. Several structures appear compatible with these spectral characteristics, namely, 5, 8, and the relatively unlikely structures 12, 13, etc. A simple way to dis-

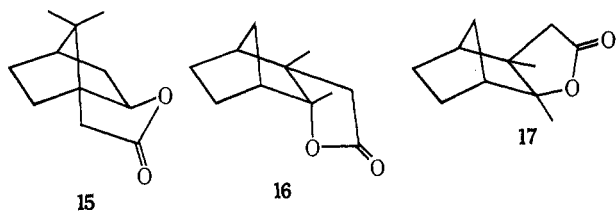


tinguish these compounds is desulfurization with  $\text{LiAlD}_4$ .<sup>1</sup> When the experiment was performed, 2-methylcamphenilol was produced. Both nmr and mass spectra clearly showed that one of the geminate dimethyls at C-3 is deuterated; thus, structure **14** was assigned to the reduction product. A trans-2,3-fused sultone ring juncture was considered highly unlikely.

The course of the rearrangement reaction could be conveniently followed by inserting sealed capillaries containing solid **1** into refluxing ethoxyethanol (bp 133–135°) and removing samples at regular time intervals. The crude data, shown in Figure 1, indicate that **1** disappears quite rapidly to **8**, which in a slower reaction goes to **2**. Heating relatively pure **8** afforded **2**. Under the same conditions **2** did not lead to any **8**. Thus, it appears that sultone **2** must be thermodynamically more stable than sultone **8**.

The rearrangement can also be performed in inert solvents like *n*-octane and tetrachloroethylene (TCE). A really simple way to do the rearrangement is to dissolve 10-isobornyl sultone in refluxing *n*-octane (bp 124°) for 2–3 hr, cool, and collect crystalline **2** in 80% yield. The rearrangement in *n*-octane was difficult to follow kinetically; after an induction period of 6 min, sultone **1** was completely converted into a mixture of **2** and **8**. The rearrangement was much slower in refluxing TCE (bp 121°) solvent, and the course of the reaction could be easily followed by nmr. Here again sultone **8** could be observed, and it was possible, using dibenzyl ether as an internal standard, to show that there were no side reactions of **1**, **2**, and **8**, such as formation of camphene.

The crude kinetic data shown in Figure 1 do not tell whether sultone **8** is on the pathway to the formation of **2**, *i.e.*, mechanism A, or just a dead-end product. In other words, does the conversion of **8** → **2** involve **7** → **4** → **6** → **2** or **7** → **9** → **10** → **6** → **2**? It is interesting to note that lactones **15**, **16**, and **17** are known<sup>4</sup>



and that it appears that the thermodynamic stability order is **15** < **16** < **17**. The exo lactone **17** just as the exo sultone **2** has a singlet methylene ( $\text{CH}_2\text{X}$ ,  $\text{X} = \text{CO}$  or  $\text{SO}_2$ ) in its nmr spectrum, and the endo lactone **16** like the endo sultone **8** has an AB quartet for this methylene group.

Our first approach to distinguish mechanisms A and B was to synthesize and study the rearrangement of 4-methyl-10-isobornyl sultone (**18**). If **18** were to rearrange *via* an endo-methyl shift mechanism such as B, the product should be **19**; however, if an exo-methyl shift mechanism such as A prevailed, the product should be **20** (eq 2).

The synthesis of **18** is shown in Scheme II. The synthesis of **26** from either fenchone (**21**) or camphor (**27**) represents an improvement of our earlier reported

(4) W. R. Vaughan, J. Wolinsky, R. S. Dueltgen, S. Grey, and F. S. Seichter, *J. Org. Chem.*, **35**, 400 (1970).

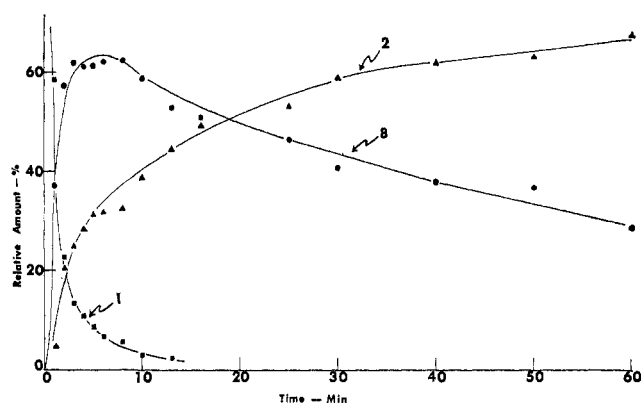
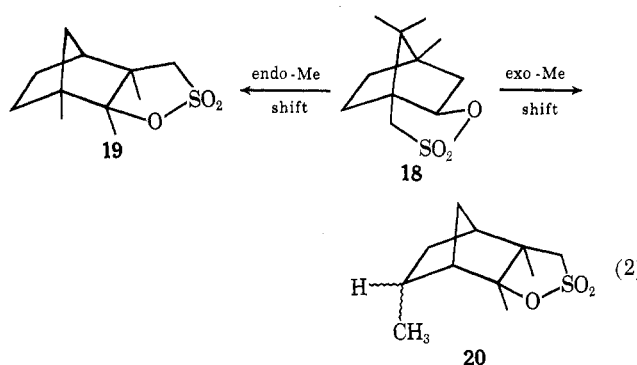
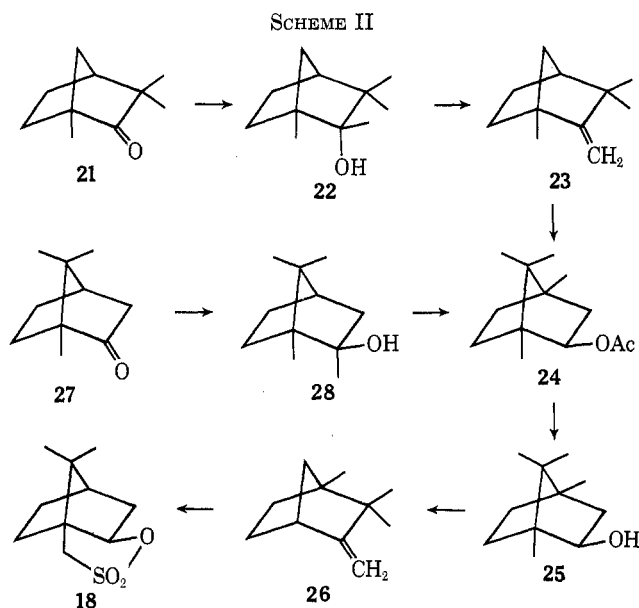


Figure 1.—Product composition resulting from the neat thermal rearrangement of 10-isobornyl sultone (**1**) at 133–135°: ■, amount of sultone **1**; ●, amount of sultone **8**; ▲, amount of sultone **2**.

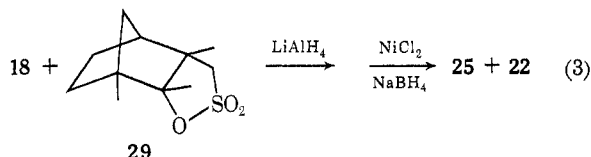


synthesis (see Experimental Section).<sup>1</sup> The thermal rearrangement of **18** was accomplished by heating at 75–85° for 3 hr and subliming out the volatile materials.



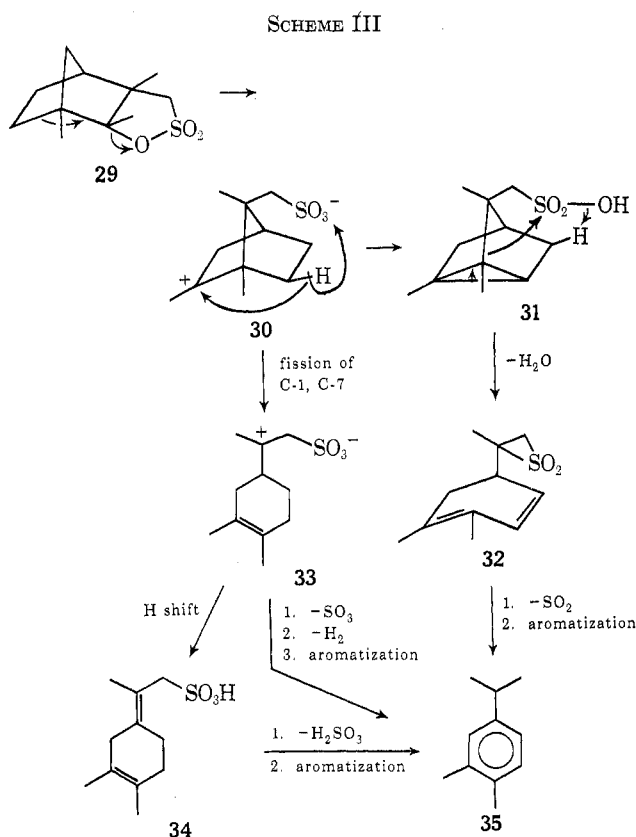
The product mixture was found to be composed of one part of **18** to three parts of a new compound, a sultone. An nmr spectrum of the mixture suggested that the new sultone has structure **29**, singlet methyls at  $\delta$  1.15, 1.32, and 1.44 and an AB quartet ( $J = 14$  Hz) for the  $-\text{CH}_2\text{SO}_2-$  group, one doublet at 2.83 and the other at 3.41.<sup>4</sup> Reduction of the sultone mixture with  $\text{LiAlH}_4$ , followed by nickel boride, gave a 1:3 mixture of **25**

and 1,2-dimethylcamphenilol (22). The endo OH of 22 supports the endo sultone ring juncture of 29.



1-Methylcamphene hydrate (the exo isomer of 22) was shown not to be present.

If 18 or the mixture of 18 and 29 were heated at higher temperatures in an attempt to get either 19 or 20, desulfonation with subsequent aromatization occurred, giving the hydrocarbon 3,4-dimethylcumene (35). The structural proof of this latter compound was based on spectral comparison to reported values.<sup>5</sup> Aromatization of bicyclo[2.2.1]heptanes has occurred in other systems as well.<sup>6,7</sup> The possible mechanisms for this transformation are presented in Scheme III. The



mechanism involving loss of  $\text{SO}_2$  via an episulfone extrusion reaction is based on some work of Paquette.<sup>8</sup> Mechanisms involving loss of  $\text{H}_2\text{SO}_3$  or  $\text{SO}_3$  and  $\text{H}_2$  can also be envisioned.

### Conclusions

The rearrangement of 10-isobornyl sultone (1) not only affords *exo*-camphene sultone (2), as reported earlier,<sup>1</sup> but also *endo*-camphene sultone (8). The

(5) Sadtler Infrared Spectra Index No. 26048 and Sadtler Nmr Spectra Index No. 420M.

(6) R. P. Lutz and J. D. Roberts, *J. Amer. Chem. Soc.*, **84**, 3715 (1962).

(7) A. Coulombeau, C. Coulombeau, and A. Rassat, *Bull. Soc. Chim. Fr.*, 4389 (1970).

(8) L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *J. Amer. Chem. Soc.*, **93**, 1048 (1971).

*endo* sultone is formed first in the reaction, but then gradually rearranges to the more stable *exo* sultone. Although it is tempting to conclude that the *endo* sultone is an intermediate along the pathway that gives the *exo* isomer, we cannot rule out the possibility that the *endo* sultone is a dead-end product which is in equilibrium with an intermediate that gives the *exo* isomer at a slow rate.

It was anticipated that the thermal rearrangement of 4-methyl-10-isobornyl sultone (18) would allow us to establish the mechanisms of these sultone rearrangements. However, heating 18 only gave the *endo* sultone 29 at moderate temperatures and 3,4-dimethylcumene (34) at high temperatures. The fact that no *exo* sultone was observed could be interpreted to favor either an *exo*- or *endo*-3,2-methyl shift. The C-4 bridgehead methyl could retard an *endo*-3,2-methyl shift (pathway B, 4  $\rightarrow$  6) by an eclipsing effect<sup>9</sup> that would result between the *exo*-3-methyl and the bridgehead methyl as the C-3 flattens out. Alternatively, the C-4 methyl could have a large effect on the mechanism of rearrangement if pathway A prevailed. This methyl would end up on the carbonium site of structure 9, *i.e.*, structure 30. The ion now is tertiary and should, therefore, have less tendency to go onto a secondary carbonium ion via a 6,2-hydride shift, as depicted in 9  $\rightarrow$  10. The longer lived ion 30 might then find alternate ways of reacting, such as shown in Scheme III.

The question of what type of 3,2-methyl shift prevails remains unanswered. Our next paper,<sup>10</sup> dealing with deuterated analogs of 10-isobornyl sultone, attempts to provide the answer.

### Experimental Section<sup>11</sup>

**Kinetic Measurements of Thermal Rearrangement of 10-Isobornyl Sultone (1).** A.—Sealed capillaries containing 1 were immersed in a constant-boiling bath of ethoxyethanol (bp 133–135°). The rate of rearrangement was followed by measuring the relative intensities of the proton nmr signals of the  $-\text{CH}_2\text{SO}_2-$  group.

B.—10-Isobornyl sultone (1.8 g) was dissolved in 12 ml of refluxing tetrachloroethylene (TCE, bp 121°). Samples were withdrawn at regular time intervals and their nmr spectra recorded.

C.—To 10 ml of refluxing *n*-octane (bp 124°) was added 2.5 g of sultone 1. Samples were withdrawn at regular time intervals. Upon cooling, a solid was isolated by filtration. The proton nmr spectra of all the withdrawn samples showed that 8 was not present. In a separate run sultone 2 was isolated in 80% yield after a reaction time of 3 hr.

D.—No side reactions, such as the extrusion of sulfur trioxide to form camphene, were observed in the nmr spectrum. Furthermore, when dibenzyl ether was mixed with 1 in refluxing TCE, the relative ratio of the benzylic protons to  $-\text{CH}_2\text{SO}_2-$  protons remained unchanged under the same reaction conditions as in B.

***endo*-Camphene Sultone (8).**—10-Isobornyl sultone (1.0 g, 4.6 mmol) was heated at 125° for 5 min. The resulting dark brown solid was shown (by nmr) to be a mixture of *exo*- and *endo*-

(9) P. v. R. Schleyer, *ibid.*, **89**, 699, 701 (1967).

(10) D. R. Dimmel and W. Y. Fu, *J. Org. Chem.*, **38**, 3782 (1973).

(11) All boiling points and melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer, Model 137B. Nmr spectra were obtained on a Varian A-60A spectrometer, using TMS as an internal standard and  $\text{CCl}_4$  as solvent. Mass spectra were obtained using a CEC 21-103 mass spectrometer. Unless otherwise stated, gas chromatographic analyses and preparative vpc were performed on a 6 ft  $\times$  0.25 in. aluminum column packed with 20% SE-30 on 60–80 mesh Chromosorb W or an 8 ft  $\times$  0.25 in. aluminum column packed with 20% diethylene glycol succinate (DEGS) on 30–60 mesh Chromosorb W using an F&M Model 700 gas chromatograph. Elemental analyses were performed by Chemalytic, Inc., Tempe, Ariz.

camphene sultones and 10-isobornyl sultone. The mixture was placed on an alumina column (70 g, pH 10.2) and eluted with 140 ml of hexane, followed by 80 ml of 95% hexane–5% benzene, 80 ml of 80% hexane–20% benzene, 240 ml of 60% hexane–40% benzene, and 150 ml of 50% hexane–50% benzene. Fractions of 40 ml each were collected. Upon evaporation of the solvent, fractions 9–16 gave a white residue. Recrystallization of the residue from cold hexane gave 103 mg of a white solid: mp 159.5–160°; nmr (CCl<sub>4</sub>)  $\delta$  3.38 (d, 1,  $J$  = 14 Hz), 2.83 (d, 1,  $J$  = 14 Hz), 1.52 (s, CH<sub>3</sub>), 1.34 (s, CH<sub>3</sub>); ir (CCl<sub>4</sub>) 1360, 1185 (SO<sub>2</sub>) and 905, 875, 860, 832 cm<sup>-1</sup> (sultone).

Anal. Calcd for C<sub>10</sub>H<sub>16</sub>O<sub>3</sub>S: C, 55.51; H, 7.46; S, 14.82. Found: C, 55.16; H, 7.60; S, 14.55.

**Reduction of *endo*-Camphene Sultone (8).**—A 1.0-g (4.6 mmol) sample of a mixture of sultones, shown by nmr to be 50:50 *exo*-(2)-*endo*-camphene sultone (8), was combined with 0.75 g (20 mmol, 80 mequiv) of lithium aluminum hydride in anhydrous tetrahydrofuran (THF) and refluxed for 10 days. After being quenched with saturated aqueous sodium sulfate, the salts were filtered and washed several times with fresh ether. The filtrate was distilled and the residue sublimed. A liquid sublimate was collected which smelled of sulfur. Analysis by vpc and nmr indicated that the product was probably a mixture of hydroxy sulfides.

The crude product mixture was dissolved in a small amount of 95% ethanol and added to a solution of 5.0 g (20 mmol) of hexa-aquonickel(II) chloride in 95% ethanol. The solution was swept with nitrogen for 10 min and then cooled in an ice bath. While cold, an aqueous solution of 2.25 g (60 mmol) of sodium borohydride was added dropwise to the stirred solution. When the addition was complete, the ice bath was removed and the reaction mixture refluxed for 4 hr. The solution was then cooled, diluted with water, and filtered. The filtered black catalyst was washed several times with ether. The ether layer was separated from the filtrate, washed, dried (MgSO<sub>4</sub>), and concentrated and the residue sublimed to yield approximately 100 mg of a mushy solid.

The nmr spectrum of the product indicated that it was a 50:50 mixture of camphene hydrate and 2-methylcamphenilol. After several columns were tried, the two components were partially separated by vpc using a 8 ft  $\times$  1/8 in. 20% Quadrol on 60–80 mesh Chromosorb W column. One alcohol had a retention time of 18.5 min and the other 19 min. Enriching the 50:50 sample with either pure alcohol to determine which peak corresponded to which led to a coalescence of the peaks. Another more definitive answer to the structure of sultone 8 is discussed next.

A 175-mg sample of 8, purified by column chromatography and recrystallized from hexane, was dissolved in anhydrous ether and combined with 350 mg (tenfold excess) of lithium aluminum deuteride. The mixture was stirred for 2 weeks at room temperature, quenched with saturated sodium sulfate solution, and filtered. After the salts were washed several times with ether, the filtrate was dried (MgSO<sub>4</sub>), filtered, evaporated, and sublimed to give 30 mg of solid. An nmr spectrum of the solid agreed with the spectrum of 2-methylcamphenilol except for a decrease in the methyl signal at 53.6 Hz; the other methyl signals at 55.2 and 70.7 Hz were unchanged. A mass spectrum clearly showed that the product was a 2,3,3-trimethyl-2-norbornanol compound with deuterium located on one of the C-3 methyl groups (the *m/e* 41 shifted substantially to *m/e* 42; *m/e* 43 did not shift to *m/e* 44; and *m/e* 71, the base peak, was not shifted in comparison to the nondeuterated compound). The solid was assigned the structure 14.

**1,2-Dimethylcamphenilol (22).**—An ethereal solution of 85 g (0.6 mol) of methyl iodide was added dropwise to 20.0 g (1.67 g-atoms) of magnesium in 100 ml of anhydrous ether. A solution of 53 g (0.35 mol) of fenchone in ether was added dropwise to the freshly prepared Grignard reagent. The resulting dark gray solution was refluxed for 5 hr. The reaction mixture was poured into a beaker of 40 ml of cold, saturated ammonium chloride. The ether layer was separated and the aqueous layer was extracted twice with ether. The combined ether extracts were dried (MgSO<sub>4</sub>) and concentrated to give 58.1 g (99.2%) of a mixture of 22 and 21: ir 3510, 1095 (–OH), 1740 cm<sup>-1</sup> (C=O). This mixture was used directly in the next step.

**1-Methylcamphene (23).**—To an ice-cold solution of 58.1 g of the alcohol–ketone mixture obtained above in 70 ml of anhydrous pyridine was slowly added 40 ml of thionyl chloride. After refluxing for 12 hr the mixture was poured into water and extracted with ether. The ether extracts were washed successively with 5% HCl, 5% NaHCO<sub>3</sub>, and water. The resulting brown solution was

dried (MgSO<sub>4</sub>), concentrated, and distilled to give 38.5 g of a colorless liquid: bp 125° (110 mm); ir 3080, 1650, 900 cm<sup>-1</sup> (–C=CH<sub>2</sub>) [lit.<sup>12</sup> bp 170–172° (737 mm)]. A small amount of fenchone was present (ir).

**1,2,7,7-Tetramethyl-*exo*-2-norbornanol (28).**—An ethereal solution of 40 g (0.26 mol) of camphor was slowly added to an ethereal solution of methylmagnesium iodide prepared from 67 g (0.47 mol) of methyl iodide and 20.2 g (1.66 g-atoms) of magnesium. The reaction mixture was refluxed in a nitrogen atmosphere for 40 hr. The mixture was poured into 40 ml of cold and saturated ammonium chloride and the organic layer separated. The aqueous phase was extracted twice with fresh ether. The combined ether extracts were dried (MgSO<sub>4</sub>) and concentrated to afford 41 g of a mixture of 74% 28 and 26% camphor (by vpc analysis). The mixture was refluxed for 3 hr with 12 g of hydroxylamine hydrochloride, 20 g of potassium hydroxide, and 75 ml of 95% ethanol. The ethanolic solution was poured into 150 ml of cold water, and extracted twice with ether, and the combined ether extracts were washed twice with 10% NaOH, dried (MgSO<sub>4</sub>), and concentrated to give 35 g (79%) of a solid: mp 164–167°; nmr (CCl<sub>4</sub>)  $\delta$  1.18 (s, CH<sub>3</sub>), 1.06 (s, CH<sub>3</sub>) 0.84 (s, CH<sub>3</sub>), and 0.80 (s, CH<sub>3</sub>) (lit.<sup>13</sup> mp 168°).

**4-Methylisobornyl Acetate (24). A. From 1-Methylcamphene (23).**—1-Methylcamphene (38.5 g, 0.23 mol) was mixed with 90 ml of glacial acetic acid and 3 ml of 50% H<sub>2</sub>SO<sub>4</sub> and kept at 60° for 20 hr. After cooling, the solution was poured into 250 ml of cold water and extracted with ether. The ether extracts were washed with saturated NaHCO<sub>3</sub>, dried over magnesium sulfate, concentrated, and distilled to give 30.0 g (62%) of a colorless liquid: bp 97–110° (25 mm); ir 1735, 1240 cm<sup>-1</sup> (acetate); nmr (CCl<sub>4</sub>)  $\delta$  4.62 (dd, 1, CHOH,  $J$  = 4.5, 7.5 Hz), 1.92 (s, CH<sub>3</sub>), 0.88 (s, CH<sub>3</sub>), 0.83 (s, 2 CH<sub>3</sub>), and 0.68 (s, CH<sub>3</sub>) [lit.<sup>1</sup> bp 126–128° (28 mm)].

**B. From 1,2,7,7-Tetramethyl-*exo*-2-norbornanol (28).**—A mixture of 35 g (0.21 mol) of 28, 120 ml of glacial acetic acid, and 6 ml of 50% H<sub>2</sub>SO<sub>4</sub> was kept at 60° for 3 days. After cooling, the mixture was poured into 90 g of ice–water slurry and extracted three times with ether. The combined ether extracts were washed successively with 5% NaOH and water until the aqueous wash was neutral to litmus. The ether layer was then dried (MgSO<sub>4</sub>), concentrated, and distilled to give 25 g (57%) of a colorless liquid whose boiling point and ir and nmr spectra were identical with those obtained from A.

**1,4,7,7-Tetramethyl-*exo*-2-norbornanol (25).**—A mixture of 30 g (0.14 mol) of 24, 54 ml of water, 54 ml of methanol, and 31 g of potassium hydroxide was refluxed with stirring for 20 hr. The reaction mixture was poured into 200 ml of water and extracted three times with ether. The combined ether extracts were dried (MgSO<sub>4</sub>) and concentrated to give 15 g (62%) of a white solid: mp 193–194°; ir 3510, 1040 cm<sup>-1</sup> (–OH); nmr (CCl<sub>4</sub>)  $\delta$  3.54 (dd, 1,  $J$  = 4.5, 7.5 Hz, CHOH), 0.87 (s, 2 CH<sub>3</sub>), 0.83 (s, CH<sub>3</sub>), 0.66 (s, CH<sub>3</sub>); mass spectrum (70 eV) *m/e* (rel intensity) 150 (10), 135 (16), 125 (17), 109 (100), 107 (20), 55 (34), 43 (37), 41 (63), 39 (33), 29 (30), 27 (37) (lit.<sup>12</sup> mp 190–191°).

**$\beta$ -Methylcamphene (26).**—To a cold solution of 24 g (142 mmol) of 25 in 25 ml of freshly distilled pyridine was slowly added 10 ml of thionyl chloride. After being stirred for 3 hr, the mixture was poured into ether and water. The ether layer was separated and washed successively with 5% HCl, saturated NaHCO<sub>3</sub>, and water. After the ether was removed, the residue was eluted through an alumina column with pentane to give, after sublimation, 16.64 g (78%) of a solid: mp 87–96°; ir 3080, 1650, 1415, 880 cm<sup>-1</sup> (–C=CH<sub>2</sub>); nmr (CCl<sub>4</sub>)  $\delta$  4.60 (d, 2,  $J$  = 12 Hz, –C=CH<sub>2</sub>), 2.61 (m, 1, methine proton at C-1), 1.02 (s, CH<sub>3</sub>), 0.98 (s, CH<sub>3</sub>), 0.92 (s, CH<sub>3</sub>) (lit.<sup>12</sup> mp 100–110°). Analysis by vpc (SE-30) showed approximately 55% 26 and 45% tricyclene.

**4-Methyl-10-isobornyl Sultone (18).**—To a cooled solution of 6 g (75 mmol) of sulfur trioxide in 50 ml of tetrachloroethylene (TCE) was added dropwise with rapid stirring 8.2 g (94 mmol) of *p*-dioxane in 50 ml of TCE. The SO<sub>3</sub>–dioxane complex was formed immediately. 4-Methylcamphene (4.0 g, 26.7 mmol) dissolved in 10 ml of TCE was then added slowly with rapid stirring. After stirring at room temperature for 16 hr, the reaction mixture was poured into 60 ml of saturated NaHCO<sub>3</sub>.

(12) A. I. Sherygin, *Zh. Obshch. Khim.*, **18**, 499 (1948); *Chem. Abstr.*, **42**, 7276h (1948).

(13) M. L. Chapman, W. Chodkiewicz, and P. Cadot, *Tetrahedron Lett.*, 1619 (1965).

The organic layer was separated and the aqueous phase was extracted with methylene chloride. The combined organic phases were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated under reduced pressure at room temperature. The viscous residue was recrystallized twice from pentane to yield 0.402 g (6.7%) of a colorless solid: mp 74–75°; nmr ( $\text{CCl}_4$ )  $\delta$  4.36 (dd, 1,  $J = 5, 7$  Hz,  $-\text{CHOSO}_2$ ), 3.22 (s, 2,  $-\text{CH}_2\text{SO}_2$ ), 0.97 (s, 2  $\text{CH}_3$ ), 0.89 (s,  $\text{CH}_3$ ).

Anal. Calcd for  $\text{C}_{11}\text{H}_{18}\text{O}_3\text{S}$ : C, 57.37; H, 7.88; S, 13.60. Found: C, 57.37; H, 7.91; S, 13.72.

**Thermal Rearrangement of 4-Methyl-10-isobornyl Sultone (18).**—4-Methyl-10-isobornyl sultone (280 mg) was placed in a sublimator and maintained between 75 and 85° for 3 hr. Sublimation gave 202 mg of a solid [75° (0.1 mm)]. Analysis by nmr showed a 1:3 mixture of 18 and a rearranged sultone, respectively. In addition to the starting material the nmr showed two doublets centered at  $\delta$  3.41 ( $J = 14$  Hz) and 2.83 ( $J = 14$  Hz) and three singlet methyls at 1.44, 1.32, and 1.15, which suggested structure 29.<sup>4</sup>

**Reduction of Sultone Mixture 18 and 29.**—A procedure similar to the reduction of 8 was used. Thus, 200 mg of the sultone mixture was first treated with 1.1 g (29 mmol) of lithium aluminum hydride in ether and then with 2.4 g (10 mmol) of hexa-aquanickel(II) chloride and 1.23 g (33 mmol) of sodium boro-

hydride in absolute ethanol. Analysis by vpc showed a 1:3 mixture. The spectroscopic properties (ir and mass spectrum) of the major component, collected by preparative vpc, were identical with those of 22. The minor component was likewise isolated by preparative vpc, and its ir and mass spectrum data were identical with those of 25.

**3,4-Dimethylcumene (35) from 4-Methyl-10-isobornyl Sultone (18).**—Sultone 18, 0.25 g, was heated to 100° for 2 hr. The resulting brown solution was found to be an aromatic hydrocarbon: ir 882, 818, 718  $\text{cm}^{-1}$  (1,2,4-trisubstituted aromatic); nmr ( $\text{CCl}_4$ )  $\delta$  6.90 (s, 3, aryl protons), 2.78 (m, 1, ArCH), 2.20 (s, 6, 2  $\text{CH}_3$ ) and 1.21 (d, 6,  $J = 7$  Hz,  $-\text{CH}(\text{C}_3)\text{H}_2$ ); mass spectrum (70 eV)  $m/e$  (rel intensity) 149 (3), 148 (25), 134 (13), 133 (100), 117 (12), 105 (13), 91 (14), 77 (8), 51 (6), 41 (11), 39 (12), and 29 (12). The ir and nmr spectra were in complete agreement with those of 2,3-dimethylcumene. A vpc collected sample showed the same spectral properties.<sup>5</sup>

Registry No.—1, 13131-57-2; 8, 41366-78-3; 14, 41429-86-1; 18, 41366-79-4; 21, 1195-79-5; 22, 28462-85-3; 23, 13567-57-2; 24, 10470-41-4; 25, 41366-83-0; 26, 13144-43-9; 28, 2371-42-8; 29, 41366-86-3; 35, 4132-77-8; methyl iodide, 74-88-4; camphor, 76-22-2.

## Sultone Rearrangements. II. Deuterated Analogs of 10-Isobornyl Sultone. Evidence for Exo-3,2-Methyl Shifts and Discrete 2-Norbornyl Cations

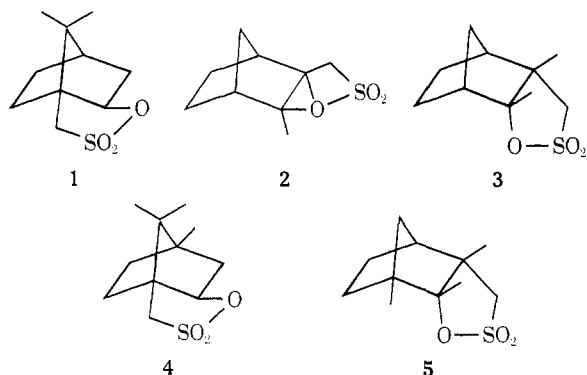
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The 3,3- $d_2$  and 9- $d_1$  analogs of 10-isobornyl sultone (1) were synthesized. There is no scrambling of the deuterium label during the syntheses, even though a 2-norbornyl cation is a likely intermediate in one of the steps. The deuterated 10-isobornyl sultones were thermally converted to deuterated *exo*-camphene sultones (2) in hopes of clarifying the nature of the 3,2-methyl shifts which occur during the rearrangement reactions. The label at C-9 is scrambled during the thermal reactions such that a distinction between *exo*- vs. *endo*-3,2-methyl shifts cannot be made. However, analysis of the deuterium atom position in the product of the thermal rearrangement of 1-3,3- $d_2$  shows that an *exo*-3,2-methyl shift prevails over *endo* shift in the formation of *exo*-camphene sultone. Studies using optically active reagents showed that the two methods of synthesizing 10-isobornyl sultone were highly stereospecific, meaning that the probable 2-norbornyl cation intermediate does undergo racemizing 6,2-hydride shifts. However, racemization does occur during the thermal rearrangement of 1 to 2.

In the previous paper we described the thermal rearrangement of 10-isobornyl sultone (1) to *exo*- and *endo*-camphene sultones (2 and 3).<sup>1</sup> Rearrangement of a methyl analog, sultone 4, gave only an *endo* sultone 5 and 3,4-dimethylisopropylbenzene and no *exo* sultone



comparable to 2. The formation of the *endo* sultones 3 and 5 most likely occurs *via* a *exo*-3,2-methyl shift. The exact manner by which the *exo* sultone 2 is formed is still in doubt. It was anticipated that its formation may be a result of a relatively rare rearrangement,

namely an *endo*-3,2-methyl shift.<sup>2</sup> Previous results<sup>1</sup> suggested, but did not prove, that the *endo* sultone 3 may be the precursor of 2 and, consequently, *endo*-3,2-methyl shifts do not have to be involved.

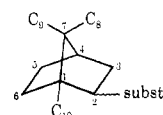
Since introduction of a methyl group changed the course of the reaction, we decided to keep the structural variations to a minimum by employing deuterium labeling. In order to get deuterium into the structure we had to develop a new way of synthesizing 10-isobornyl sultone. The previous methods<sup>3</sup> usually employed camphene as the starting material and the task of synthesizing specifically labeled camphene derivatives appeared to be both expensive and involved. A synthesis of 10-isobornyl sultone from camphene is shown in eq 1.

A major problem in specifically deuterating these systems is the ease with which these compounds undergo rapid rearrangements, *i.e.*, Wagner–Meerwein and 6,2- and 3,2-hydride shifts.<sup>4</sup> For example, a rapid

(2) See footnote 3 of ref 1.

(3) J. Wolinsky, D. R. Dimmel, and T. W. Gibson, *J. Org. Chem.*, **32**, 2087 (1967).

(4) The number system for bicyclo[2.2.1]heptanes is as follows:



(1) D. R. Dimmel and W. Y. Fu, *J. Org. Chem.*, **38**, 3778 (1973).