(ε 20,300). It formed a maroon 2,4-dinitrophenylhydrazone, mp 162–163°.

Anal. Calcd for $C_{16}H_{16}N_4O_4$: C, 58.53; H, 4.91; N, 17.06. Found: C, 58.79; H, 4.91; N, 16.80.

A second experiment using boron trifluoride etherate as the acid catalyst gave the same product in 81% isolated yield.

Registry No.—2, 10271-04-2; 3, 10294-80-1; 4, 10271-05-3; 2,4-dinitrophenylhydrazone of 4, 10271-06-4; 5, 10271-07-5; 6, 10271-08-6; 2,4-dinitrophenylhydrazone of 6, 10271-09-7; 10, 10271-10-0; 2,4-dinitrophenylhydrazone of 10, 10271-11-7.

Rearrangement of α-Bromocamphoric Anhydride[1a-c]

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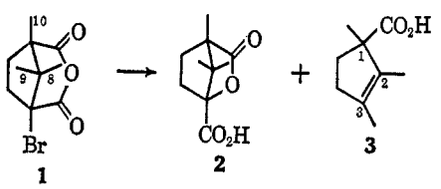
α-Bromocamphoric anhydride (1) is converted by aqueous sodium carbonate into camphanic acid (2) and the rearranged product laurolenic acid (3). Camphanic acid is not converted to laurolenic acid under the same conditions, and thus is not an intermediate in the rearrangement. D-(−)-α-Bromocamphoric anhydride-9,9,9-d_3 was prepared from D-(+)-isoketopinic acid (14) by lithium aluminum deuteride reduction of the corresponding methyl ester to 9-hydroxyisoborneol-2,9,9-d_3, selective preparation of the 9-*p*-toluenesulfonate, lithium aluminum deuteride reduction to D-(−)-isoborneol-2,9,9,9-d_4, Sarett oxidation to D-(+)-camphor-9,9,9-d_3 (shown to be optically pure), oxidation with selenium dioxide and then alkaline hydrogen peroxide to D-(+)-camphoric acid-9,9,9-d_3, and bromination. Rearrangement of this labeled bromo anhydride produced D-(+)-laurolenic acid in which the deuteriomethyl group is located exclusively at the 2 position. Consequently the rearrangement involves stereospecific migration of the methyl which is *cis* to the carboxyls of α-bromocamphoric acid. These results indicate that methyl migration is concerted with bromide loss, and that neither α-carboxylate participation in bromide loss (through an α-lactone or its mechanistic equivalent) or carbene formation is involved.

In 1885 Fittig and Woringer reported that α-bromocamphoric anhydride (1) was converted by boiling water into a mixture of an unsaturated acid, laurolenic acid (called lauronolic acid in the older literature), and the lactonic acid, camphanic acid (2).[2] Aschan[3] found that the yield of laurolenic acid was improved somewhat at higher pH, and that the α-chloro anhydride gave similar results. The correct structure for laurolenic acid (3) was first suggested by Lapworth,[4] and this assignment has been confirmed by subsequent physical and degradative evidence[5-9] and our recent synthesis.[10]



Although laurolenic acid is the minor product of the bromo anhydride hydrolysis (15% yield), it is in many respects the more interesting owing to the unusual combination of structural changes which accompany its formation. The rearrangement of bromonorcedrenedicarboxylic acid[11,12] is the only other known reaction in which a 1,2-methyl migration accompanies loss of bromide and carbon dioxide from an α-bromo acid. In order to allow a mechanistic interpretation of this unusual rearrangement we wished to learn (a) whether there is any stereospecificity of methyl migration, and if so which methyl migrates, and (b) which of the two carboxyl groups is lost, since the symmetry of this system (unlike that of the cedrene derivative) does not allow an unequivocal *a priori* assignment. We have attempted to answer these questions by studying the rearrangement of suitably labeled α-bromocamphoric anhydride. At this time we are able to report that the methyl migration is completely stereospecific, involving only the methyl which is *cis* to the two carboxyl groups; work is in progress which will ascertain whether carboxyl loss is equally specific.

One of the initial points to be established about the bromo anhydride rearrangement was that camphanic acid (2) is not an intermediate in the formation of laurolenic acid (3). It is known, for example, that laurolenic acid is produced upon pyrolysis of the lactonic acid.[2,3,9,13,14] However, the conditions which convert the bromo anhydride reproducibly to 14–16% laurolenic acid and 55–65% camphanic acid leave camphanic acid unchanged. Thus its intermediacy in the bromo anhydride rearrangement is excluded, and the two products are formed by competitive reaction pathways.

(1) (a) Abstracted in part from the Ph.D. dissertation of A. P. L., Indiana University, 1966; (b) supported in part by National Science Foundation Research Grant GB-1606; (c) presented in part at the 2nd Midwest Regional Meeting of the A. C. S., Lawrence, Kan., Oct 27–28, 1966; (d) U. S. Government Grantee, 1960–1962, administered by the Institute of International Education; Coulter Jones Scholar, University of Arkansas, 1965–1966; (e) correspondence regarding this work should be directed to W. L. M. at this address.

(2) R. Fittig and L. Woringer, *Ann.*, **227**, 1 (1885).

(3) O. Aschan, *Ber.*, **27**, 2112, 3504 (1894); *Ann.*, **290**, 185 (1896).

(4) A. Lapworth, *Brit. Assoc. Advance. Sci. Rept.*, 299 (1900); A. Lapworth, *J. Chem. Soc.*, **77**, 1053 (1900); A. Lapworth and W. H. Lenton, *ibid.*, **79**, 1284 (1901).

(5) J. F. Eykman, *Rec. Trav. Chim.*, **12**, 157 (1893); *Chem. Weekblad*, **4**, 41 (1906).

(6) J. Bredt, J. Houben, and P. Levy, *Ber.*, **35**, 1286 (1902).

(7) W. A. Noyes and C. G. Derrick, *J. Am. Chem. Soc.*, **31**, 669 (1909); **32**, 1061 (1910); W. A. Noyes, *ibid.*, **31**, 1368 (1909); **32**, 1068 (1910); W. A. Noyes and L. P. Kyriakides, *ibid.*, **32**, 1064 (1910).

(8) A. W. Crossley and N. Renouf, *J. Chem. Soc.*, **89**, 26 (1906).

(9) F. Tiemann and H. Tigges, *Ber.*, **33**, 2935 (1900).

(10) W. L. Meyer, A. P. Lobo, and E. T. Marquis, *J. Org. Chem.*, **30**, 181 (1965).

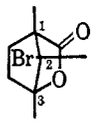
(11) L. Ruzicka and J. A. vanMelsen, *Ann.*, **471**, 40 (1929); L. Ruzicka, Pl. A. Plattner, and G. W. Kusserow, *Helv. Chim. Acta*, **25**, 85 (1942); Pl. A. Plattner, G. W. Kusserow, and H. Kläui, *ibid.*, **25**, 1345 (1942).

(12) G. Stork and R. Breslow, *J. Am. Chem. Soc.*, **75**, 3292 (1953). They suggested (without evidence) that this reaction is "essentially one of solvolysis of a neopentyl type, undoubtedly facilitated by cancellation of the positive charge on the relevant carbonyl group by formation of a carboxylate anion."

(13) J. Bredt and A. Amann, *J. Prakt. Chem.*, [2] **87**, 12 (1913).

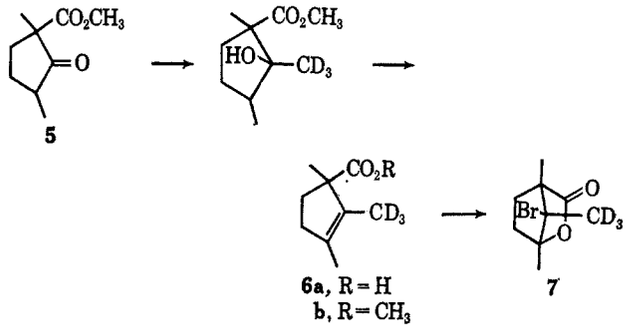
(14) G. S. Skinner, *J. Am. Chem. Soc.*, **45**, 1498 (1923).

The technique chosen to follow the methyl groups through the rearrangement involved specific deuterium labeling of either the 8- or the 9-methyl[15] of the bromo anhydride and nmr analysis of the product. Thus we needed an unequivocal assignment of the methyl resonances in the spectrum of laurolenic acid or a suitable derivative. The acid itself is not useful for such analysis, for, although the C-1 methyl absorbs as a sharp singlet at τ 8.77, the resonances of the two allylic methyls at C-2 and C-3 are broad as a result of homoallylic spin coupling and are nearly superimposed at τ 8.38.[10] In spectra of the corresponding methyl ester and amide the C-2 and C-3 methyl resonances are resolvable (τ 8.42 and 8.50 in the former and 8.33 and 8.42 in the latter[10]), but owing to their breadth they still overlap substantially near the base line. This partial overlap would render quantitative deuterium analysis difficult by the nmr technique, particularly if methyl migration proved to be nonspecific so that only part of the deuterium content was located in each methyl group.



4

The bromo lactone **4**, mp 194°,[3,9,14,16,17] is a well-characterized derivative of laurolenic acid, and its nmr spectrum proved to be ideally suited for potential deuterium analysis. In the absence of homoallylic coupling all three quaternary methyl resonances of this derivative are sharp singlets, they occur well away from the methylene proton signals of C-4 and C-5, and they are cleanly separated from each other, falling at τ 8.38, 8.50, and 8.75. The τ 8.75 resonance, from its chemical shift, clearly results from the C-1 methyl (CH_3CCO_2R).[18] The other two methyl resonances were assigned to the appropriate methyls by preparation of the bromo lactone of *dl*-laurolenic acid in which the 2-methyl was specifically deuterated. The synthesis was identical with our published synthesis of *dl*-laurolenic acid,[10] save that trideuteriomethyl iodide[19] was substituted for methyl iodide in preparation of the Grignard reagent which is added to 2,5-dimethyl-2-carbomethoxycyclopentanone (**5**). The *dl*-laurolenic acid-d_3 so derived (**6a**) retains the sharp 1-methyl absorption at τ 8.77 and has only a three-proton allylic methyl resonance at 8.38. The spectrum of its bromo lactone (**7**) shows sharp singlets at τ 8.75 (C-1) and 8.50 (C-3), but is completely devoid of the 8.38 singlet, which therefore must result from the 2-methyl of the parent (**4**).



5 **6a**, R = H; **b**, R = CH_3 **7**

In order to prepare α-bromocamphoric anhydride with a specific deuterium label in either the 8- or the 9-methyl group, we utilized the known tendency of camphor to undergo electrophilic π substitution as an introduction to compounds in which the *gem*-methyls are functionally distinguished. Bromination of camphor or 3-bromocamphor in chlorosulfonic acid solution produces π-bromo derivatives,[20] and these have been clearly shown to contain the bromine exclusively on the carbon which is *anti* to the ketonic group (C-9).[21-23] D-(+)-Camphor itself leads to a partially racemic product under these conditions,[20] but substantially more optical activity is retained if 3-bromocamphor is brominated.[20] In fact it will be shown below that the retention of configuration is complete in the latter case. Inasmuch as it seemed possible that the configurational result as well as the isotopic scrambling result of the bromoanhydride rearrangement would be of use in deducing its mechanism, we chose to carry out 9 functionalization of 3-bromocamphor.

The early stages of our synthesis of D-(+)-camphor-9,9,9-d_3 were adapted from the work of Corey (Scheme I).[24,25] D-(+)-Camphor (**8**) was converted to D-(+)-isoketopinic acid (**14**) by the sequence 3-bromination in acetic acid, 9-bromination in chlorosulfonic acid,[24] 3-debromination by zinc–hydrogen bromide,[24] 9-bromide displacement by acetate,[26] saponification,[25] and chromic anhydride–manganous sulfate oxidation[25] (**8** → **9** → **10** → **11** → **12** → **13** → **14**, Scheme I). To determine whether variable amounts of racemization were occurring at any stage in this sequence, particularly in the 9-bromination reaction (**9** → **10**) which involves several carbon-skeleton rearrangements of the intermediate carbonium ions, the molecular amplitude (*a*) of the Cotton effect of each preparation of isoketopinic acid (**14**) was carefully determined. This was identical within experimental error (±1.2%) from run to run; so either no racemization takes place or the amount of racemization is constant. Subsequent data exclude the latter alternative; thus these intermediates are optically pure.

Diazomethane esterification of the keto acid **14** followed by reduction of the keto ester with a 50% molar excess of lithium aluminum hydride at 72° produced a mixture of two diols in the ratio 9:1, the pre-

(15) We retain the camphor numbering system for the methyl groups in camphoric acid and its anhydride, *i.e.*, C-9 in these derivatives is the methyl which is *trans* to the carboxyls; *cf.* structures **1** and **8**.

(16) W. A. Noyes and C. E. Burke, *J. Am. Chem. Soc.*, **34**, 174 (1912).

(17) O. Aschan, *Acta Soc. Sci. Fennicae*, **21**, 1 (1895); *Chem. Zentr.*, **66II**, 967 (1895).

(18) The methyl resonances of CH_3CCO_2H or CH_3CCO_2R of 43 compounds selected from our own unpublished results and the literature fall within the range τ 8.70–8.93 in the absence of adjacent anisotropic substitution: (a) "High-Resolution NMR Spectra Catalog," Vol. 1 and 2, Varian Associates, Palo Alto, Calif., 1962, 1963; (b) E. Wenkert, A. Afonso, P. Beak, R. W. J. Carney, P. W. Jeffs, and J. D. McChesney, *J. Org. Chem.*, **30**, 713 (1965); (c) K. L. Williamson, T. Howell, and T. A. Spencer, *J. Am. Chem. Soc.*, **88**, 325 (1966).

(19) F. A. Cotton, J. H. Fasmacht, W. D. Horrocks, and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).

(20) H. Nishimitsu, M. Nishikawa, and H. Hagiwara, *Proc. Japan Acad.*, **27**, 285 (1951); *Chem. Abstr.*, **46**, 6112 (1952).

(21) E. Wedekind and R. Stusser, *Ber.*, **56**, 1557 (1923).

(22) T. Hasselström, *J. Am. Chem. Soc.*, **53**, 1097 (1931).

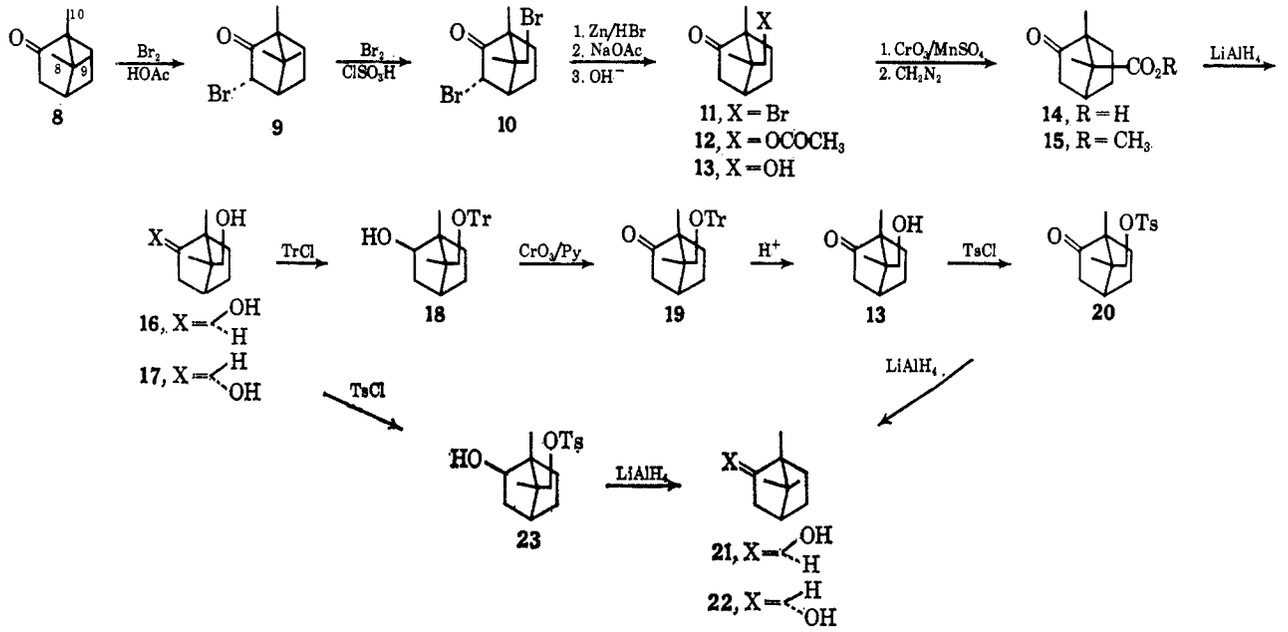
(23) Y. Asahina and M. Ishidate, *Ber.*, **66**, 1673 (1933); **68**, 947 (1935).

(24) E. J. Corey, S. W. Chow, and R. A. Scherrer, *J. Am. Chem. Soc.*, **79**, 5773 (1957).

(25) E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *ibid.*, **81**, 6305 (1959).

(26) P. C. Guha and S. C. Bhattacharyya, *J. Indian Chem. Soc.*, **21**, 271 (1944).

SCHEME I



ponderant isomer being 9-hydroxyisoborneol (**16**) and the minor isomer being 9-hydroxyborneol (**17**).[27] Reaction of this mixture with 1.5 equivalents of *p*-toluenesulfonyl chloride in pyridine proceeded in nearly quantitative yield to produce an oily *p*-toluenesulfonate (**23**) which clearly corresponded to a monotosyl derivative according to its nmr spectrum. That the selective *p*-toluenesulfonation occurs at the primary hydroxyl was confirmed by Sarett oxidation[28] to a keto tosylate (**20**) which was also obtained from 9-hydroxycamphor (**13**), and by independent preparation of the hydroxy tosylate **23** by borohydride reduction of the keto tosylate **20**. The crude hydroxy tosylate (prepared from the 9:1 mixture of stereoisomeric diols) was reduced by excess lithium aluminum hydride to a 9:1 mixture of isoborneol (**21**) and borneol (**22**)[29] containing 5–10% of the diols **16** and **17**.[30] Sarett oxidation[28] of the isoborneol–borneol mixture affords D-(+)-camphor, the over-all yield from keto ester **15** being 45%. The camphor obtained in this way is identical in all respects, including its optical rotation and the molecular amplitude (a) of its optical rotatory dispersion curve, with the starting material used for the synthesis. Consequently all intermediates in the synthesis, as well as the ultimate camphor, are optically pure ($\pm 0.5\%$, the uncertainty in determination of a).

Before conditions were developed to tosylate the diol **16** at the 9-hydroxyl selectively, an alternate, but less efficient, path from diol **16** to isoborneol (**21**) was explored. The diol **16** was converted to a 9-monotrityl ether (**18**) which was oxidized by the chromium trioxide–pyridine complex[28] to the keto trityl ether **19**. This was identical with the ether prepared by tritylation of ketol **13**, and the trityl group could be removed by methanolic hydrogen chloride to produce the ketol. Although they were not used in the subsequent synthesis of camphor-d_3, these reactions were not without utility, for they served to confirm that no solvolytic rearrangements of the carbon skeleton occurred in the reduction, tritylation, or detritylation steps. The ketol **13** was converted to the keto *p*-toluenesulfonate (**20**) which was reduced by lithium aluminum hydride to the 9:1 mixture of isoborneol and borneol.[29]

Repetition of the sequence **14** → **15** → **16** → **23** → **21** → **8** with the substitution of lithium aluminum deuteride for lithium aluminum hydride in the steps **15** → **16** and **23** → **21** produced D-(+)-camphor-9,9,9-d_3 (**24**) by way of the corresponding 2,9-perdeuterated intermediates. These derivatives had nmr spectra which were identical with those of their protio analogs except the C-2 and C-9 proton resonances were absent and effects of spin coupling to C-2 and C-9 protons had disappeared from the remainder of the spectra. The mass spectrum of the camphor-d_3 showed that it consisted to the extent of 98% as a d_3 species, 2% as d_2, and undetectable amounts of d_1 or d_0.[31] We have commented elsewhere on the unusual rotatory dispersion properties of the camphor-d_3.[32]

The preferred procedure for conversion of D-(+)-camphor-9,9,9-d_3 to D-(−)-3-bromocamphoric anhydride-9,9,9-d_3[15] (**27**) involved selenium dioxide oxidation[33] to D-(−)-camphorquinone-9,9,9-d_3 (**25**), alkaline hydrogen peroxide cleavage[34] to D-(+)-camphoric acid-9,9,9-d_3 (**26**), and treatment of the latter with phosphorus pentachloride and bromine (Scheme II).[3] Nmr spectra of the deuterated derivatives were compared with those

(27) Compare this stereoselectivity with the 9:1 ratio of isoborneol–borneol produced by lithium aluminum hydride reduction of camphor: D. S. Noyce and D. B. Denney, *J. Am. Chem. Soc.*, **72**, 5743 (1950). We did not separate the diols **16** and **17**. The ratio was determined by integration of the C-methyl resonances in the nmr spectrum of the mixture; the configurational assignment follows from conversion of the mixture to a 9:1 mixture of isoborneol and borneol. With less than this excess of hydride at 72° or with this amount of hydride at 25°, only the keto group was reduced.

(28) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *ibid.*, **75**, 422 (1953).

(29) The relative configurations and proportions of the alcohols were deduced from the nmr spectrum of the mixture; see the Experimental Section.

(30) If the tetrahydrofuran solvent is not scrupulously dried prior to use in the reduction, a much higher proportion of diol (25–35%) is produced.

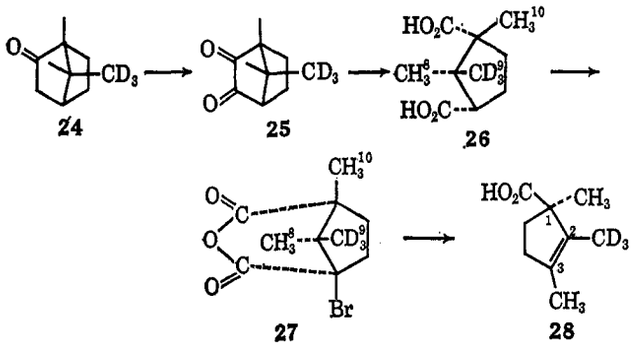
(31) We are grateful to Professor J. Wolinsky and Dr. D. Dimmel of Purdue University, for the mass spectra.

(32) W. L. Meyer and A. P. Lobo, *J. Am. Chem. Soc.*, **88**, 3181 (1966).

(33) W. C. Evans, J. M. Ridgion, and J. L. Simonsen, *J. Chem. Soc.*, 137 (1934).

(34) M. O. Forster and H. Holmes, *ibid.*, **93**, 242 (1908).

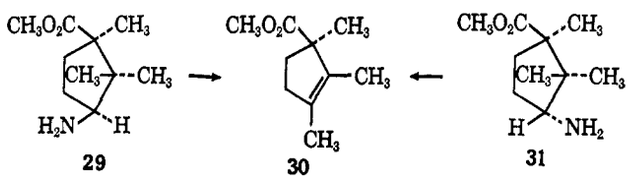
SCHEME II



of their protio analogs, and in each instance the spectra were identical with the exception that one of the three C-methyl singlets (C-9) was completely absent from the spectrum of the deuterio derivative and another C-methyl singlet (C-8) was substantially narrower (as a result of the decreased long-range coupling) in those spectra. The mass spectrum of the deuteriobromo anhydride **27** provided evidence for the presence of at least 98% of the trideuterio species, 2% of the dideuterio derivative, and inconsequential quantities of less deuterated species.[31]

Exposure of the bromo anhydride-d_3 (**27**) to 15% sodium carbonate produced labeled laurolenic acid (**28**) (Scheme II). The nmr spectrum of this derivative had a broad, three-proton methyl resonance at τ 8.38 (2-methyl or 3-methyl) and a sharp, three-proton singlet at 8.75 (1-methyl). Consequently the labeled methyl is at C-2 and/or C-3, but not at C-1. The corresponding bromo lactone (**7**) had an nmr spectrum with only two sharp methyl singlets, at τ 8.50 (3-methyl) and at 8.75 (1-methyl). There was no observable trace of the τ 8.38 2-methyl resonance, and careful integration of the spectrum showed that the two methyl resonances had the same relative intensities (±2%) as do those of the parent protio bromo lactone (**4**). Consequently *it is the 8-methyl, trans to the departing bromine in the bromo anhydride, which migrates exclusively in the rearrangement.* It is coincidental that the rearrangement product was identical in the position of label with the *dl*-laurolenic acid-d_3 (**6a**) produced by synthesis. However this good fortune allowed a direct comparison of the infrared and nmr spectra of the two samples and their derived bromo lactones; these, of course, were completely superimposable.

Before discussing the implications of this tracer experiment on the mechanism of the bromo anhydride rearrangement, it is pertinent to consider such data as are available concerning the configurational consequences of the reaction. Although there is no unequivocal evidence concerning its optical purity, several authors[9,13,16] have found substantially identical rotations for the dextrorotatory laurolenic acid which results from rearrangement of the (−)-bromo anhydride.[35,36] This (+)-laurolenic acid affords the (+)-bromo lactone. Noyes and Skinner[14,37] reported that nitrosation of methyl *cis*-3-amino-1,2,2-trimethylcyclopentanecarboxylate (**29**) or its *trans* isomer **31**, both of which were derived from D-(+)-camphoric acid by sequences which should not affect the C-1 configuration, afforded a methyl laurolenate (**30**) which upon hydrolysis and bromination gave the dextrorotatory bromo lactone. Since the C-1 carboxyl is protected as an ester during the deamination process, it is improbable that any configurational change occurred at that center. If this is true, (+)-laurolenic acid must have the same C-1 configuration as does D-(+)-camphoric acid, and the predominant or exclusive course of the bromo anhydride rearrangement involves retention of configuration at C-1.[38]



The pathways which have been considered for conversion of the bromo anhydride to laurolenic acid are protrayed in Scheme III. Presumably the first stage involves saponification of the anhydride to the dibasic acid, which at pH 11 should exist predominently as its dibasic salt **32**.[39] One possible course of solvolysis of the bromo salt involves participation of the α-carboxylate to form an intermediate α-lactone (**33**)[40,41] or its mechanistic equivalent.[42] Such species are commonly considered to be intermediates in solvolyses of α-halocarboxylic acid salts, which thus proceed with retention of configuration (double inversion).[41,42] Three modes of decomposition of such an α-lactone have been considered: path D in which the lactone opens without methyl participation to produce the α-carbonium ion **35** which is not configurationally protected on either side, path E in which lactone opening is accompanied by migration of the β-methyl *from the side of the ring trans to the leaving oxygen* (methyl-9),

(35) The (−)-bromo anhydride corresponds to D-(+)-camphoric acid and D-(+)-camphor.

(36) This is not true for the laurolenic acid obtained by pyrolysis of camphanic acid.[9,13,16] Although invariably dextrorotatory when prepared from (−)-camphanic acid (which in turn is the product derived from the (−)-bromo anhydride (see ref 35), the magnitude of the rotation is variable from report to report, never exceeding that recorded for laurolenic acid derived from the bromo anhydride. It is possible that the mechanism of the camphanic acid pyrolysis is such that partial racemization of the unsaturated acid is its direct result, the extent of racemization depending on reaction conditions. It is also possible, however, that the variable rotations result from contamination of laurolenic acid by camphonenic acid, a reported by-product of the pyrolysis (see ref 9). These points are under consideration in our laboratories.

(37) W. A. Noyes and G. S. Skinner, *J. Am. Chem. Soc.*, **39**, 2692 (1917).

(38) Although the optical purity of the laurolenic acid has not been directly determined, we feel it is unlikely that any racemization accompanies the halo anhydride rearrangement. It seems improbable that a constant value of rotation would be obtained for the acid produced in several laboratories under different reaction conditions or that identical values would result for laurolenic acid obtained from either the bromo or the chloro anhydride[14] if partial racemization were involved. Furthermore, none of the reasonable mechanisms which accommodate the stereospecific methyl migration allow any simultaneous racemization.

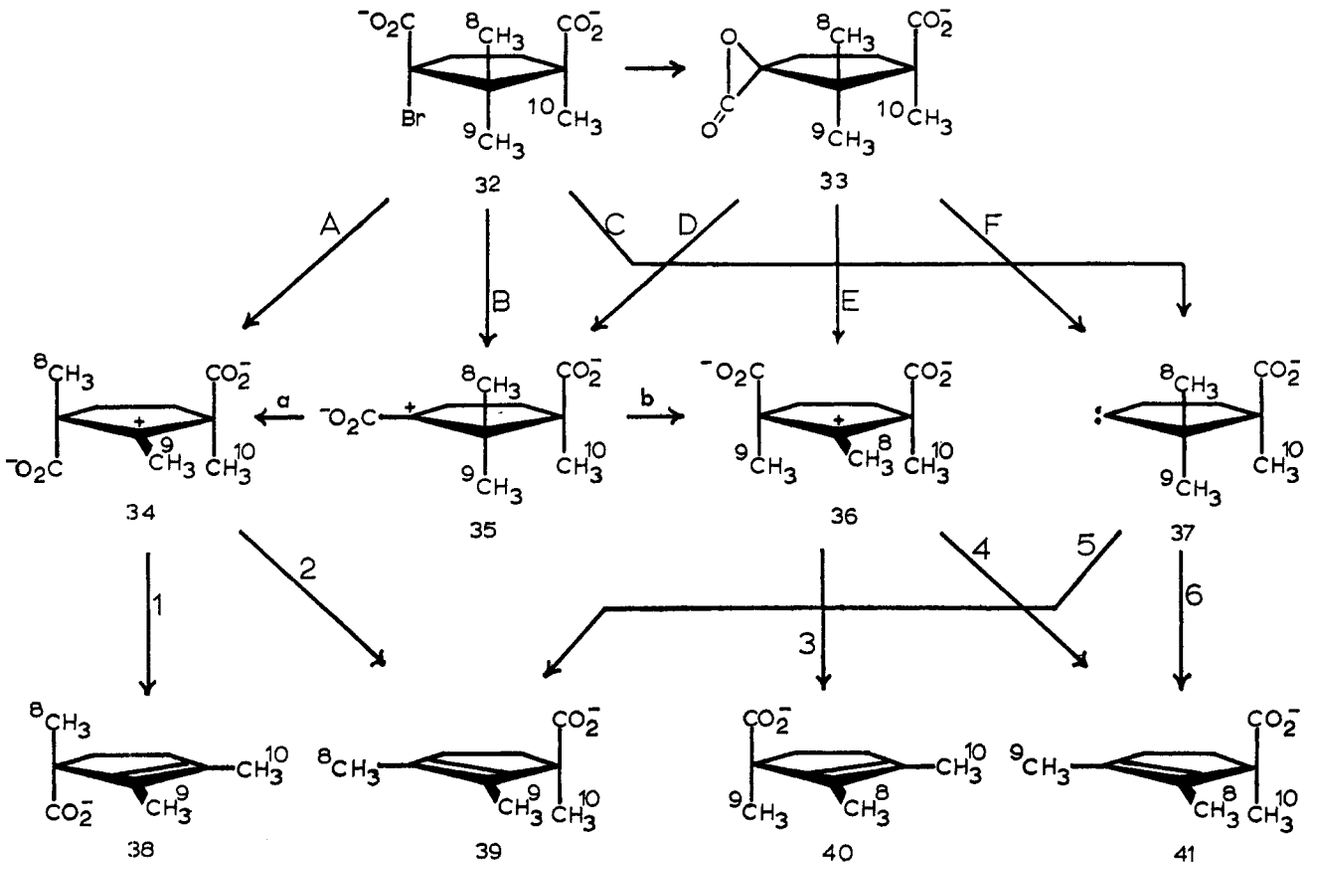
(39) The pK values of camphoric acid are 4.64 and 5.87; *cf.* W. Dieckmann and A. Hardt, *Ber.*, **52**, 1134 (1919). Introduction of the 3-bromine should not have a large influence on the second ionization, which almost certainly involves the 1-carboxyl.

(40) J. F. King and P. de Mayo in "Molecular Rearrangements," Vol. II, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 803.

(41) (a) C. M. Bean, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 303 (1936); (b) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **61**, 1576 (1939); (c) S. Winstein, *ibid.*, **61**, 1635 (1939); (d) S. Winstein and R. B. Henderson, *ibid.*, **65**, 2196 (1943); (e) E. Grunwald and S. Winstein, *ibid.*, **70**, 841 (1948); (f) *cf.* A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 116–120.

(42) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman, and A. D. Scott [*J. Chem. Soc.*, 1252 (1937)] prefer to consider α-carboxylate participation as an electrostatic stabilization of the α-carbonium ion rather than actual C–O bond formation. The stereochemical consequence of this process are the same as α-lactonization.

SCHEME III



and path F in which more or less concerted loss of the lactone ring as carbon dioxide generates a carbenoid species (**37**) at C-3.[40] Path D should be followed by a nonspecific methyl migration, methyl-8 and methyl-9 rearranging to approximately equal extents to produce a nearly 50:50 mixture of β-carbonium ions **34** and **36**.[43] β-Carbonium ion **36** alone is the product of path E. As in ion **35**, methyl migration to the electron-deficient center in carbene **37** should be nonselective,[43] and should afford a mixture of products **39** and **41** by paths 5 and 6, respectively. The final stage of the ionic processes, leading to product from ions **34** or **36**, is loss of one of the carboxylate groups as carbon dioxide. The product composition will depend on whether this decarboxylation is concerted with or subsequent to formation of the ion. If decarboxylation accompanies methyl migration, one of the two carboxyls could well be specifically involved and **34**, for example, could lead either to **38** alone (C-1 carboxyl loss) or **39** alone (C-3 carboxyl loss); if the ion **34** had discrete existence, its symmetry requires 50:50 loss of each carboxyl, and the product should be a 50:50 mixture of **38** and **39**, *which differs only in the origin of the methyls on C-1 and C-3*. Similarly, ion **36** could follow path 3 (C-1 decarboxylation concerted with methyl migration), path 4 (C-3 decarboxylation concerted with methyl migration), or both, and lead to products **40** or **41**, or both. Similar pathways (A, B, and C) lead directly from the bromo anion **32** to ions **34**, **35**, and **36**, or carbene **37** and thence to products. Pathway A involves a backside (methyl-8) alkyl shift concerted with bromide loss; pathway B involves solvolysis of bromine with no methyl participation and thus produces **35** which should give both **34** and **36**;[43] pathway C is α-bromodecarboxylation to the carbene **37**.[40] It should be noted that we have not included as likely possibilities the solvolysis of bromide or α-lactone oxygen with concerted *cis*-methyl migration, *i.e.*, **32** → **36** stereospecifically or **33** → **34** stereospecifically. There is no analogy for this type of stereospecific frontside participation in nucleophilic rearrangements of the type RABX → ABR + X, whereas stereospecific *trans* rearrangements are ubiquitous.[44] However, if *cis*-rearrangement processes were considered, their structural consequences would be identical with those of a *trans* shift in the other solvolytic series (bromide **32** or lactone **33**).

The products to be expected for each of the processes of Scheme III, together with the deuterium distribution from an initial 9-deuteriomethyl derivative and the configuration of the product are summarized in Table I. Of the sequences discussed, only pathways A-1 and/or A-2 predict sole location of the deuteriomethyl group at C-2 in a product of retained configuration. Thus the bromo acid rearrangement proceeds by a *trans*-methyl shift which accompanies bromide loss, and neither an α-lactone nor a carbene intervenes. Whether the carboxyl loss is specific (paths 1 or 2) or

(43) The methyl-8 to methyl-9 migration might well not be exactly 50:50 even if isotope effects are ignored, owing to differential buttressing of the methyls by the C-1 carboxylate and methyl-10, respectively. It is also possible that the C-1 carboxylate could provide some preferential stabilization of the developing positive charge as one of the methyls migrated. We doubt that these effects would be sufficient to direct reaction *via* path a to the complete exclusion of path b. Paths B, C, D, and F are excluded by the data only if this assumption is justified.

(44) D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 5.

TABLE I

PRODUCTS OF REARRANGEMENT PATHWAYS IN SCHEME III

Pathway	Products	Position of deuterated methyl	Configuration
A-1	**38**	2	Retained
A-2	**39**	2	Retained
A-1 and A-2	**38** and **39**	2	Retained
B-1,[a] B-2,[a] B-3,[a] and B-4[a]	**38, 39, 40,** and **41**	1, 2, and 3	Partially racemized (net retention)
C-5 and C-6	**39** and **41**	2 and 3	Retained
D-1,[a] D-2,[a] D-3,[a] and D-4[a]	**38, 39, 40,** and **41**	1, 2, and 3	Partially racemized (net retention)
E-3	**40**	1	Inverted
E-4	**41**	3	Retained
E-3 and E-4	**40** and **41**	1 and 3	Racemic
F-5 and F-6	**39** and **41**	2 and 3	Retained

[a] Both a and b.

random (paths 1 and 2) will be determined by rearrangement of camphor-8,8,8-d_3, synthesis of which is in progress.

It is interesting to observe that this result indicates that in this system β-methyl participation in bromide solvolysis (**32** → **34**) is apparently favored over α-carboxylate participation (**32** → **33**). This may not, however, be a general relationship. The solvolyzing bromide of the bromocamphorate ion is tertiary, and even in solvolytic substitutions of simple α-bromocarboxylate salts participation of the α-carboxylate group is of much less importance with tertiary bromides (*e.g.*, α-bromoisobutyrate) than it is with primary or secondary derivatives (*e.g.*, α-bromopropionate).[41e] In addition, carboxylate participation in the present system involves formation of a small spiro ring system, and the attendant ring strain undoubtedly renders this pathway less effective than it would be in an acyclic or larger cyclic compound. Further studies will be necessary to assess the importance of these factors in the general case.

Experimental Section[45]

(+)-Laurolenic Acid (3) from D-(−)-α-Bromocamphoric Anhydride.—The procedure is a modification of that of Aschan.[3] A suspension of 1.582 g (0.0061 mole) of D-(−)-α-bromocamphoric anhydride[3] (mp 215°) in 150 ml of 15% sodium carbonate solution was warmed on the steam bath until solution was complete, 2.5–3.5 hr being required. The solution (pH 11) was cooled, neutralized to pH 8 with concentrated sulfuric acid, allowed to stand overnight, saturated with salt, and continuously extracted with ether for 2 days to afford 0.156 g (17%) of crude (+)-laurolenic acid. Distillation afforded 0.141 g (15%) of pure (+)-acid:[38] n^{27}D 1.4740; bp (bath temperature) 75–80° (1–1.5 mm); $[\alpha]^{23}$D +155° (*c* 0.64, $CHCl_3$); RD (*c* 0.116) positive plain curve to 250 mμ, $[\alpha]^{29}_{290}$ +1340°, $[\alpha]^{29}_{250}$ +6730° [lit.[16,37] n^{25}D 1.4792, bp 139–140° (17 mm), $[\alpha]^{25}$D +152° (*c* 4.53, absolute ethanol)]. Infrared and nmr spectra of this sample were identical with those of synthetic *dl*-laurolenic acid.[10] Spectra of the methyl ester, prepared from the (+) acid with diazomethane, were identical with spectra of the synthetic *dl* ester.[10] The (+)-bromo lactone (mp 194°) was identical in melting point and infrared and nmr spectra with the *dl*-bromo lactone[10] (lit. melting point of (+)-bromo lactone 187°,[3,9,16] 194°;[14,37] $[\alpha]$D +51.0°[14]). The (+)-bromo lactone has a plain positive RD curve between 450 and 260 mμ (*c* 0.115), $[\alpha]_{450}$ +100°, $[\alpha]_{400}$ +140°, $[\alpha]_{300}$ +530°, $[\alpha]_{260}$ +1540°.[46] Its mass spectrum has prominent peaks at *m/e* 125, 109, 93, and 91.[31] The rearrangement was done several times using this procedure; yields varied from 14 to 16%. The yield was much less reproducible when Aschan's[3] isolation technique (steam distillation) was applied on this small scale.

The aqueous solution remaining after extraction of (+)-laurolenic acid was acidified to pH 1 with concentrated sulfuric acid, allowed to stand overnight, saturated with salt, and continuously extracted with ether for 2 days to afford 0.612 g (64%) of (−)-camphanic acid (**2**) which was purified by sublimation or recrystallization from water to afford colorless rhombic crystals: mp 200°; $\lambda_{max}^{CHCl_3}$ 3.4 (broad), 5.60, 5.78 μ; nmr ($CDCl_3$) τ 7.95 (m), 8.86 (s), 8.90 (s), 8.98 (s); RD (*c* 0.10) negative plain curve to 250 mμ, $[\alpha]^{29}_{250}$ −120° (lit. mp 200–201°;[47] $[\alpha]$D −9.3°[48]).

Substitution of (−)-camphanic acid (**2**) for the bromo anhydride in this procedure led to its recovery in 99% yield; no laurolenic acid was obtained. In control experiments as little as 1–2% of added laurolenic acid was isolable by extraction techniques used.

Methyl *dl*-1,3-Dimethyl-2-trideuteriomethyl-2-hydroxycyclopentane-1-carboxylate.—The procedure was identical with that used for preparation of the protio analog,[10] the only difference being the use of trideuteriomethyl iodide[19] instead of methyl iodide. The crude mixture of hydroxy ester and keto ester **4** was used for the dehydration step. A pure sample of the hydroxy ester (isomer mixture) was collected by gas chromatography. It had $\lambda_{max}^{CHCl_3}$ 2.80, 4.49, and 5.82 μ; its nmr spectrum was identical with that of the protio counterpart[10] save that resonances owing to the 2-methyl were absent.

Methyl *dl*-1,3-Dimethyl-2-trideuteriomethylcyclopent-2-ene-1-carboxylate (6b).—Dehydration of the deuterated hydroxy ester with 50% sulfuric acid by the procedure used with its protio analog[10] yielded crude deuterio ester **6b** which was purified by gas chromatography. It had $\lambda_{max}^{CHCl_3}$ 4.50, 4.56, and 5.78 μ. Its nmr spectrum was identical with that of synthetic *dl*-methyl laurolenate[10] save that the τ 8.50 methyl resonance was absent.

***dl*-1,3-Dimethyl-2-trideuteriomethylcylopent-2-ene Carboxylic Acid (6a).**—Eschenmoser hydrolysis[49] as used for the preparation of *dl*-laurolenic acid[10] afforded 80% of crude trideuteriolaurolenic acid (**6a**): $\lambda_{max}^{CHCl_3}$ 2.8 (broad), 4.48, 4.55, 5.89 μ; nmr (CCl_4) τ 8.38 (less broad than in the spectrum of laurolenic acid, three protons), 8.77 (s). The crude acid was converted to the bromo lactone **7**, which was obtained by sublimation as white rosettes: mp 194°; $\lambda_{max}^{CHCl_3}$ 4.12, 4.17, 5.59 μ; nmr ($CDCl_3$) τ 8.50 (s), 8.77 (s). This nmr spectrum was identical with that of the protio bromo lactone except for the absence of the τ 8.38 singlet.

D-(+)-Camphor (8).—This starting material, obtained from Eastman Kodak Co., had mp 178–179°; $[\alpha]^{23}$D +49.5° (*c* 1.2); RD (*c* 0.12), $[\alpha]^{24}_{550}$ +50°, $[\alpha]^{24}_{500}$ +75°, $[\alpha]^{24}_{450}$ +125°, $[\alpha]^{24}_{400}$ +175°, $[\alpha]^{24}_{350}$ +395°, $[\alpha]^{24}_{330}$ +760°, $[\alpha]^{24}_{320}$ +1240°, $[\alpha]^{24}_{312}$ +1942° (peak), $[\alpha]^{24}_{300}$ +1405°, $[\alpha]^{24}_{290}$ −930°, $[\alpha]^{24}_{274}$ −2195° (trough), $[\alpha]^{24}_{260}$ −1915°; a = +62.89 ± 0.31 [lit. $[\alpha]^{20}$D +40.2° (*c* 1.0) and +47.3° (*c* 50);[50] $[\alpha]_{312.5}$ +2009° (peak), $[\alpha]_{265}$ −3305°

(45) Infrared spectra were obtained on Perkin-Elmer Model 21, 137, and 337 spectrophotometers. Nmr spectra were obtained from dilute solutions with tetramethylsilane as internal standard using a Varian A-60 spectrometer or a Varian DP-60 spectrometer operating at 60 Mcps and equipped with a Model 3506 flux stabilizer. First-order multiplets in nmr spectra are described by use of abbrevations, s for singlet, d for doublet, t for triplet, q for quartet, neq for AB quartet; m is used for multiplets not described by other symbols. Rotatory dispersion (RD) spectra were run in methanol solution on a Durrum-Jasco Model ORD/UV-5 spectropolarimeter with a 500-w dc Xenon arc tube, at a scanning speed of 13.3 mμ/min and a sensitivity of 300 mdeg. Unless otherwise stated the accuracy in measuring molecular amplitudes (a) of RD curves is ±2%; uncertainty in the rotation at a given wavelength is ±20°. Optical rotations at the sodium D line were observed in 95% ethanol solution unless otherwise stated, using a Rudolph Model 80 polarimeter and a 2-dm polarimeter tube. Gas chromatographic purifications were run on a Perkin-Elmer Model 154D vapor fractometer with helium as carrier gas using a 2-m 9% silicone gum (SE 30) on Chromosorb W column at 125°. Microanalyses were by Alfred Bernhardt, Mülheim (Ruhr), Germany (indicated B), and by Midwest Microanalytical Laboratory, Indianapolis, Ind. (indicated M). Melting points were observed in sealed evacuated capillary tubes unless marked (o), in which case open capillaries were used. Melting points are corrected for stem exposure unless otherwise indicated.

(46) This spectrum was obtained on a Cary Model 60 spectropolarimeter. We are grateful to Mr. W. Thaanum of the Applied Physics Corp., for making the instrument available for our use.

(47) F. Wreden, *Ann.*, **163**, 323 (1872).

(48) N. Zelinsky and N. Lepeschkin, *ibid.*, **319**, 303 (1901).

(49) A. Eschenmoser, F. Elsinger, and J. Schreiber, *Helv. Chim. Acta*, **43**, 113 (1960).

(50) C. F. Poe and E. M. Plein, *J. Phys. Chem.*, **38**, 883 (1934).

(trough)[51]]. The amplitude of this Cotton effect was determined to ±0.5%, see below.

High-Precision RD Determinations of Camphor and Camphor-9,9,9-d_3.—A 10-mg sample of the carefully purified substance was weighed to ±0.000005 g and dissolved in 10.00 ± 0.05 ml of absolute methanol. The 10-mm RD cell was rinsed six times with the solution, filled, and placed at the same spot in the cell compartment for each determination. The RD determination was repeated with a second aliquot from the same solution. This process was repeated with six independently weighed samples of the starting camphor and with two independently weighed samples from each of three independently synthesized batches of camphor and camphor-d_3 (12 determinations of the RD curve for each substance). The amplitudes of the 12 curves for each substance were averaged; the standard deviation in a was 0.5%. The RD determinations were made on all 36 samples within the shortest time possible (18 hr) so as to minimize long-term instrumental fluctuations owing to temperature, lamp stability, etc. The determinations were done in random sequence.

D-(+)-**3-Bromocamphor** (**9**).—A solution of 100 g (0.66 mole) of D-(+)-camphor in 480 ml of glacial acetic acid was warmed to 80° and 40 ml (118 g, 1.3 moles) of bromine in 40 ml of glacial acetic acid was added dropwise over 3 hr. The mixture was stirred at 80° for 22 hr, poured onto ice, and filtered to afford 142 g (93%) of crude D-(+)-3-bromocamphor, mp 56–72°. Recrystallization from 95% ethanol afforded 129 g (85%) of the pure bromo ketone as colorless needles: mp 76°; $[\alpha]^{23}D$ +125° (c 1.0); $\lambda_{max}^{CHCl_3}$ 5.69, 7.22, 7.28 μ; nmr ($CDCl_3$) τ 5.38 (d, J = 5 cps), 8.92 (s), 9.04 (s), 9.06 (s); RD (c 0.090), $[\alpha]^{29}_{550}$ +170°, $[\alpha]^{29}_{500}$ +200°, $[\alpha]^{29}_{450}$ +300°, $[\alpha]^{29}_{400}$ +430, $[\alpha]^{29}_{350}$ +1100°, $[\alpha]^{29}_{340}$ +1600°, $[\alpha]^{29}_{334}$ +1900° (peak), $[\alpha]^{29}_{320}$ +1130°, $[\alpha]^{29}_{310}$ −70°, $[\alpha]^{29}_{300}$ −1230°, $[\alpha]^{29}_{292}$ −1470° (trough), $[\alpha]^{29}_{280}$ −1130°, $[\alpha]^{29}_{260}$ −500°, $[\alpha]^{29}_{250}$ −300°; a = +77.8 [lit. mp 76°;[24] $[\alpha]^{24}_{546}$ +165°;[24] $[\alpha]_{335}$ +1970° (peak), $[\alpha]_{290}$ −1472° (trough)[51]].

D-(+)-**3,9-Dibromocamphor** (**10**).—This compound was prepared in 50–55% yield according to the procedure of Corey, Chow, and Scherrer.[24] The dibromo ketone **10** had mp 156.5°; $\lambda_{max}^{CHCl_3}$ 5.68 μ; nmr ($CDCl_3$) τ 5.45 (d, J = 5 cps), 6.38 and 6.65 (neq, J = 10.2 cps), 8.89 (s), 8.97 (s); RD (c 0.085), $[\alpha]^{29}_{550}$ +110°, $[\alpha]^{29}_{500}$ +140°, $[\alpha]^{29}_{450}$ +230°, $[\alpha]^{29}_{400}$ +350°, $[\alpha]^{29}_{350}$ +880°, $[\alpha]^{29}_{340}$ +1450°, $[\alpha]^{29}_{332}$ +1770° (peak), $[\alpha]^{29}_{320}$ +1090°, $[\alpha]^{29}_{310}$ −280°, $[\alpha]^{29}_{300}$ −1410°, $[\alpha]^{29}_{290}$ −1690° (trough), $[\alpha]^{29}_{270}$ −1160°, $[\alpha]^{29}_{250}$ −1060°; a = +107.6 [lit.[52] mp 152–153°; $[\alpha]D$ +98.8° (c 4.0, $CHCl_3$)].

D-(+)-**9-Bromocamphor** (**11**).—This compound was prepared in 65–70% yield by zinc debromination of 3,9-dibromocamphor following the procedure of Corey, Chow, and Scherrer.[24] The bromo ketone **11** had mp 93–95°; $\lambda_{max}^{CHCl_3}$ 5.71 μ; nmr ($CDCl_3$), τ 6.45 and 6.72 (neq, J = 10.3 cps), 8.98 (d, J = 1 cps), 9.02 (s); $[\alpha]^{23}D$ +109° (c 0.93); RD (c 0.087), $[\alpha]^{29}_{550}$ +50°, $[\alpha]^{29}_{500}$ +80°, $[\alpha]^{29}_{450}$ +240°, $[\alpha]^{29}_{400}$ +410°, $[\alpha]^{29}_{350}$ +970°, $[\alpha]^{29}_{330}$ +1720°, $[\alpha]^{29}_{320}$ +2970°, $[\alpha]^{29}_{312}$ +4420° (peak), $[\alpha]^{29}_{300}$ +3450°, $[\alpha]^{29}_{290}$ −620°, $[\alpha]^{29}_{270}$ −5110° (trough), $[\alpha]^{29}_{260}$ −4770°, $[\alpha]^{29}_{250}$ −4140°; a = +212.05 [lit.[52] mp 93–94°; $[\alpha]D$ +116° (c 6.0, $CHCl_3$)].

D-(+)-**9-Acetoxycamphor** (**12**).—This compound was prepared in 90–95% yield by treatment of the bromo ketone **11** (mp 93–95°) with sodium acetate following the procedure of Guha and Bhattacharyya[26] with the following modification. Final purification was effected by fractional evaporative distillation in a micro Hickman flask at 50° (bath temperature) (0.2 mm) [lit.[26] bp 123° (5 mm)], thereby affording the acetate **12** as a colorless oil with no resonances of starting material visible in its nmr spectrum. This sample had $\lambda_{max}^{CHCl_3}$ 5.71 μ; nmr ($CDCl_3$) τ 5.83 and 6.00 (neq, J = 11.2 cps), 7.92 (s), 9.02 (s), 9.05 (s); RD (c 0.091), $[\alpha]^{29}_{550}$ +80°, $[\alpha]^{29}_{500}$ +100°, $[\alpha]^{29}_{450}$ +160°, $[\alpha]^{29}_{400}$ +230°, $[\alpha]^{29}_{350}$ +560°, $[\alpha]^{29}_{330}$ +1020°, $[\alpha]^{29}_{320}$ + 1880°, $[\alpha]^{29}_{314}$ +2410° (peak), $[\alpha]^{29}_{300}$ +1090°, $[\alpha]^{29}_{290}$ −990°, $[\alpha]^{29}_{272}$ −2510° (trough), $[\alpha]^{29}_{260}$ −2180°, $[\alpha]^{29}_{250}$ −1880°; a = +103.3.

D-(+)-**9-Hydroxycamphor** (**13**).—9-Acetoxycamphor (**12**, crude material as obtained by the procedure of Guha and Bhattacharyya[26]) was saponified in 85% yield by the procedure of Corey, *et al.*,[25] to produce the ketol **13** which was recrystallized from ether–pentane as colorless needles: mp 243.5–244°; $[\alpha]^{23}D$ +63.1° (c 0.87); $\lambda_{max}^{CHCl_3}$ 2.86, 5.75 μ; nmr ($CDCl_3$) τ 6.27 and 6.50 (neq, J = 10.9 cps), 9.04 (s, six protons); RD (c 0.086), $[\alpha]^{30}_{550}$ +50°, $[\alpha]^{30}_{500}$ +70°, $[\alpha]^{30}_{450}$ +110°, $[\alpha]^{30}_{400}$ +180°, $[\alpha]^{30}_{350}$ +490°, $[\alpha]^{30}_{330}$ +980°, $[\alpha]^{30}_{320}$ +1750°, $[\alpha]^{30}_{314}$ + 2130° (peak), $[\alpha]^{30}_{300}$ +770°, $[\alpha]^{30}_{290}$ −1120°, $[\alpha]^{30}_{276}$ −2140° (trough), $[\alpha]^{30}_{260}$ −1710°, $[\alpha]^{30}_{250}$ −1430°; a = +72.2 (lit.[25] mp 238–240°; $[\alpha]^{23}D$ +63.6°).

D-(+)-*trans*-**Isoketopinic Acid** (**14**).—Oxidation of the ketol **13** (mp 243.5–244° followed the procedure of Corey, *et al.*[25] The crude isoketopinic acid (**14**) was purified by sublimation to afford colorless rhombic crystals: mp 257–258°; $\lambda_{max}^{CHCl_3}$ 3.0 (broad), 5.74, 5.88 μ; nmr ($CDCl_3$) τ 8.77 (s), 8.82 (s); $[\alpha]^{23}D$ +5.9° (c 0.90); RD (c 0.1175), $[\alpha]^{24}_{550}$ +1°, $[\alpha]^{24}_{500}$ +2°, $[\alpha]^{24}_{450}$ +26°, $[\alpha]^{24}_{400}$ +26°, $[\alpha]^{24}_{350}$ +119°, $[\alpha]^{24}_{330}$ +281°, $[\alpha]^{24}_{320}$ +587°, $[\alpha]^{24}_{314}$ +817° (peak), $[\alpha]^{24}_{300}$ +179°, $[\alpha]^{24}_{290}$ −664°, $[\alpha]^{24}_{282}$ −1072° (trough), $[\alpha]^{24}_{260}$ −920°; a = +34.41 ± 0.44 [lit.[23] mp 249–250°; $[\alpha]^{27}D$ +3.2° (c 5.0 absolute ethanol)]. The amplitude of this Cotton effect was determined to ±1.2% by the technique described above for camphor. Eight determinations per preparation from four independently synthesized samples were made.

Methyl D-(+)-*trans*-**Isoketopinate** (**15**).—To 1.698 g (0.00968 mole) of isoketopinic acid (**14**), mp 257–258°, in 45 ml of anhydrous ether at 0° was added 150 ml of ether containing diazomethane prepared from 7 g (0.07 mole) of N-methyl-N-nitrosourea. The mixture was allowed to stand at 0° for 2 hr. Excess diazomethane was destroyed by acetic acid and the solution was extracted with 10% sodium hydroxide and dried over sodium sulfate. Removal of solvent afforded 1.8585 g of a crude product, mp 63–68°, which was purified by sublimation to yield 1.625 g (89%) of the keto ester **15** as white leaflets: mp 76°; $\lambda_{max}^{CHCl_3}$ 5.74, 5.82 μ; nmr ($CDCl_3$) τ 6.28 (s), 8.78 (s), 8.90 (s); $[\alpha]^{23}D$ +2.7° (c 0.87); RD (c 0.098), $[\alpha]^{29}_{550}$ +30°, $[\alpha]^{29}_{500}$ +50°, $[\alpha]^{29}_{450}$ +60°, $[\alpha]^{29}_{400}$ +90°, $[\alpha]^{29}_{350}$ +180°, $[\alpha]^{29}_{330}$ +340°, $[\alpha]^{29}_{320}$ +610°, $[\alpha]^{29}_{312}$ +950° (peak), $[\alpha]^{29}_{300}$ +520°, $[\alpha]^{29}_{290}$ −400°, $[\alpha]^{29}_{280}$ −920°, $[\alpha]^{29}_{274}$ −1040° (trough), $[\alpha]^{29}_{260}$ −920°, $[\alpha]^{29}_{250}$ −830°; a = +39.0 (lit.[23] mp 72–73°).

D-**9-Hydroxyisoborneol and** D-**9-Hydroxyborneol** (**16** and **17**).—A solution of 1.576 g (0.00803 mole) of methyl *trans*-isoketopinate (mp 76°) in 15 ml of dry tetrahydrofuran was added dropwise to a solution of 0.596 g (0.01205 mole) of lithium aluminum hydride in 30 ml of dry tetrahydrofuran (distilled over lithium aluminum hydride). The mixture was refluxed at 72–74° for 25–30 hr and excess lithium aluminum hydride was destroyed by cautious addition of water and concentrated sodium hydroxide. The diol mixture was extracted with ether and dried over sodium sulfate. Evaporation of solvent afforded 1.381 g of crude diol which was purified by differential sublimation to yield 1.238 g (90%) of a white solid diol mixture: mp 275–277°; λ_{max}^{KBr} 3.00 μ (broad); nmr (CD_3COCD_3) τ 6.38–6.67 (m), 8.87 (s), 9.03 (s), 9.08 (s), 9.15 (s); $[\alpha]^{23}D$ −11.3° (c 1.0); RD (c 0.109), negative plain curve to 250 mμ; $[\alpha]^{24}_{250}$ −200°. The ratio of the *exo* isomer to the *endo* isomer in this mixture was 9:1, as ascertained by integration of the methyl resonances of the diol **16** (τ 8.87 and 9.08) and diol **17** (τ 9.03 and 9.15). The mass spectrum of this sample had prominent peaks at m/e 152, 140, 139, 126, 121, 95, and 31.[31]

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.65. Found (B): C, 70.29; H, 10.44.

D-(−)-**9-Hydroxyisoborneol-9-triphenylmethy Ether** (**18**). **A. From** D-**9-Hydroxyisoborneol** (**16**).—A solution of 500 mg (0.0029 mole) of diol **16** [mp 270–271° (o), contaminated with *ca.* 10% of diol **17**] and 1.1 g (0.0042 mole) of triphenylmethyl chloride in 60 ml of dry pyridine was warmed on a steam bath for 5 min and then stirred at room temperature overnight. The solution was poured into 250 ml of ice–water and extracted with two 100-ml portions of ether which were washed with water, dried over magnesium sulfate, and evaporated. The residual oil was crystallized from aqueous ethanol to afford 1.23 g (90%) of the trityl ether **18** as colorless prisms: mp 168.5–170° (o); $[\alpha]^{23}D$ −12.5° (c 1.1). This product has infrared and nmr spectra which are identical with those of the analytical sample described below, and a mixture melting point was undepressed.

B. From D-(+)-**9-Hydroxycamphor Triphenylmethyl Ether** (**19**).—To a solution of 350 mg (0.00085 mole) of the keto trityl ether **19** [mp 130–130.5° (o)] in 25 ml of methanol containing a trace of potassium hydroxide was added 1.0 g (0.026 mole) of sodium borohydride and the mixture was stirred overnight at room temperature. Methanol was distilled *in vacuo* and the residue was taken up in 20 ml of water and extracted exhaustively with ether which was dried over magnesium sulfate and evapo-

(51) C. Djerassi, J. Osiecki, R. Riniker, and B. Riniker, *J. Am. Chem. Soc.*, **80**, 1216 (1958). The discrepency between our value and theirs for the wavelength and rotation at the trough of the camphor spectrum is probably due to the reduced accuracy at short wavelength of the instrumentation available for the early work.

(52) F. S. Kipping and W. J. Pope, *J. Chem. Soc.*, **67**, 371 (1895).

rated to afford 296 mg (85%) of crude D-(−)-9-hydroxyisoborneol trityl ether (**18**), mp 138–145° (o). Recrystallization from aqueous ethanol afforded 260 mg (74%) of pure trityl ether **18** as colorless prisms: mp 169–170° (o); $[\alpha]^{23}D$ −12.5° (*c* 1.0); RD (*c* 0.529), negative plain curve to 250 mμ, $[\alpha]^{24}_{250}$ −140°; $\lambda^{CHCl_3}_{max}$ 6.7, 6.9 μ; nmr ($CDCl_3$) τ 2.7 (m), 7.08 (s), 8.71 (s), 9.16 (s).

Anal. Calcd for $C_{29}H_{32}O_2$: C, 84.42; H, 7.81. Found (B): C, 83.95; H, 7.65.

D-(+)-9-Hydroxycamphor Triphenylmethyl Ether (19). A. From D-(−)-9-Hydroxyisoborneol-9-triphenylmethyl Ether (18).—Chromic anhydride (500 mg, 0.0050 mole) was dissolved in 5 ml of dry pyridine[28] and cooled to 0° in an ice bath, a cold solution of 700 mg (0.0018 mole) of crude hydroxy trityl ether **18** [mp 138–145° (o)] in 14 ml of dry pyridine was added, and the mixture was shaken and allowed to stand overnight. The mixture was poured into 100 ml of ice–water and extracted with three 35-ml portions of ether which were washed with 2% hydrochloric acid, 5% sodium bicarbonate, and water, dried over sodium sulfate, and evaporated to afford 455 mg (66%) of crude keto trityl ether **19**, mp 101–108°. This was recrystallized from ether–hexane to give 432 mg (60%) of trityl ether **19** as colorless prisms: mp 130–130.5° (o); $\lambda^{CHCl_3}_{max}$ 5.75 μ; $[\alpha]^{23}D$ +28.2° (*c* 0.47). This product was identical with that described below.

B. From D-(+)-9-Hydroxycamphor (13).—To a solution of 250 mg (0.0036 mole) of ketol **13** [mp 231–233° (o)] in 3 ml of dry pyridine was added 293 mg (0.0036 mole) of chlorotriphenylmethane, mp 109–111°. The mixture was warmed on a steam bath for 2 hr, stirred at room temperature overnight, poured into *ca.* 125 ml of water, and extracted with 100 ml of ether which was dried with magnesium sulfate and evaporated to dryness. The crude material was chromatographed on 10 g of grade I Giulini neutral alumina using 200 ml of cyclohexane to elute 410 mg (91%) of trityl ether **19** which was recrystallized from ether–hexane to give 372 mg (87%) of (+)-9-hydroxycamphor triphenylmethyl ether **19** as colorless prisms: mp 130–130.5° (o); $[\alpha]^{23}D$ +28.0° (*c* 0.44); RD (*c* 0.0889), $[\alpha]^{24}_{700}$ +50°, $[\alpha]^{24}_{589}$ +50°, $[\alpha]^{24}_{500}$ +60°, $[\alpha]^{24}_{450}$ +80°, $[\alpha]^{24}_{400}$ +120°, $[\alpha]^{24}_{350}$ +300°, $[\alpha]^{24}_{310}$ +1380° (peak), $[\alpha]^{24}_{272}$ −1530° (trough), $[\alpha]^{24}_{250}$ −1140°; *a* = +119.5; $\lambda^{CHCl_3}_{max}$ 5.75 μ; nmr ($CDCl_3$) τ 2.65 (m), 6.95 (s), 8.90 (s), 9.16 (s).

Anal. Calcd for $C_{29}H_{30}O_2$: C, 84.81; H, 7.36. Found (B): C, 84.51; H, 7.35.

D-(+)-9-Hydroxycamphor *p*-Toluenesulfonate (20).—A stirred solution of 5 g (0.03 mole) of (+)-9-hydroxycamphor [**13**, mp 233–235° (o)] in 5 ml of dry pyridine was cooled to 0° and 6.2 g (0.033 mole) of *p*-toluenesulfonyl chloride was added. The mixture was stirred for 4 hr at 0° and for 5 hr at room temperature, poured into 200 ml of ice–water, and after 0.5 hr was extracted with 100 ml of ether which was washed with 100 ml of 10% hydrochloric acid and 100 ml of 5% sodium bicarbonate and dried over sodium sulfate. Evaporation afforded 6.9 g (71%) of crude tosylate **20** (mp 79–83°) which was recrystallized from ether–hexane to afford 5.7 g (60%) of purified tosylate as colorless plates: mp 110–112° (o); $\lambda^{CHCl_3}_{max}$ 5.78 μ; $[\alpha]^{23}D$ +34.9° (*c* 0.73); RD (*c* 0.115), $[\alpha]^{24}_{700}$ +25°, $[\alpha]^{24}_{589}$ +25°, $[\alpha]^{24}_{500}$ +50°, $[\alpha]^{24}_{450}$ +80°, $[\alpha]^{24}_{400}$ +130°, $[\alpha]^{24}_{350}$ +310°, $[\alpha]^{24}_{311}$ +1340° (peak), $[\alpha]^{24}_{270}$ −1420° (trough), $[\alpha]^{24}_{250}$ −1200°; *a* = +89.0; nmr ($CDCl_3$) τ 2.15 and 2.58 (m, A_2B_2, J_{ortho} = 8 cps), 5.93 and 6.17 (neq, *J* = 9.6 cps), 7.55 (s), 9.10 (s), 9.13 (s).

Anal. Calcd for $C_{17}H_{22}O_4S$: C, 63.32; H, 6.87; S, 9.94. Found (B): C, 63.40; H, 7.01; S, 9.90.

D-9-Hydroxyisoborneol and D-9-Hydroxyborneol 9-*p*-Toluenesulfonates (23).—To 1.263 g (0.007421 mole) of the sublimed diol (9:1 mixture of **16** and **17**, mp 275–277°) in 20 ml of pyridine (dried by distillation from barium oxide) was added 2.140 g (0.0112 mole) of *p*-toluenesulfonyl chloride (mp 68–69°) and the mixture was stirred at room temperature for 18–20 hr. Ethyl acetate and 5% sodium bicarbonate were added to the solution,[53] the mixture was extracted with chloroform, the extract was dried over sodium sulfate, chloroform was removed in a rotary evaporator, and the last traces of pyridine were removed by coevaporation with benzene to yield 2.464 g (100%) of a liquid product which was used as such for the next reaction. This had λ^{film}_{max} 2.82, 2.90, 6.25, 7.35, 8.40, 8.65 μ; nmr ($CDCl_3$) τ 2.25 and 2.73 (m, A_2B_2, J_{ortho} = 9 cps), 6.00–6.58 (m), 7.62 (s), 8.92 (s, major isomer), 9.12 (s, major isomer), and 9.17 (s, minor isomer).

D-(−)-Isoborneol and D-(+)-Borneol (21 and 22). A. From D-9-Hydroxyisoborneol 9-*p*-Toluenesulfonate (23).—A solution of 2.107 g (0.00650 mole) of crude monotosylate **23** in 25 ml of dry tetrahydrofuran was added dropwise to a solution of 0.740 g (0.0195 mole) of lithium aluminum hydride in 20 ml of dry tetrahydrofuran. The mixture was refluxed at 72–74° for 29 hr. Excess lithium aluminum hydride was destroyed by dropwise addition of water and concentrated sodium hydroxide. The mixture was extracted with ether and dried over sodium sulfate. Removal of solvent afforded 1.042 g of a mixture of **16–17** and **21–22**, the ratio varying from 1:10 to 1:20, determined by isolation of the products (if the tetrahydrofuran was not scrupulously dried over lithium aluminum hydride immediately before use, this ratio was 1:2–1:3). Chromatography over grade III neutral Woelm alumina yielded in the benzene eluate 0.842 g (84%) of a mixture of the desired alcohols **21** and **22**: mp 215–216°; $[\alpha]^{23}D$ −24.2° (*c* 0.98); $\lambda^{CHCl_3}_{max}$ 2.74 μ; nmr ($CDCl_3$) τ 8.98 (s), 9.11 (s), 9.14 (s), 9.17 (s). The alcohols were not separated, but the ratio of isoborneol to borneol was determined to be 9:1 by comparing the areas of the C-methyl resonances of isoborneol (τ 8.98, 9.11, and 9.17[54]) with that of borneol (τ 9.14, all three resonances superimposed[54]).

Elution with ether yielded 0.058 g (6%) of the diol **16–17** mixture (9:1).

B. From D-(+)-9-Hydroxycamphor *p*-Toluenesulfonate (20).—A solution of 1.0 g (0.0031 mole) of keto tosylate **20** (mp 79–83) in 15 ml of freshly distilled tetrahydrofuran was refluxed for 4 hr with 120 mg (0.0032 mole) of lithium aluminum hydride and then allowed to stand at room temperature overnight. Water was added to decompose excess lithium aluminum hydride and 20 ml of 35% aqueous sodium hydroxide was added. The mixture was extracted with ether, dried over sodium sulfate, and evaporated to afford 394 mg (85%) of an alcohol mixture (mp 207–210°) which was sublimed at 40° (30 mm) to afford 386 mg (73%) of a 9:1 isoborneol–borneol mixture as colorless prisms: mp 213–214°; $[\alpha]^{23}D$ −24.6° (*c* 1.2); $\lambda^{CHCl_3}_{max}$ 2.74 μ; nmr τ 6.42 (t, *J* = 6 cps), 8.98 (s), 9.11 (s), 9.14 (s), 9.17 (s).

D-(+)-Camphor (8).—According to the general procedure of Sarett[28] a yellow chromium trioxide–pyridine complex was prepared by addition of 1.252 g (0.0125 mole) of chromium trioxide to 10 ml of pyridine at 0°. A solution of 0.647 g of isoborneol–borneol (**21–22**, 9:1 mixture) in 10 ml of pyridine was added dropwise and the mixture was stirred at room temperature for 19 hr. The mixture was filtered, the residue was washed with ether, water was added to the filtrate, and the aqueous phase was extracted with ether. The extracts were washed with 200 ml of 3% hydrochloric acid in 10-ml portions, dried over sodium sulfate, and carefully distilled to dryness leaving 0.537 g (84%) of crude camphor which was sublimed at 35 mm (bath temperature 120–140°) to yield 0.415 g (65%) of camphor: mp 178°; $\lambda^{CHCl_3}_{max}$ 5.72 μ; nmr ($CDCl_3$) τ 9.04 (s), 9.09 (s), 9.17 (s); $[\alpha]^{23}D$ +48.7° (*c* 0.91); RD (*c* 0.11), $[\alpha]^{24}_{550}$ +50°, $[\alpha]^{24}_{500}$ +74°, $[\alpha]^{24}_{450}$ +114°, $[\alpha]^{24}_{400}$ +170°, $[\alpha]^{24}_{350}$ +397°, $[\alpha]^{24}_{330}$ +766°, $[\alpha]^{24}_{320}$ +1363°, $[\alpha]^{24}_{312}$ +1958° (peak), $[\alpha]^{24}_{300}$ +1163°, $[\alpha]^{24}_{290}$ −766°, $[\alpha]^{24}_{274}$ −2157° (trough), $[\alpha]^{24}_{260}$ −1845°; *a* = +62.56 ± 0.54. The amplitude of this Cotton effect was determined to ±0.5%. The mass spectrum showed prominent peaks at *m/e* 152, 137, 109, 108, 95, 81, 69, 55, and 41.[31]

D-9-Hydroxyisoborneol-2,9,9-d_3 and D-9-Hydroxyborneol-2,9,9-d_3.—The procedure was similar to that for preparation of **16–17**, the only difference being the use of lithium aluminum deuteride instead of lithium aluminum hydride. The product had mp 274–276°; λ^{KBr}_{max} 3.00 (broad), 4.49, 4.75 μ; nmr (CD_3COCD_3) τ 7.13 (s, hydroxyl proton), 8.87 (s), 9.03 (s), 9.08 (s), 9.15 (s). As in the protio series the ratio of the *exo* to the *endo* isomer was 9:1. The mass spectrum showed prominent peaks at *m/e* 155, 140, 139, 128, 122, 95, and 33.[31]

D-9-Hydroxyisoborneol-2,9,9-d_3 and D-9-Hydroxyborneol-2,9,9-d_3 9-*p*-Toluenesulfonates.—The procedure was identical with that used for the preparation of **23**. The product had λ^{film}_{max} 2.82, 2.90, 3.39, 3.46, 4.45, 4.65, 6.25, 7.35, 8.40, 8.65 μ; nmr ($CDCl_3$) τ 2.25 and 2.73 (m, A_2B_2, J_{ortho} = 9 cps), 7.62 (s), 8.92 (s), 9.12 (s), 9.18 (s).

D-Isoborneol-2,9,9,9-d_4 and D-Borneol-2,9,9,9-d_4.—The procedure was identical with that used for preparation of **21–22** except that instead of lithium aluminum hydride, lithium aluminum deuteride was used. The purified product had mp 215–216°;

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$\lambda_{max}^{CHCl_3}$ 2.74, 3.33, 3.40, 3.48, 4.49, 4.54, 7.26, 7.30 μ; nmr ($CDCl_3$) τ 8.98 (s), 9.11 (s), 9.14 (s). The methyl peaks at τ 8.97 and 9.11 correspond to the major isomer (isoborneol-d_4) while the 9.14 peak corresponds to the minor isomer (borneol-d_4). The major and minor isomers were in a 9:1 ratio.

D-(+)-**Camphor-9,9,9-d_3 (24)**.—The procedure was identical with that used for preparation of the protio compound. The product had mp 177–178°; $\lambda_{max}^{CHCl_3}$ 4.46, 4.50, 5.74 μ; nmr ($CDCl_3$) τ 9.09 (s), 9.17 (s); RD (*c* 0.1150), $[\alpha]_{550}^{24}$ +52°, $[\alpha]_{500}^{24}$ +78°, $[\alpha]_{450}^{24}$ +105°, $[\alpha]_{400}^{24}$ +157°, $[\alpha]_{350}^{24}$ +365°, $[\alpha]_{330}^{24}$ +757°, $[\alpha]_{320}^{24}$ +1356°, $[\alpha]_{312}^{24}$ +1874° (peak), $[\alpha]_{300}^{24}$ +1018°, $[\alpha]_{290}^{24}$ −835°, $[\alpha]_{274}^{24}$ −2061° (trough), $[\alpha]_{260}^{24}$ −1487°; a = +60.92 ±0.23. The amplitude of this Cotton effect was determined to ±0.5%. The mass spectrum showed prominent peaks at *m/e* 155, 140, 137, 112, 111, 98, 95, 81, 69, 58, 55, 44, and 41.[31]

D-(−)-**Camphorquinone and** D-(−)-**Camphorquinone-9,9,9-d_3 (25)**.—The procedure is a modification of that of Evans, Ridgion, and Simonsen.[33] To 2.324 g (0.0153 mole) of D-camphor (**8**, mp 178–179°, Eastman Kodak) was added 3.888 g (0.0350 mole) of selenium dioxide in 2.5 ml of acetic anhydride. The mixture was heated at 140–146° for 4.5 hr, cooled, and filtered, and the residue was washed with acetic acid. The filtrate was neutralized with 20% sodium hydroxide; the yellow solid which precipitated was extracted with ether and dried over sodium sulfate. Removal of solvent yielded 2.469 g (97%) of a crude product which was purified by sublimation to yield 2.115 g (84%) of the quinone as a yellow, crystalline solid: mp 198–199° (o); $\lambda_{max}^{CHCl_3}$ 5.64, 5.70 μ; nmr ($CDCl_3$) τ 7.38 (d, J = 4.5 cps), 8.89 (s), 8.92 (s), 9.07 (s) (lit.[33] mp 198°). The mass spectrum had prominent peaks at *m/e* 166, 152, 138, 123, 110, and 95.[31]

The deuterated derivative **25** was prepared from camphor-d_3 by an identical procedure, and had mp 198–199°; $\lambda_{max}^{CHCl_3}$ 4.54, 5.65, 5.71 μ; nmr ($CDCl_3$) τ 7.38 (d, J = 4.5 cps), 8.89 (s), 9.07 (s). The mass spectrum had prominent peaks at *m/e* 169, 155, 141, 126, 123, 113, 98, and 95.[31]

D-(+)-**Camphoric Acid and** D-(+)-**Camphoric Acid-d_3 (26)**.—According to a modification of the procedure of Hassel,[55] 50 ml of 5% sodium hydroxide was added to 2.168 g (0.01305 mole) of camphorquinone (mp 198–199°), the mixture was stirred at room temperature, and 7-ml portions (0.0522 mole) of 30% hydrogen peroxide were added initially, after 6 hr, and after 12 hr. Stirring was continued for 25–30 hr after the last peroxide addition, and the mixture was filtered and acidified with concentrated hydrochloric acid to precipitate camphoric acid. The suspension was cooled and extracted with ether, the extract was dried over sodium sulfate, and solvent was distilled to yield 2.455 g (94%) of the crude acid which was purified by sublimation to yield 2.325 g (89%) of the pure acid: mp 186–187° (o) (lit.[56] mp 187°); λ_{max}^{KBr} 3.4 (broad), 5.9, 7.12, 7.30 μ; nmr (CD_3COCD_3) τ 8.71 (s), 8.75 (s), 9.12 (s).

The d_3-analog (**26**) was prepared in an identical manner from camphorquinone-d_3 (**25**). It had mp 187–188° (o); λ_{max}^{KBr} 3.4 (broad), 4.48, 5.92, 7.09, 7.19, 7.41 μ; nmr (CD_3COCD_3) τ 8.75 (s), 9.12 (s).

D-(−)-α-**Bromocamphoric Anhydride-d_3 (27)**.—The procedure is modified from that of Aschan.[3] To 1.062 g (0.00526 mole) of camphoric acid-d_3 (mp 187–188°) was added 2.218 g (0.01065 mole) of phosphorus pentachloride and the mixture was warmed at 80–87° for 4.5 hr without stirring to yield a clear solution. This solution was cooled, 0.985 g (0.00616 mole) of bromine was added all at once, and the mixture was heated at 60–65° for 6.5 hr. The mixture was poured into 24 g of ice–water, stirred for 0.5 hr, and extracted with ether, and the ether was dried over sodium sulfate. Evaporation yielded 1.440 g of a semisolid which was purified by recrystallization from chloroform–ether to afford 0.953 g (70%) of colorless, rhombic crystals of the bromo anhydride: mp 216° (o); $\lambda_{max}^{CHCl_3}$ 4.45, 5.47, 5.62, 7.14, 7.57, 8.55 μ; nmr ($CDCl_3$) τ 7.67 (m), 8.62 (s), 8.93 (s). The mass spectrum had prominent peaks at *m/e* 175, 173, 137, 109, 94, and 93 which correspond to peaks at *m/e* 178, 176, 175, 173, 140, 112, 97, 96, 94, and 93 in the spectrum of the protio analog.[31]

Rearrangement of D-(−)-α-**Bromocamphoric Anhydride-d_3**.—A 0.707-g sample (95–98% pure, 0.00268 mole) of α-bromocamphoric anhydride-d_3 (mp 214°) was treated with 125 ml of 15% sodium carbonate solution in the manner described for the protio analog. This afforded 0.064 g (15%) of a deuterium-labeled (+)-laurolenic acid. Infrared and nmr spectra of this sample were identical with those of synthetic 1,3-dimethyl-2-trideuteriomethylcyclopent-2-enecarboxylic acid (**5**). The bromo lactone of this labeled laurolenic acid was idential in melting point and infrared and nmr spectra with the *dl*-bromo lactone **6** prepared from the corresponding *dl* acid **5**. Repeated integration of the τ 8.77 and 8.50 methyl resonances showed their intensity ratio to be 1.01 ± 0.02; analogous integration of the corresponding resonances in the spectrum of the protio bromo lactone gave a value of 0.99 ± 0.03. The mass spectrum of deuteriobromo lactone has prominent peaks at *m/e* 128, 112, 96, 93, 94, and 91.[31]

In addition 0.342 g (63%) of (−)-camphanic acid-d_3 was obtained. This was purified by sublimation to afford colorless rhombic crystals: mp 200°; $\lambda_{max}^{CHCl_3}$ 3.4 (broad), 4.44, 5.60, 5.78 μ; nmr ($CDCl_3$) τ 7.95 (m), 8.86 (s), 8.98 (s). This nmr spectrum was identical with that of camphanic acid (**2**) except for the absence of the τ 8.90 singlet.

Registry No.—**1**, 10333-96-7; **2**, 10333-97-8; **3**, 10333-98-9; **4**, 10333-99-0; **6a**, 10334-00-6; **6b**, 10334-01-7; **7**, 10353-25-0; **8**, 464-49-3; **9**, 10293-06-8; **10**, 10293-10-4; **11**, 10293-09-1; **12**, 10353-26-1; **13**, 10334-06-2; **14**, 10334-07-3; **15**, 10334-08-4; **16**, 10334-09-5; **17**, 10334-10-8; **18**, 10334-11-9; **19**, 10380-96-8; **20**, 10334-12-0; **21**, 10334-13-1; **22**, 10334-14-2; **23**, 10334-15-3; **24**, 10224-31-4; **25**, 10334-17-5; **26**, 10334-18-6; **27**, 10334-19-7; **28**, 10334-20-0; methyl *dl*-1,3-dimethyl-2-trideuteriomethyl-2-hydroxycyclopentane-1-carboxylate, 10385-44-1; D-9-hydroxyisoborneol, 10334-21-1; D-9-hydroxyisoborneol-2,9,9-d_3, 10353-27-2; D-9-hydroxyborneol-2,9,9-d_3, 10334-22-2; D-9-hydroxyisoborneol-2,9,9-d_3 9-*p*-toluenesulfonate, 10334-23-3; D-9-hydroxyborneol-2,9,9-d_3 9-*p*-toluenesulfonate, 10334-24-4; D-isoborneol-2,9,9,9-d_4, 10385-45-2; D-borneol-2,9,9,9-d_4, 10334-25-5; D-(−)-camphorquinone, 10334-26-6; D-(+)-camphoric acid, 10334-27-7; (−)-camphanic acid-d_3, 10380-97-9.

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