pure aldehyde, b.p. 71–73° (0.05 mm.), $n^{25}D$ 1.5002; ν_{max}^{liquid} 2720, 1690, 1640, 1625, 1210, 1180, 1080, 1005, and 903 cm.$^{-1}$. This material was shown to be homogeneous by vapor phase chromatography and possessed a retention time identical with that of the major component of the mixture.

The major C_{15}-aldehyde, upon treatment with Brady reagent, yielded a 2,4-dinitrophenylhydrazone which was obtained (from ethanol) as orange colored prisms, m.p. 188–189°.

Anal. Calcd. for $C_{21}H_{28}N_4O_4$: C, 63.05; H, 7.06; N, 14.01. Found: C, 62.96; H, 7.24; N, 13.87.

***cis*- and *trans*-2-Methyl-4-(1,3,3-trimethyl-2-methylenecyclohexyl)crotonaldehyde Tosylhydrazones (8 and 9).**—A solution of 5.06 g. (23 mmoles) of the mixture of **6** and **7** and 5.40 g. (29 mmoles) of tosylhydrazine in 100 ml. of ethanol was allowed to stand at room temperature for 24 hr. Water (150 ml.) was added and 7.12 g. (81%) of an oily mixture of the *cis*- and *trans*-tosylhydrazones **8** and **9** was collected. This mixture was taken up in hot aqueous ethanol which was allowed to cool slowly with seeding to precipitate the tosylhydrazone of the major C_{15}-aldehyde. Recrystallization from aqueous ethanol followed by drying *in vacuo* afforded the major tosylhydrazone as colorless prisms, m.p. 91–93° dec.; λ_{max}^{EtOH} 227 and 253 mμ; $\nu_{max}^{CHCl_3}$ 3230, 1640, 1605, 1500, 1365, 1320, 1165, 1095, 1045, 1025, 953, 909, and 817 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{32}N_2O_2S$: C, 68.10; H, 8.31; N, 7.22. Found: C, 67.88; H, 8.19; N, 7.27.

Chromatography of 1.20 g. of the oily mixture of tosylhydrazones on Merck acid-washed alumina yielded 920 mg. of pure major tosylhydrazone and 78 mg. of the minor isomer (*ca.* 90% pure). The infrared spectra of the two tosylhydrazones were similar, but differences of band position and intensity were apparent in the 800–1300 cm.$^{-1}$ region. Thin layer chromatography indicated that the major isomer possessed the larger R_f value on both silica gel and alumina.

Irradiation of the Sodium Salts of *cis*- and *trans*-2-Methyl-4-(1,3,3-trimethyl-2-methylenecyclohexyl)crotonaldehyde Tosylhydrazones.—The irradiation apparatus consisted of a reaction vessel surrounding a quartz water-cooling jacket of slightly smaller diameter, leaving an annular space of 160-ml. capacity. The reaction vessel was equipped with a gas inlet at its base and a side-arm to which was attached a reflux condenser. A 450-watt Hanovia high pressure mercury arc surrounded with a Pyrex sleeve was placed in an immersion well in the water jacket.

A solution of 3.42 g. (8.8 mmoles) of the mixture of **8** and **9** in 150 ml. of isooctane (Fischer Spectranalyzed) containing 10 ml. of dry monoglyme was placed in the irradiation vessel and purged with a stream of dry nitrogen. Sodium hydride (0.5 g.) was added and the sodium salts of the tosylhydrazones formed as a yellow suspension with evolution of hydrogen. When hydrogen evolution had ceased (after 5 min.), the suspension, which was kept agitated with a brisk stream of nitrogen, was irradiated for 1 hr., during which a copious precipitate of the *p*-toluenesulfinate salt settled out. The photolysate was poured into 250 ml. of water and extracted with pentane. The pentane extract was dried (magnesium sulfate) and the solvent removed to yield 1.81 g. of a yellow oil which was chromatographed on Woelm neutral (Activity I) alumina. The first fraction to be eluted with hexane consisted of 171 mg. (10%) of virtually pure **10**, ν_{max}^{liquid} 3160, 1780, 1630, 1180, 1095, 978, 901, and 697 cm.$^{-1}$. This hydrocarbon polymerizes rapidly at room temperature. Subsequent fractions were found to be mixtures and were combined (127 mg.) and subjected to vapor phase chromatographic analysis. The major component (51%, 4% based on tosylhydrazone) possessed a retention time identical with that of natural thujopsene and, when collected and distilled, had an infrared spectrum and mass spectral fragmentation pattern identical with those of the natural product.[27]

Acknowledgment.—We are indebted to the National Science Foundation (G-22647) for financial support.

(27) A sample of natural thujopsene was kindly supplied by Drs. M. Stoll and E. Demole, Firmench et Cie., Geneva, Switzerland.

[CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES, CINCINNATI 39, OHIO]

The Condensation of Camphene and Phenol. Product Formation *via* a Direct 2,6-Hydride Transfer[1]

BY WILLIAM F. ERMAN

RECEIVED FEBRUARY 3, 1964

Reaction of *dl*-camphene and phenol at 0° with catalytic quantities of boron trifluoride etherate yielded isobornyl phenyl ether (**1**) in 80% yield. In contrast, treatment of camphene and phenol with boron trifluoride etherate under C-alkylation conditions (100°) afforded not only the *o*- and *p*-isobornylphenols (**2** and **3**) but also the *o*- and *p*-6-*exo*-hydroxyphenyl-*exo*-isocamphanes (**4** and **5**). Product formation was stereospecific as evidenced by absence of the bornylphenols **7** and **8**, the camphenehydrophenols **9** and **10**, and the 6-*exo*-hydroxyphenyl-*endo*-isocamphanes (**11** and **12**) in the reaction mixture. Reaction of *l*-bornyl acetate, $[\alpha]^{26}D$ −38.3°, with phenol afforded the same completely racemic products in comparable yields. The corresponding 6-*exo*-acetoxy-*exo*-isocamphane (**29**) was not detected in the product mixture when camphene was treated with acetic acid under the same conditions. A mechanism to account for the observed facts is presented.

The formation of products from carbonium ions *via* a 1,3-hydride transfer is well documented for acyclic,[2] cyclic,[3] and bicyclic systems.[4] In each of these recorded examples, however, the 1,3-hydride shift proceeds *via* transition from a less stable (higher energy) carbonium ion to a more stable ion (*i.e.*, primary ion → secondary or tertiary ion; secondary ion → tertiary ion) or by interconversion of two equienergetic secondary ions. We wish to report the first example of a reaction in which products are formed *via* a 1,3-hydride transformation involving conversion of a tertiary carbonium ion to a secondary ion[5]: the condensation of camphene and phenol.[6] We have found in fact that

(1) Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

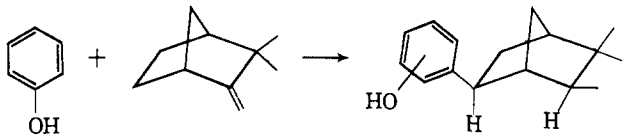
(2) (a) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **84**, 3962 (1962); (b) P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962), and reference cited therein; (c) W. A. Mosher and J. C. Cox, *ibid.*, **72**, 3701 (1950); (d) N. L. Wendler, R. P. Graber, and F. W. Bollinger, *Chem. Ind.* (London), 1312 (1956).

(3) (a) A. C. Cope, H. E. Johnson, and J. S. Stevenson, *J. Am. Chem. Soc.*, **78**, 5599 (1956), and references cited therein; (b) V. Prelog and W. Küng, *Helv. Chim. Acta*, **39**, 1394 (1956), and references cited therein.

(4) W. von E. Doering and A. P. Wolf, 12th International Congress of Pure and Applied Chemistry, New York, N. Y., 1951, Abstracts, p. 437; *Perfumery Essent. Oil Record*, **42**, 414 (1951); *Chem. Abstr.*, **46**, 7080 (1952); (b) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954); J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951); (c) P. de Mayo, "The Chemistry of Natural Products. Vol. II. Mono- and Sesquiterpenoids," Interscience Publishers, Inc., New York, N. Y., 1959, pp. 161–170; (d) J. A. Berson, "Carbonium Ion Rearrangements in Bridged Bicyclic Systems," Chapter 3 in "Molecular Rearrangements," edited by P. de Mayo, Interscience Publishers, Inc., New York, N. Y., 1963, pp. 139–155.

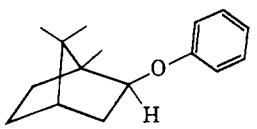
(5) Product formation *via* a 1,3-hydride transfer involving transition from a tertiary to a secondary carbonium ion does have a possible analogy in the Lewis acid catalyzed conversion of *endo*-tetrahydrodicyclopentadiene to adamantane. The driving force for this transformation has been postulated as relief of strain in the bicyclo[2.2.1]heptane ring. Since the over-all process is irreversible, the equilibrium is shifted from an initially formed tertiary carbonium ion to a secondary ion. P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960).

the C-alkylation of phenol by camphene affords as the *predominant* products the isomeric *o*- and *p*-6-*exo*-hydroxyphenyl-*exo*-isocamphanes.



4, *ortho* **5**, *para*

Although acid-catalyzed condensation of camphene or bornyl and isobornyl derivatives with phenolic compounds of many and varied structure have been studied by numerous investigators over the course of the past 50 years,[8-11] the structures of the products from these condensation reactions have never been clearly delineated. In the first definitive study of the camphene–phenol reaction Kitchen[12] showed that O-alkylation occurred almost exclusively when these two compounds were treated with catalytic quantities of boron trifluoride etherate in benzene solution at 0° and that isobornyl phenyl ether (**1**) was the predominate product of the reaction. The ether **1** was



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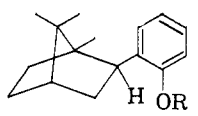
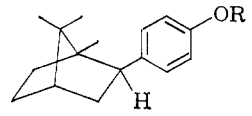
reported to rearrange on treatment with boron trifluoride etherate to a mixture of alkylphenols. A 1:1 camphene–phenol adduct, m.p. 77.8–78.6°, was isolated from this mixture in 26% yield and assigned the structure *o*-isobornylphenol (**2**). More recently Kheifits and Belov[13] in studying this reaction isolated the same *o*-substituted camphene–phenol adduct, m.p. 77°, and a *p*-isomer, m.p. 103°. These authors similarly assigned the *o*-isobornyl-(**2**) and *p*-isobornylphenol (**3**) structures to the compounds solely on the basis of reaction mechanism considerations. We have found that the two compounds, m.p. 77° and 103°, are actually 6-*exo*-*o*-hydroxyphenyl-*exo*-isocamphane (**4**) and 6-*exo*-*p*-hydroxyphenyl-*exo*-isocamphane (**5**).

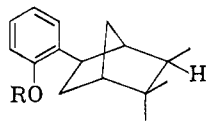
Results.—When a mixture of camphene and phenol was treated at 0°[5] with catalytic quantities of boron trifluoride etherate, isobornyl phenyl ether (**1**) was isolated as a gas chromatographically homogeneous liquid, b.p. 99–101° (0.3 mm.), in 80% yield. Kitchen's



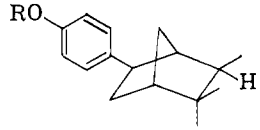
2, R = H
19, R = CH_3



3, R = H
39, R = CH_3

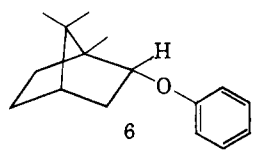


4, R = H
22, R = CH_3



5, R = H
36, R = CH_3

original structure assignment was confirmed by comparison of the n.m.r. and infrared spectra and the gas chromatography retention time with an authentic sample prepared by an independent route.[14] It should be pointed out that the chemical shift of the C-2-α-methyne in isobornyl phenyl ether was well separated from that of bornyl phenyl ether (**6**) so that the presence of any of the latter ether in the product could have been easily recognized. The spin-coupling pattern of the C-2 proton of the ether **1**[15] was typical of monosubstituted isobornyl derivatives.[16]



6

When a mixture of camphene and phenol was treated at 100° for 3 hr. with catalytic quantities of boron trifluoride etherate, there was isolated a mixture of four monoalkylphenol adducts in 30% yield. The product consisted of *o*-isobornylphenol (**2**, 33%, m.p. 85.5–86.0°), *p*-isobornylphenol (**3**, 7%, m.p. 151–152°), 6-*exo*-*o*-hydroxyphenyl-*exo*-isocamphane (**4**, 49%, m.p. 84–85°),[17] and 6-*exo*-*p*-hydroxyphenyl-*exo*-isocamphane (**5**, 10%, m.p. 101–103°).

The corresponding *o*- and *p*-bornylphenols (**7**, **8**), *o*- and *p*-camphene hydrophenols (**9**, **10**), and *o*- and *p*-6-*exo*-hydroxyphenyl-*endo*-isocamphanes (**11**, **12**) were not detected in the reaction mixture.

(6) Although Roberts[7a] and Vaughan[7b,c] have suggested that acid-catalyzed racemization of camphene at 100–110° may proceed at least in part by a 1,3-hydride shift, this process probably occurs during or subsequent to Wagner–Meerwein rearrangement to the bornyl cation. Such a 1,3-hydride shift would then involve exchange of hydride between two secondary carbonium ions and would not be analogous to the transition discussed here.

(7) (a) J. D. Roberts and J. A. Yancey, *J. Am. Chem. Soc.*, **75**, 3165 (1953); (b) W. R. Vaughan and R. Perry, Jr., *ibid.*, **75**, 3168 (1953); (c) W. R. Vaughan, C. R. Goeschel, M. H. Goodrow, and C. L. Warren, *ibid.*, **85**, 2282 (1963).

(8) Y. Watanabe, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **63**, 1420 (1960).

(9) A. R. Abdurasuleva and S. Achiava, *Zh. Obschch. Khim.*, **32**, 707 (1962) [*Abstr. Ind. Org. Chem.*, **12**, 520 (1962)].

(10) Vl. Kabaivanov, M. Mikhailov, M. Natov, and L. Popova, *Khim. Ind.*, **31**, 107 (1959) [*Chem. Abstr.*, **54**, 21172 (1960)].

(11) For other references to the acid-catalyzed reactions of alicyclic terpenes and phenol see W. F. Erman and T. J. Flautt, *J. Org. Chem.*, **27**, 1526 (1962).

(12) See ref. 5–7, footnote 11.

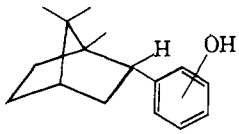
(13) See ref. 9a, footnote 11.

(14) The author is indebted to Dr. R. Wehr for a sample of isobornyl phenyl ether prepared essentially by the method of Kursanov for preparation of menthyl phenyl ethers: N. I. Kursanov, *J. Russ. Phys. Chem. Soc.*, **46**, 815 (1914) [*Chem. Abstr.*, **9**, 1751 (1915); *Chem. Zentr.*, **86**, 894 (1915)].

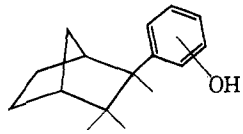
(15) The n.m.r. data, when critical, are listed in the Experimental section along with significant infrared, mass, and ultraviolet spectra data.

(16) In general, monosubstituted isobornyl and bornyl derivatives are readily distinguished by their contrasting spin coupling patterns. The pattern of the C-2 proton in bornyl derivatives appears as a quartet, the spin coupling constants of which range from 2.4 to 4.6 c.p.s. for $J_{endo\text{-}exo}$ and from 6.0 to 11.4 for $J_{exo\text{-}exo}$. In contrast, the coupling constants of the C-2 proton in isobornyl derivatives are more nearly equivalent and range from 5.2–8.7 c.p.s. For a discussion of the n.m.r. spectra of bornanes and related systems and exceptions to this rule see (a) T. J. Flautt and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 3212 (1963); (b) K. L. Williamson, *ibid.*, **85**, 516 (1963); (c) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2709 (1963).

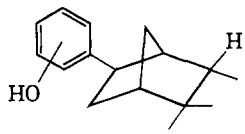
(17) The phenol **4** was isolated as a crystalline material, m.p. 76.2–77.1, the melting point of which was elevated to 84–85° only after chromatography over alumina and repeated recrystallization. The 3,5-dinitrobenzoate derivative of **4** had m.p. 165–167°, strikingly similar to that reported by Kheifits and Belov for their phenol, m.p. 77°. When the product mixture was recrystallized directly from petroleum ether it was possible to isolate only the compound, m.p. 76.2–77.1° (84–85°), according to the method of the previous authors.[12,13] The *o*-isobornyl phenol (**3**), on the other hand, was isolated in pure form only by column chromatography. There is, then, little doubt that our compound, m.p. 84–85°, is identical with the compound, m.p. 77°, reported by Kheifits and Belov[13] and by Kitchen.[12]



7, *ortho*
8, *para*



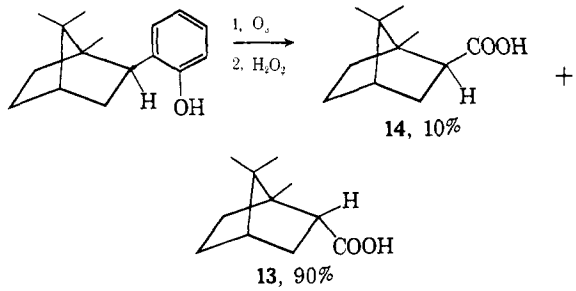
9, *ortho*
10, *para*



11, *ortho*
12, *para*

Structure Elucidation of Products. The Isobornyl Phenols.—The compound, m.p. 151–152°, was readily identified as *p*-isobornylphenol (**3**) by comparison of the n.m.r., infrared, and mass spectra and the gas chromatography retention times of this compound and its methyl ether derivative with an authentic sample of **3** and its methyl ether derivative **39**.[11] A mixture melting point of the phenol and the authentic **3** showed no depression.

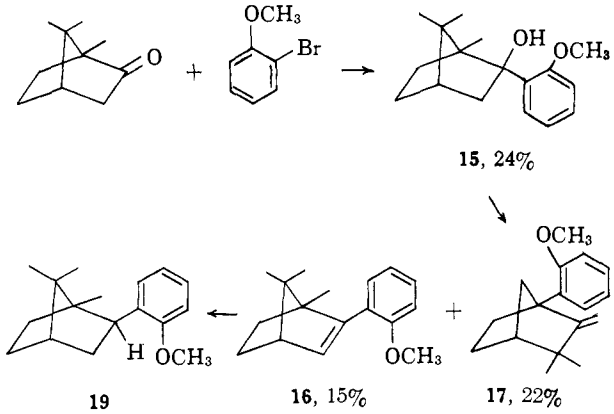
The general structure of the phenol, m.p. 85.5–86.0, was determined as a 2-substituted bornane by ozonolysis to a mixture of bornylcarboxylic acid (**13**, 90%) and isobornylcarboxylic acid (**14**, 10%)[18] using the general procedure of Bartlett, *et al.*[19] The phenol, m.p. 85.5–86.0°, was tentatively described as *o*-isobornylphenol (**2**) by comparison of the n.m.r.



14, 10%

13, 90%

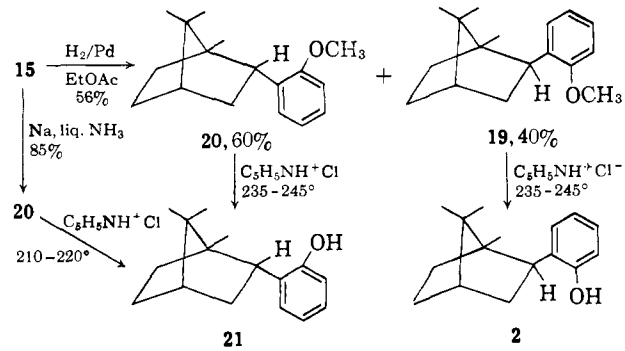
spectrum of this compound with that of the *p*-isobornylphenol (**3**). Three singlets at 8.92, 9.07, and 9.25 τ (methyl protons) and a multiplet at 6.87 ($J_1 = J_2 =$ 8.7 c.p.s.) (*endo*-C-2-proton) in the ratio 9:1 were characteristic of the isobornyl epimer. Since an unambiguous synthesis of the phenol **2** had not been described previously, we pursued the synthesis as outlined in Fig. 1 using the procedure of Erman and Flautt[11] for the synthesis of *p*-isobornylphenol (**3**). Grignard reaction of camphor and *o*-bromoanisole afforded *o*-anisylborneol (**15**) in 24% yield. When **15** was treated with minute quantities of boron trifluoride etherate in ether at room temperature or below, a low yield (22%) of the desired *o*-anisylbornylene (**16**) was obtained. The principal product of the dehydration was *o*-anisylcamphene (**17**, 77%), formed by Wagner–Meerwein rearrangement of **15**.[20]



15, 24%

19 **16**, 15% **17**, 22%

Figure 1.



21 **2**

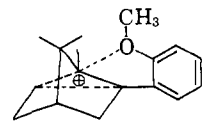
Figure 2.

Since conditions for dehydration of **15** without rearrangement could not be found, the alcohol **15** was reduced directly with palladium-on-carbon to a mixture of *o*-isobornylanisole (**19**, 40%) and *o*-bornylanisole (**20**, 60%) (Fig. 2). Demethylation gave the corresponding phenols *o*-isobornylphenol (**2**) and *o*-bornylphenol (**21**). Reduction of **15** with sodium in liquid ammonia gave only the bornyl epimer **20** thus securing its structure.[22]

The n.m.r., infrared, and mass spectra of synthetic **2** were identical with those of the compound, m.p. 85.5–86.0°, from the reaction of camphene and phenol. A mixture melting point of the two phenols conclusively revealed their identity.

The Isocamphanylphenols.—The two compounds, m.p. 84–85° and 101–103°, from the reaction of camphene and phenol were shown to be identical except for *o*- and *p*-isomerism[23] by oxidation to the same carboxylic acid: *exo*-isocamphane-6-*exo*-carboxylic acid (**23**). The n.m.r. spectra of the two phenols were strikingly similar except, of course, for the aromatic region and anticipated differences in chemical shifts

may be facilitated by the so-called "*o*-effect"[21] or by stabilization of the carbonium ion i by the *o*-methoxyl group.



i

(18) Botton has shown that isobornylcarboxylic acid is converted by acid to a mixture consisting of approximately 94% bornyl- and 6% isobornylcarboxylic acid at equilibrium: M. de Botton, *Bull. soc. chim. France*, 816 (1955).

(19) P. D. Bartlett, E. R. Webster, C. E. Dills, and H. G. Richey, Jr., *Liebigs Ann.*, **623**, 217 (1959).

(20) Preponderance of olefin **17** in this reaction seems somewhat surprising in light of the fact that *p*-anisylbornylene was the only product when *p*-anisylisoborneol was treated with boron trifluoride etherate under even more vigorous conditions.[11] The rearrangement of the alcohol **15** to the olefin **17**

(21) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 648–652.

(22) Analogously, reduction of *p*-anisylbornylene with sodium in liquid ammonia afforded only the more stable *p*-bornylanisole, ref. 11.

(23) The n.m.r. and infrared spectra clearly defined the compound, m.p. 83–85°, as the *ortho* isomer and the compound, m.p. 101–103°, as the *para* isomer.

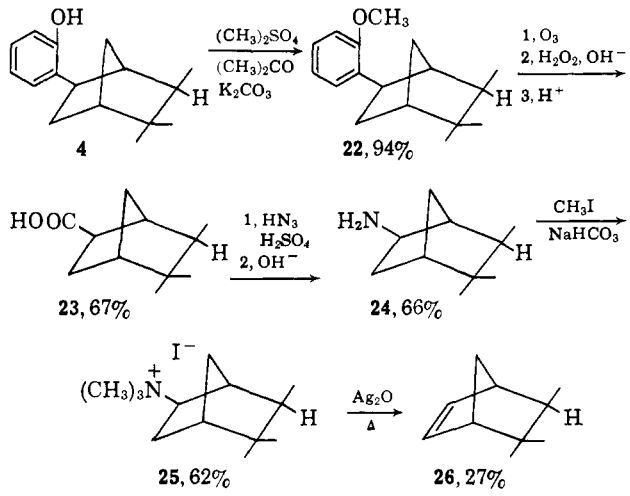


Figure 3.

between *o*- and *p*-isomers. Therefore structure proof of only the *o*-isomer will be described.

Examination of the n.m.r. spectrum of **4** revealed the multiplet pattern of the aromatic protons at 2.8–3.5 τ [4.0]; the phenolic proton 4.9 τ (s) [1.1]; the benzyl C-6 proton as a multiplet centered at 7.12 τ ($J_1 \sim J_2 \sim 7.2$ c.p.s.) [0.9]; the bridgehead C-1 proton, 7.94 τ broad signal [0.8]; the C-2, C-4, C-5, and C-7 bridgehead protons as multiplets at 7.79 τ [0.9] and 8.1–8.8 τ [6.2]; and the methyl groups at 8.97 (s), 9.12 (s), and 9.13 (d, $J = 6.1$ c.p.s.) [8.9].[24]

The *o*-phenol (**2**) was degraded to the known *exo*-isocamphene (**26**) as outlined in Fig. 3. The structure of the olefin **26** was defined by the n.m.r. spectrum which showed a triplet at 3.88 τ ($J_1 = 1.5$ c.p.s.; C-5,6 vinyl protons), a multiplet at 7.70 τ (C-1 and C-4 bridgehead protons), and an AB quartet with doublets centered at 8.25 and 8.70 τ ($J_{AB} = 10$ c.p.s., bridge protons) in the ratio 2.0:1.9:2.1. The methyne proton α to the methyl group appears upfield (8.7–9.1 τ) as a multiplet superimposed by the methyl proton pattern, probably a consequence of the location of the α-proton above the plane of the olefinic bond.[25,26] The *gem*-dimethyl protons appear as singlets at 8.98 and 9.15 τ, while the splitting pattern of the C-2 methyl proton is superimposed with the *gem*-dimethyl at 8.98 and the C-2 α-proton. The structure of **26** was more definitively ascertained by comparison of the n.m.r. and infrared spectra with those of an authentic specimen of *dl-exo*-isocamphene[27] and by a mixture melting point determination with the authentic **26** and the phenyl azide derivative[28] of **26**.

The transformation of the phenol **2** to the olefin **26** established the stereochemistry of the methyl at C-2 but did not delineate the position of the aromatic group between C-5 and C-6 or define the stereochemistry of this function. The position of the aromatic group was established by degradation to 6-*exo*-acetoxy-*exo*-isocamphane (**29**) by the procedure outlined in Fig. 4. The gas chromatography retention time, and n.m.r. and infrared spectra of the acetate **29** obtained by degradation of the phenol **2** were identical with those of an authentic sample of 6-*exo*-acetoxy-*exo*-isocamphane (**29**) prepared by hydroboration of olefin **26**[27] and subsequent acetylation (Fig. 4). In the latter synthesis two isomeric acetates were isolated. Since the hydroboration of norbornene is known to occur from the *exo* side[29] the structure of the two acetates must be 6-*exo*-acetoxy-*exo*-isocamphane (**29**) and 5-*exo*-acetoxy-*exo*-isocamphane (**30**). The lower boiling acetate was defined as the 5-acetoxy derivative **30** by comparison of the n.m.r. spectra with that of an authentic sample of the hydrogen phthalate derivative (**30b**) of 5-*exo*-hydroxy-*exo*-isocamphane.[28] The higher boiling acetate after saponification and treatment with phthalic anhydride afforded a hydrogen phthalate derivative (**29b**), the physical constants and n.m.r. spectrum of which contrasted markedly with that of the authentic hydrogen phthalate derivative[28] **30b** of the 5-*exo*- alcohol. The acetate obtained by degradation of the phenol **4** is therefore confirmed as the 6-*exo*-acetate **29**.

Since strong arguments can be presented to establish that each step of the degradation from phenol **4** to acetate **29** proceeded without epimerization,[30] the *exo* configuration is assigned to the phenol **4**. Further support for the *exo* stereochemistry is given by the n.m.r. splitting pattern of the benzyl proton. This proton appears as a multiplet with almost equal spacings of 7.2 c.p.s.[34] Since the dihedral angle between the C_6–C_1 protons is ~79°, the spin coupling between these protons should be ~0.[37] The resulting pattern should be similar to that of the isobornylphenols which do indeed appear as multiplets with approximately equal coupling constants.[9] In contrast, the benzyl proton of the 6-*endo*-hydroxyphenyl isomer should appear as a complex multiplet of unequal spacings of 8–10, 3–4, and 2–4 c.p.s.[16,36]

Discussion.—The reaction of camphene with phenol at 0° proceeds in accord with previously documented examples of the addition of organic acids to camphene

(24) Chemical shifts are expressed in conventional τ-values. Coupling patterns, shown in parentheses, are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants, J, are expressed in cycles per second. Relative ratio of peak areas are shown in brackets.

(25) L. N. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 129.

(26) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(27) Prepared by the method of S. Beckmann and B. Geiger, *Chem. Ber.*, **94**, 1910 (1961).

(28) Kindly supplied by Professor S. Beckmann, Chem. Inst. der Landwirtschaftlichen Hochschule, Stuttgart, Hohenheim, West Germany.

(29) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 126.

(30) A 70:30 mixture of norbornane-*exo*-carboxylic acid and norbornane-*endo*-carboxylic acid was not equilibrated after treatment for 8 hr. with 15% sodium hydroxide in aqueous methanol at reflux.[31] Thus it is doubtful that complete epimerization from *endo*-acid to *exo*-acid could have occurred under the oxidative conditions employed here. Hart and Chloupek[32] and Bartlett and Pincock[31] have shown that the *endo*- and *exo*-norbornanecarboxylic acids are not epimerized during acid chloride formation with thionyl chloride. The subsequent steps of amide formation and Grignard work-up were mild and yielded only one isomeric amide and ketone, respectively. If equilibration occurred during these steps a mixture of products would have been detected. The Baeyer–Villiger reaction is known to proceed with retention of configuration.[33]

(31) P. D. Bartlett and R. E. Pincock, *J. Am. Chem. Soc.*, **84**, 2445 (1962).

(32) H. Hart and F. J. Chloupek, *ibid.*, **85**, 1155 (1963).

(33) C. H. Hassall, "Organic Reactions," Vol. 9, John Wiley and Sons, Inc., New York, N. Y. 1957, p. 73.

(34) The peaks are broad relative to the pattern of the isobornyl phenols, probably a result of spin coupling with the C-7-*trans* proton. Coupling of this type is reported to be of the order of 2–4 c.p.s.[35,36]

(35) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

(36) P. Laszlo and P. von R. Schleyer, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 9, 1963.

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

at low temperatures.[38] The product of kinetic control—camphene hydrophenyl ether (**31**, Fig. 5)—is probably formed initially from the cation **32** in accordance with Berson's generalizations.[39] However, owing to the well-recognized instability of *t*-alkyl phenyl ethers,[40] the ether **31** would be expected to undergo extremely rapid rearrangement to the more stable isobornyl phenyl ether (**1**). Since a thermodynamic equilibria is hardly approached under these conditions, it is not surprising that bornyl phenyl ether (**6**) is absent from the reaction mixture.

The condensation of camphene and phenol under C-alkylation conditions, however, contrasts markedly not only with the low temperature camphene–phenol reaction but also with the reaction of other organic acids—*e.g.*, acetic acid—with camphene at higher temperatures. Thus, in the C-alkylation of phenol by camphene the 6-substituted isocamphanes **4** and **5** were the principal products of the reaction while no bornyl isomers were formed at all. In contrast, isobornyl acetate and bornyl acetate were the principal products when camphene was treated with acetic acid under the same conditions while the corresponding 6-*exo*-acetoxy-*exo*-isocamphane derivative **29** was not detected in the product mixture.[41]

The apparent anomalies between the acetic acid and phenol reactions can be reconciled by visualizing a rapid equilibrium between cations **32** and **33**[42] (Fig. 6) and making the following assumptions: (1) Although the initial products of kinetic control—the camphene hydrophenols **9** and **10**—may be completely by-passed due to steric retardation of alkylation at the highly hindered 2-carbon, it is more probable that the *t*-phenols **9** and **10** are formed initially but, being unstable to acid at 100°,[43] are subsequently converted to the more stable secondary phenols **2, 3, 4,** and **5**.

(2) The rate of alkylation of cation **32** is slow compared with the rate of addition to the cation **33**. Examination of the molecular models of *p*-isobornylphenol (**3**) and 6-*exo*-*p*-hydroxyphenyl-*exo*-isocamphane (**5**) lends credence to this argument.[44] The bulky aromatic group shows considerable interaction with the C-3-methyl group in its attack on the ion **32** but is completely unaffected when approaching the ion **33** from the *exo* side.

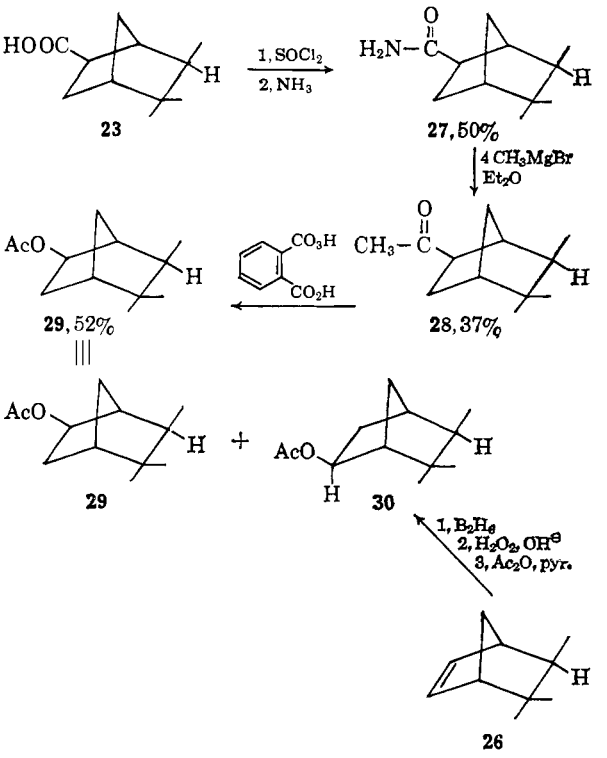


Figure 4.

(3) Although the equilibrium under thermodynamically controlled conditions should lie strongly in the direction of the cation **32**,[45] two factors lead to the formation of 6-substituted products—the comparative rates between alkylation of **32** and **33**, as mentioned above, and the fact that once alkylation occurs the process is irreversible. The irreversible nature of the secondary phenol C–C bond formation under these conditions was firmly established by results from demethylation of the methyl ethers of the phenols **2, 3, 4, 5, 7,** and **8**. Under extremely vigorous acid conditions the corresponding phenols were isolated without concurrent rearrangement of the alicyclic system. For example, treatment of *o*-isobornylanisole (**19**) with pyridine hydrochloride at 245–250° for 4 hr. afforded the phenol **2** in 88% yield. The stability of the phenols **2, 3, 4,** and **5** to acid at elevated tempera-

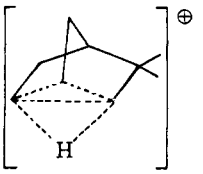
(38) For the most recent review on the subject of acid-catalyzed addition reactions to camphene and related systems refer to footnote 4b.

(39) J. A. Berson, *Tetrahedron Letters*, 17 (1960).

(40) R. A. Smith, *J. Am. Chem. Soc.*, **55**, 3718 (1933).

(41) Although principal products from the reaction of camphene and acetic acid are isobornyl acetate and bornyl acetate, a complexity of minor products accompanies the two acetates and the yields of these compounds are highly dependent upon the exact conditions of the reaction. One such reaction is listed in the Experimental section for comparison with the camphene–phenol condensation.

(42) The intermediates may be represented as rapidly equilibrating nonclassical ions on the one hand, or as a single nonclassical species ii at the other extreme. We have used the nonclassical representations **32** and **33** for purposes of clarity only.

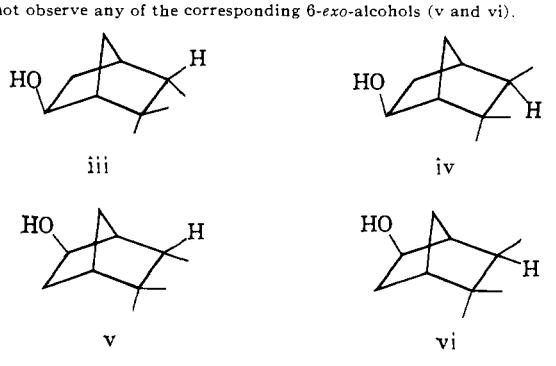


ii

(43) *t*-Butylphenol, for example, is converted almost completely to *t*-butylbenzene and phenol on treatment with Lewis acids in benzene solution at 80°: (a) R. A. Smith, *J. Am. Chem. Soc.*, **59**, 899 (1937); (b) *ibid.*, **56**, 717 (1934); (c) S. Natekon, *ibid.*, **56**, 1583 (1934); (d) I. Tzukervanik and Z. Nazarova, *J. Gen. Chem. USSR*, **5**, 767 (1935) [*Chem. Abstr.*, **30**, 443 (1936)].

(44) It is assumed that in the transition state the structure begins to approach that of product by partial bond formation.

(45) That this is the direction of equilibrium between **32** and **33** is validated by the work of Beckmann and Geiger[46] who, on hydration of 6-*exo*-isocamphene (**26**), isolated 2,2,3-*endo*- and 2,2,3-*exo*-trimethylbicyclo[1.2.2]heptan-5-*exo*-hexanol (iii and iv [48%]) and isoborneol (50%) but did not observe any of the corresponding 6-*exo*-alcohols (v and vi).



(46) S. Beckmann and B. Geiger, *Chem. Ber.*, **95**, 2101 (1962).

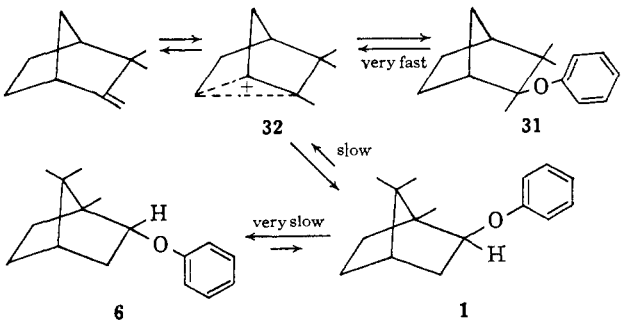


Figure 5.

tures also accounts for the absence of bornylphenols in the product mixture. Bornyl isomers are generated from the initially formed isobornyl isomers quite slowly even when such isomers are readily eliminated by acid.[4b]

Thus the products from the phenol reaction are basically those of kinetic control owing to the relative stability of the secondary phenols. The formation of 6-substituted isomers is accounted for by enhanced competition of alkylation at the C-6 site as a consequence of retardation of alkylation at the C-2 position. In contrast, the acetate products from the reaction of acetic acid and camphene are unstable to the reaction conditions employed here. Thus any 6-acetoxyisocamphane formed in this reaction would be rapidly converted to the camphene ion **32**[45] or to other elimination products. Similarly, isobornyl acetate would undergo slow isomerization to bornyl acetate.

This mechanistic picture would be consistent except for the suprising absence of the phenols **11** and **12** which would arise from attack at position C-1 of the ion **33** (path d). Since there is no obvious reason for predicting a faster rate of addition at position 6 than position 1 of cation **33**, it is tempting to treat the process of phenol attack as concerted with 2,6-hydride transfer.[47] If attack by phenol at C-6 is competitive with 1,3-hydride transfer, then product formation should proceed with some degree of optical integrity. When phenol was treated with *l*-bornyl acetate, $[\alpha]^{26}D$ $-38.3°$, under the same conditions as the *dl*-camphene–phenol condensation, the same completely racemic products **2–5** were isolated in comparable yields (**2**, 26%; **3**, 12%; **4**, 44%; **5**, 13%). This observation implies that racemization *via* one of three carbonium ion paths—1,2-methyl migration, tricyclene formation, or 2,6-hydride transfer—is much faster than and precedes the alkylation step.

Although other explanations may be presented to account for the absence of the phenols **11** and **12**, these interpretations are entirely speculative at this stage and further experimentation will be necessary to establish the exact details of this process.[49]

Experimental

General.—Melting points were determined in an Ace Glass Hershberg melting point bath using calibrated Anschutz ther-

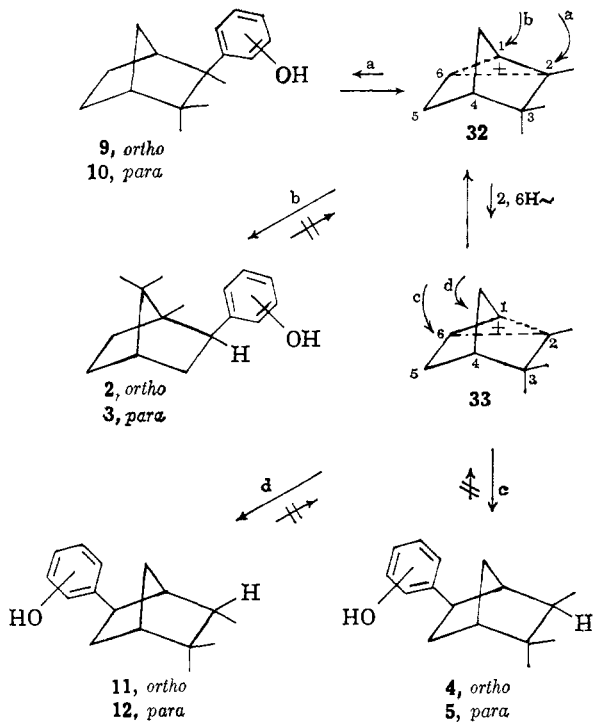


Figure 6.

mometers or on a micro hot stage apparatus and are corrected. Boiling points were observed on standard thermometers and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer Infracord spectrophotometer. Microanalyses were performed by Dr. F. L. Jackson and associates or by Spang Microanalytical Laboratories, Ann Arbor, Mich. The n.m.r. spectra were obtained with a Varian A-60 instrument in carbon tetrachloride or deuterated chloroform using tetramethylsilane as an internal reference. Molecular weights were determined on a Bendix Time of Flight mass spectrophotometer. Gas chromatography separations were made on one of five columns designated as columns 1–5. Column 1: a 10-ft., 0.25 in. stainless steel column packed with 30% succinic acid–triethylene glycol polymer on 60/80 mesh Chromosorb; column 2: a 10-ft. × 0.25 in. stainless steel column packed with 25% adipic acid–ethylene glycol polymer on 60/80 mesh Chromosorb; column 3: a 5-ft., 0.25 in. stainless steel column packed with 20% GE-SF-96 silicone on 60/80 mesh Chromosorb; column 4: a 10-ft., 0.25 in. copper column packed with 20% GE-SF-96 silicone on 60/80 mesh acid-washed Chromosorb W; column 5: a 10-ft., 0.25 in. copper column packed with 20% Reoplex on 60/80 mesh acid-washed Chromosorb W.

The petroleum ether used in this work was purified by distillation, b.p. 30–60°.

Condensation of Camphene and Phenol. A. At 0°.—To 408.6 g. (3.0 moles) of *dl*-camphene and 282.3 g. (3 moles) of phenol maintained at 0–5° was added dropwise with vigorous stirring over a period of 30 min. 1.73 g. (0.012 mole) of boron trifluoride etherate. The mixture was stirred an additional 2.5 hr. at 0–5°, then diluted with ether, the ethereal solution washed with 50 ml. of 10% sodium hydroxide and water, and dried over magnesium sulfate. The ether was removed under reduced pressure and the product distilled from a 1-ft. Vigreux column to yield 80.0 g. of forerun, b.p. 65–160°, and 539 g. (78%) of isobornyl phenyl ether (**1**), b.p. 160° (8.0 mm.). A 5.0-g. portion of the product was redistilled for analysis from an 18-in. spinning band column, b.p. 99–101° (0.3 mm.), $n^{25}D$ 1.5260; infrared spectrum: λ 8.05 μ (aromatic ether); 13.3, 14.5 μ (monosubstitution); n.m.r. spectrum: 6.02 τ (t, J = 5.2 c.p.s.) [1] (C-2 proton); 8.95, 9.02, 9.14 τ (s) [9] (methyl protons).

Anal. Calcd. for $C_{18}H_{22}O$: C, 83.4; H, 9.6. Found: C, 83.5; H, 9.8.

Condensation of Camphene and Phenol. B. At 100°.—To a mixture of 584.3 g. (4.30 moles) of camphene, $[\alpha]D$ 1.0°, fractionally distilled over sodium, b.p. 157°, m.p. 48–50°, and 808.4 g. (8.60 moles) of phenol was added dropwise with stirring 3.12 g. (0.022 mole) of boron trifluoride etherate over a period of 1 hr. The temperature rose to 100–110° over this period and was main-

(47) The presence of only 5-*exo*-methyl-2-*exo*-norbornyl formate and apparent absence of 5-*endo*-methyl-2-*exo*-norbornyl formate in the formolysis of *syn*-7-methyl-2-*exo*-norbornyl acid phthalate at 95° by Beckmann and Eder[48] suggests that a more subtle explanation of product stereospecificity is necessary.

(48) S. Beckmann and G. Eder, *Chem. Ber.*, **91**, 2878 (1958).

(49) For example, a comparison of this reaction with that of the alkylation of phenol by 6-acetoxy-*exo*-isocamphane and 6-acetoxy-*endo*-isocamphane, compounds which would lead initially to the cation **33** on treatment with acid, is desirable.

TABLE I
CHROMATOGRAM 1

Fractions	Solvent	Vol., ml.	Wt., g.	Composition (%)
(1) 1–17	Petr. ether	5000	3.9	**34** (65), **35** (35)[50]
(2) 13–25	2–10% ether–petr. ether	3000	0.8	**34** (10), **35** (20), **2** (30), **4** (30)[50]
(3) 18	25% ether–petr. ether	500	25.3	**34** (10), **35** (30), **2** (40), **4** (20)[50]
(4) 19–23	25% ether–petr. ether	1500	205.5	**2** (42), **4** (58)[50]
(5) 24–30	25% ether–petr. ether	1750	85.0	**2** (18), **4** (70), **3** (4), **5** (8)[50]
(6) 31–42	25% ether–petr. ether	4750	33.9	**3** (40), **5** (60)[51]

tained with constant stirring for 3 more hours. After cooling the solution the mixture was diluted with 200 ml. of saturated sodium carbonate (40 g.) and extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and evaporated to produce 1114.8 g. of residual oil. Distillation through a 12-in. Vigreux column afforded 308.5 g. of forerun, b.p. 30–80° (0.8 mm.); 342.4 g. of distillate, b.p. 120–150° (0.8 mm.); and 564 g. of residue. Analysis of the distillate, b.p. 120–150° (0.8 mm.), on column 1 at 220° and 65 ml./min. helium flow indicated the presence of 6 components—*o*-isobornylphenol (**2**, 32%, rel. retention time 10.02 min.), 6-*exo*-*o*-hydroxyphenyl-*exo*-isocamphane (**4**, 48%, rel. ret. time 11.35 min.), *p*-isobornylphenol (**3**, 9%, rel. ret. time 13.60 min.), 6-*exo*-*p*-hydroxyphenyl-*exo*-isocamphane (**5**, 6%, rel. ret. time 14.40 min.), and two unidentified phenols (**34**, 1.5%, and **35**, 3%, relative retention times 6.08 and 8.80 min., respectively).

The 342.4 g. of distillate, b.p. 120–150° (0.8 mm.), was dissolved in 1 l. of petroleum ether (b.p. 30–60°), adsorbed on 3080 g. of Davison 100–200 mesh silica gel, and eluted as shown in Table I.

A 47.9-g. portion of fraction 4 from the above chromatogram was rechromatographed on 1502 g. of 100–200 mesh silica gel.

TABLE II
CHROMATOGRAM 2

Fraction	Solvent	Vol., ml.	Wt., g.	Composition (%)
1–39	Petr. ether	8375	15.5	**2** (80), **4** (20)[50]
	1–5% ether–petr. ether	5950		
40–105	5% ether–petr. ether	1460	18.6	**2** (60), **4** (40)[50]
105–239	5% ether–petr. ether	5860	17.0	**4** (100)[50]

A 5.2-g. sample of the material from fractions 105–239 from the chromatogram (Table II) was recrystallized from petroleum ether (b.p. 30–60°) at 0–5° to afford 4.3 g. of 6-*exo*-*o*-hydroxyphenyl-*exo*-isocamphane (**4**) as colorless rhombical prisms, m.p. 76.2–77.2°. Further recrystallization from benzene–petroleum ether (1:5) raised the m.p. to 83–85°. A mixture melting point of this compound and *o*-isobornylphenol, m.p. 83–84.2°, isolated below, showed a marked depression, m.p. 57–71°. A mixture melting point with the *o*-isobornylphenol, synthesized from camphor, m.p. 81.5–83.5°, similarly showed a marked depression, m.p. 50–65°; infrared spectrum (coconitrile mull): 2.90 μ (OH), 13.3 μ (*ortho* substitution); n.m.r. spectrum: 2.8–3.5 τ (m) [4.0] (aromatic protons); 5.18 τ (s) [1.0] (phenolic proton); 7.12 τ (m, $J_1 \sim J_2 \sim 7.2$ c.p.s.) [0.9] (C-6-benzyl proton); 7.94 τ (broad s) [0.8] (C-1 proton); 7.79 τ (m) [0.9] and 8.1–8.8 τ (m) [5.2] (C-5, C-7, C-2, C-4 protons); 8.97 τ (s), 9.12 τ (s); 9.13 τ (d, $J = 6.1$ c.p.s.) [8.9] (C-7-, C-8-, and C-2-methyl protons); mol. wt., 230.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.65; H, 9.49.

A 2.0-g. portion of the fractions 1–39 from chromatogram 2 was recrystallized from octane to yield 0.76 g. of *o*-isobornylphenol (**2**) as colorless rhombical prisms, m.p. 79.5–83°. Further recrystallization gave a constant m.p. 83–84.2°. A mixture m.p. with the phenol **4** was depressed as indicated above. A mixture melting point with the synthetic *o*-isobornylphenol, m.p. 81.5–83.5°, described below, showed no depression, m.p. 81.5–83.5°; infrared spectrum (coconitrile mull): λ 2.92 μ (OH), 13.31 μ (*o*-substitution); n.m.r. spectrum: 2.7–3.5 τ (m) [3.8] (aromatic protons); 5.51 τ (s) [1.0] (phenolic proton); 6.87 τ (m, $J_1 \sim J_2 \sim 9.0$ c.p.s.) [1.0] benzyl proton; 7.7–8.8 τ (m) [7.4] (methylene and C-4-protons); 9.11 (s), 9.15 (s), 9.24 τ (s) [8.5] (methyl protons); mol. wt., 230.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.38; H, 9.48.

The two phenols **3** and **5** could be separated as the methyl ethers by fractional distillation as described later, or by a process of fractional recrystallization. A 6.4-g. sample of the material from fraction 6 of the chromatogram 1, m.p. 87–93°, was fractionally recrystallized from benzene–petroleum ether (b.p. 30–60°). The *p*-isobornylphenol (**3**) separated first and, after six recrystallizations from petroleum ether–benzene, crystallized in colorless long needles, m.p. 150.6°. A mixture melting point of this material and authentic *p*-isobornylphenol, m.p. 151–152°,[11] was undepressed, m.p. 151–152°. The n.m.r., mass, and infrared spectra of this phenol and authentic **3**[11] were identical; mol. wt., 203.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.09; H, 9.47.

The 6-*exo*-*p*-hydroxyphenyl-*exo*-isocamphane (**5**) was recovered from the mother liquors after removal of the bulk of the phenol **3** by crystallization from benzene–petroleum ether; m.p. 92.5–94.5°. Further recrystallization from benzene–petroleum ether yielded colorless needles, m.p. 101–103°; infrared spectrum: (coconitrile mull): λ 3.0 μ (OH); 11.8, 12.2 μ (*p*-substitution); n.m.r. spectrum: 3.05, 3.41 τ (q, $J = 9.6$ c.p.s.) [4.0] (aromatic protons); 4.34 τ (s) [1.0] (phenolic proton); 7.37 τ (m, $J_1 \sim J_2 \sim 7.8$ c.p.s.) [1.0] (benzyl proton); 7.87 τ (m) [1.2] and 8.16–8.74 τ (m) [6.0] (C-5- and C-7-methylene and C-1-, C-2-, and C-4-methyne protons); 8.98 (s), 9.10 (s), and 9.12 τ (d, $J = 5.6$ c.p.s.) [9.0]; mol. wt., 230.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.05; H, 9.71.

***o*-Isobornylanisole (19) and 6-*o*-*exo*-Anisyl-*exo*-isocamphane (22).**—To a mixture of 68.8 g. (0.282 mole) of fraction 4 from chromatogram 1 above (58% **4**, 42% **2**), 125 g. (0.914 mole) of potassium carbonate, and 300 ml. of acetone heated to 50° was added dropwise with stirring over a period of 30 min. 75 g. of dimethyl sulfate. The mixture was heated at reflux under a nitrogen atmosphere for 30 min. when a second portion of 75 g. of dimethyl sulfate was added. The mixture was heated at reflux for 8 hr. and stored overnight at room temperature. The potassium sulfate was removed by filtration, the acetone removed under reduced pressure, and excess dimethyl sulfate decomposed with cautious addition of 100 ml. of concentrated ammonium hydroxide. The mixture was extracted with ether, the ethereal layer washed with water, 10% hydrochloric acid, 5% sodium bicarbonate, and water, dried over magnesium sulfate, and evaporated to yield 68.7 g. of residual liquid. Gas chromatographic analysis on column 2 at 209° and 75 ml./min. helium flow indicated the presence of 40% *o*-isobornylanisole (**19**) and 60% 6-*o*-*exo*-anisyl-*exo*-isocamphane (**22**). Fractional distillation on a 24-in. spinning band column gave 12.3 g. of distillate, b.p. 95–103° (0.1 mm.) (90% **19**, 10% **22**); 36 g. of distillate, b.p. 103 (0.1 mm.)–98° (0.06 mm.); and 18 g. of the methyl ether **22**, b.p. 98 (0.06 mm). The fraction, b.p. 95–103° (0.1 mm.), was redistilled for analysis, b.p. 61° (2.3 mm.). The distillate solidified and was recrystallized from ethanol to afford *o*-isobornylanisole (**19**) as colorless prisms, m.p. 72–74.5°. Recrystallization from ethanol gave a constant m.p. 75.8–78.5°; infrared spectrum: 8.03 μ (OCH_3); n.m.r. spectrum described in reference 16a.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.33; H, 9.76.

The ether **22**, b.p. 98° (0.6 mm.), could not be induced to crystallize but gave a single peak when analyzed on column 1 at 196° and 42 ml./min. helium flow; infrared spectrum: 8.05 μ (OCH_3); n.m.r. spectrum: 6.26 τ (s) [3.10] (OCH_3 protons); 7.03 τ (m, $J_1 \sim J_2 \sim 7.5$ c.p.s.) [1.0] (benzyl proton); 8.96 τ (s), 9.10 τ (s), 9.13 τ (d, $J = 6.1$ c.p.s.) [9.0] (methyl protons).

(50) Analyzed by gas chromatography on column 3 at 210° and 55 ml./min. flow rate.

(51) Analyzed by gas chromatography on a 1000-ft. Apiezon L capillary column at 200° and 50 ml./min. helium flow rate. The authors are indebted to Dr. C. H. Orr and associates for capillary column gas chromatograms mentioned in this work. Since the composition of fractions varied in each general fraction, the average composition for these composites is listed.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.6; H, 9.9. Found: C, 83.7; H, 9.9.

6-*exo*-*p*-Anisyl-*exo*-isocamphane (36).—A portion of the 1:1 phenol–camphene adduct mixture, b.p. 120–150° (0.8 mm.), from a separate run was methylated as above. From 50.75 g. of the phenol mixture, 111.0 g. of potassium carbonate, and 75 g. of dimethyl sulfate, there was obtained 46.8 g. of ether product. Analysis by gas chromatography on column 1 at 210° and 57 ml./min. helium flow indicated a composition of 2% of the methyl ether of **34**, 5% of the methyl ether **35**, 31% **19**, 46% **22**, 10% **39**, and 6% **36**. The product was fractionated on an 18-in. spinning band column to afford 0.60 g. of **34** as a liquid, b.p. 107–108° (0.4 mm.); infrared spectrum: λ 8.0–8.1 μ (OCH_3), 13.3 μ (*o*-disubstitution), absence of phenolic OH. There was obtained 1.2 g. of **35** as a liquid, b.p. 107.5° (0.4 mm); infrared spectrum: 8.1 (OCH_3), 13.3–13.4 μ (*o*-disubstitution). There was isolated 17.4 g. of a mixture of **19** and **22**, b.p. 96–98° (0.2 mm.); 15.3 g. of a mixture of **22** and **39**; and 1.2 g. of 6-*exo*-*p*-anisyl-*exo*-isocamphane (**36**) as a liquid, b.p. 98° (0.02 mm.); infrared spectrum λ, 8.04 μ (OCH_3); n.m.r. spectrum: 6.33 τ (s) (OCH_3); 7.48 τ (t) (benzyl proton); 9.00 τ (s), 9.17 τ (s); 9.19 τ (d, J = 6 c.p.s.) (methyl protons).

Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.25; H, 9.64.

Oxidation of *o*-Isobornylanisole (19).—Essentially the method of Flautt and Erman[16a] for oxidation of *o*-bornylanisole was employed. From 1.00 g. (0.004 mole) of *o*-isobornylanisole (**2**), m.p. 72–74.5°, treated with 3.2 g. (0.675 mole) of ozone there was isolated after peroxide treatment 0.4514 g. of colorless oil which did not solidify on long storage. The n.m.r. spectrum of the oil indicated the presence of approximately 90% bornylcarboxylic acid (**13**) and 10% isobornylcarboxylic acid (**14**).[52,53] The bornyl isomer **13** was isolated by repeated crystallization from formic acid in needles, m.p. 86–89° (0.110 g., 15%). A mixture melting point of this material and a sample of the bornylcarboxylic acid of Flautt and Erman,[16a] m.p. 90.8–92.6°, was undepressed, m.p. 87–90°.

Grignard Reaction of Camphor and *o*-Bromoanisole. Preparation of *o*-Anisylisoborneol (8).—The general procedure of Erman and Flautt[11] for preparation of *p*-anisylisoborneol using tetrahydrofuran solvent was employed. From 150 g. (0.80 mole) of *o*-bromoanisole, 20.4 g. (0.85 mole) of magnesium, and 121.6 g. (0.80 mole) of camphor was obtained 49.1 g. (23.6%) of *o*-anisylisoborneol (**15**) as rhombical prisms from petroleum ether; m.p. 77.8–81°. Further recrystallization from petroleum ether did not change the melting point appreciably, 78.4–79.6°; infrared spectrum (coconitrile mull): λ, 2.8 μ (OH), 13.4 μ (*o*-disubstitution).

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.30; H, 9.21.

Dehydration of *o*-Anisylisoborneol (15). Formation of 1-*o*-Anisylcamphene (17) and *o*-Anisylbornylene (16).—The procedure of Flautt and Erman[11] for preparation of *p*-anisylbornylene was employed for dehydration of *o*-anisylisoborneol. To 38.8 g. (0.149 mole) of *o*-anisylisoborneol dissolved in 750 ml. of ether was added 2.5 g. (0.017 mole) of boron trifluoride etherate in 250 ml. of ether. After storage at room temperature overnight the ethereal solution was washed with 5% sodium bicarbonate solution and water, dried, and evaporated to afford 27.8 g. of colorless liquid. Analysis of the liquid on column 2 at 186° and 42.5 ml./min. helium flow indicated the presence of 3 components: an unidentified isomer (1.2%, rel. ret. time 42.9 min.), 2-*o*-anisylbornylene (**16**, 21.7%, rel. ret. time 52.5 min.), and 1-*o*-anisylcamphene (**17**, 77.1%, rel. ret. time 64.8 min.). The liquid was carefully fractionated on an 18-in. spinning band column to afford 3.17 g. of forerun, b.p. 78–85° (0.15 mm.); 12.35 g. of distillate, b.p. 87–90° (0.15 mm.) (60% **17**, 30% **16**); and 17.00 g. of distillate, b.p. 97° (0.16 mm.) (**17**).

The 1-*o*-anisylcamphene (**17**) fraction, b.p. 97° (0.15 mm.), was redistilled for analysis, b.p. 122° (3.5 mm.), $n^{25}D$ 1.5415; infrared spectrum: 6.08 and 11.4 μ ($R_2C{=}CH_2$); n.m.r. spectrum: 5.52 τ (s), 5.86 τ (s) [2.0] (vinyl protons); 6.28 τ (s) [2.9] (OCH_3 protons), 7.30 τ (d, J_1 = 10.0 c.p.s., J_2 = 1.5 c.p.s.) [1.0] (C-7-*syn*-proton), 8.86 τ (s) [6.0] (methyl protons).

Anal. Calcd. for $C_{17}H_{22}O$: C, 84.3; H, 9.2. Found: C, 84.3; H, 8.9.

The fraction, b.p. 87–90° (0.15 mm.), was refractionated and the 2-*o*-anisylbornylene (**16**) isolated as a liquid, b.p. 119–120° (3.5 mm.), $n^{25}D$ 1.5410. Final purification was achieved by preparative gas chromatography on column 4 at 175° and 51 ml./min. helium flow. The *o*-anisylbornylene (**16**) separated as needles, m.p. 63–65°; infrared spectrum: absence of terminal olefin peaks; n.m.r. spectrum: 3.06 τ (d, J = 3.2 c p.s.) [1.0] (vinyl proton); 6.24 τ (s) [3.0] (OCH_3 protons); 7.65 τ (t, J = 3.0 c p.s.) [1.2] (C-4-proton); 9.07, 9.11, 9.18 τ (s) [9.0] (methyl protons).

Anal. Calcd for $C_{17}H_{22}O$: C, 84.3; H, 9.2. Found: C, 84.4; H, 9.4.

Sodium Reduction of *o*-Anisylisoborneol (8). Preparation of *o*-Bornylanisole (16).—The procedure of Erman and Flautt[11] for sodium reduction of *p*-anisylbornylene was employed. Reduction of 10.0 g. (0.038 mole) of *o*-anisylisoborneol (**15**), m.p. 75–77.5°, with 3.0 g. (0.13 mole) of sodium in 200 ml. of liquid ammonia over a period of 80 min. afforded 7.95 g. (85%) of *o*-bornylanisole (**20**) as a colorless liquid. Gas chromatographic analysis indicated the product to be 96% *o*-bornylanisole.

Distillation from an 18-in. spinning band column supplied 5.54 g. (60%) of *o*-bornylanisole (**20**), b.p. 107° (2.4 mm.), $n^{28}D$ 1.5410; infrared spectrum: absence of hydroxyl bands, 8.1 μ (OCH_3), 13.3 μ (*o*-substitution); n.m.r. spectrum: 6.20 τ (q, obscured by OCH_3) (benzyl proton), 6.32 τ (s) (OCH_3 protons) [4.0]; 8.83 (s) [2.8], 9.08 (s) [3.0]; 9.32 τ (s) [3.0] (methyl protons).

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.6; H, 9.9. Found: C, 83.9; H, 10.0.

Pyridine Hydrochloride Fusion of *o*-Bornylanisole (20). Preparation of *o*-Bornylphenol (21).—Essentially the procedure of Erman and Flautt[11] for demethylation of *p*-isobornylphenol was employed. From a mixture of 3.91 g. (0.016 mole) of *o*-bornylanisole (**20**) and 30.0 g. of pyridine hydrochloride heated at 210–220° for 4 hr., there was isolated 3.61 g. of the phenol **21** as an oil. A 3.10-g. sample of the oil was dissolved in 20 ml. of petroleum ether and chromatographed on 30 g. of 100–200 mesh Davison silica gel. Elution with petroleum ether afforded 0.120 g. of *o*-bornylanisole (**20**). Elution with 5% ether–petroleum ether afforded 2.75 g. (89%) of *o*-bornylphenol (**21**) as an oil which crystallized from octane in prisms, m.p. 62–65°. The product was recrystallized from octane for analysis, m.p. 64–66°; infrared spectrum (coconitrile mull): 2.9 μ (OH), 13.3 μ (*o*-substitution); n.m.r. spectrum described in reference 16a.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.4; H, 9.6. Found: C, 83.4; H, 10.1.

Catalytic Reduction of *o*-Anisylisoborneol. Preparation of *o*-Isobornylanisole (19) and *o*-Bornylanisole (20).—A mixture of 15.46 g. (0.06 mole) of *o*-anisylisoborneol, m.p. 75–77.5°, dissolved in 150 ml. of ethyl acetate,[54] and 1.35 g. of 10% palladium-on-carbon was hydrogenated in a Parr hydrogenator at 50 p.s.i. initial pressure and room temperature over a period of 20 hr. Complete consumption of hydrogen was observed after only 20 min., but shaking was continued overnight. After filtration of catalyst, the solvent was evaporated under reduced pressure and the colorless oily residue, 14.11 g., distilled from an 18-in. spinning band column to yield 8.26 g. (56%) of distillate, b.p. 135° (2.8 mm). The distillate consisted of 40% *o*-isobornylanisole and 60% *o*-bornylanisole. This mixture was demethylated without further separation below.

Pyridine Hydrochloride Fusion of *o*-Bornyl- (20) and *o*-Isobornylanisole (19). Preparation of *o*-Bornyl- (21) and *o*-Isobornylphenol (2).—The same procedure was used as described for demethylation of *o*-bornylanisole (**20**) above. From 8.26 g. (0.034 mole) of the *o*-bornylanisole, *o*-isobornylanisole mixture above there was isolated 8.67 g. of a yellow oil which was dissolved in 200 ml. of petroleum ether and chromatographed on 200 g. of 100–200 mesh Davison silica gel. Elution with 1850 ml. of petroleum ether, 1075 ml. of 0.1% ether in petroleum ether, and 1850 ml. of 0.5% ether in petroleum ether afforded 0.88 g. of residual oil. Elution with 1125 ml. of 1% ether in petroleum ether yielded 3.94 g. of an oil, a 0.72-g. fraction of which was crystallized from petroleum ether in needles, m.p. 52–59°. The solvent was removed from the mother liquors and the residue recrystallized from octane to afford 31 mg. of *o*-isobornylphenol as

(52) The C-2 proton of bornylcarboxylic acid occurs at 7.30 τ (m, $J_1 \sim J_2 \sim 8.0$ c.p.s.) and is separated from that of the isobornyl isomer[16a] centered at 7.67 τ (m, $J_1 \sim J_2 = 6.0$ c.p.s.). The composition of the two isomers was estimated by comparison of the area of these two signals.

(53) We are indebted to Professor M. de Botton for a sample containing approximately equimolar quantities of isobornyl- and bornylcarboxylic acid.

(54) The solvent is extremely critical in this reaction. Use of ethanol, for example, gave a smaller quantity of **19** and larger amounts of **20**.

colorless prisms, m.p. 75–79°. Recrystallization from octane gave a constant m.p. 81.5–83.5°. A mixture melting point of this material with the *o*-isobornylphenol, m.p. 83–85°, from the reaction of camphene and phenol, showed no depression. The infrared and n.m.r. spectra of the two samples were identical.

Elution with 1300 ml. of 1.0% ether in petroleum ether, 775 ml. of 2% ether–petroleum ether, and 425 ml. of 4% ether–petroleum ether gave 3.99 g. of a semisolid. Recrystallization of a 520-mg. sample of this oil from petroleum ether afforded 300 mg. of *o*-bornylphenol as colorless needles, m.p. 57.6–61.2°. Several recrystallizations from octane gave fine prisms, m.p. 63.0–64.6°. A mixture m.p. with the bornylphenol, m.p. 64–66°, from sodium reduction of *o*-anisylisoborneol (**15**), gave no depression, m.p. 62.8–65.2°. The n.m.r. and infrared spectrum of these two samples were identical.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.4; H, 9.6. Found: C, 83.5; H, 9.7.

Oxidation of 2-*exo*-*o*-Anisyl-*exo*-isocamphane (4). Preparation of *exo*-Isocamphane-6-*exo*-carboxylic Acid (23).—The oxidation of **4** was effected using the general procedure of Bartlett.[19] Treatment of 3.37 g. (0.014 mole) of **4** with 3.93 g. (0.084 mole) of ozone in 80 ml. of methylene chloride, with subsequent peroxide oxidation and acidifidation, afforded 1.70 g. (67%) of the acid **23** as a colorless oil. The oil could not be induced to crystallize even after chromatography on 42 g. of silica gel; infrared spectrum: λ 3.3–3.6, 5.90 μ (COOH); n.m.r. spectrum: 9.02 (s), 9.12 (s), 9.13 τ (d, J = 6.0 c.p.s.) (methyl protons).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0. Found: C, 72.2; H, 9.6.

Preparation of *exo*-Isocamphane-6-*exo*-carboxylic Acid Amide (27).—A solution of 1.045 g. of the acid **23** above, dissolved in 3 ml. of purified sulfonyl chloride, was heated at reflux under a nitrogen atmosphere for 90 min. The mixture was cooled to 0–5° and poured cautiously into 10 ml. of cold concentrated ammonium hydroxide. The mixture was stirred vigorously, then stored at room temperature for 30 min. The precipitated solid was collected by filtration and the *exo*-isocamphane-6-*exo*-carboxylic acid amide (**27**) crystallized in colorless needles from petroleum ether; m.p. 135.5–137° (0.670 g., 50%); infrared spectrum (coconitrile mull): λ 2.9, 3.1 (NH), 6.0–6.2 μ (broad) (NHCO); n.m.r. spectrum: 9.02 (s), 9.12 (s), 9.12 τ (d, J = 6.0 c.p.s.) (methyl protons).

Anal. Calcd for $C_{11}H_{19}ON$: C, 72.9; H, 10.6; N, 7.7. Found: C, 73.0; H, 10.6; N, 7.9.

6-*exo*-Acetyl-*exo*-isocamphane (28).—To a solution of 370 mg. (0.002 mole) of the amide **27**, m.p. 135.5–137°, in 50 ml. of anhydrous ether was added dropwise with stirring a total of 4.3 ml. of 2.99 M methylmagnesium bromide (0.013 mole) and this mixture heated at reflux for 16 hr. (The mole ratio of methylmagnesium bromide to amide (4:1) and reaction time (16 hr.) were critical in this experiment.) To the cooled reaction mixture was added 10 ml. of water, then 25 ml. of 10% hydrochloric acid. The ethereal solution was washed with water, 5% sodium bicarbonate and water, and dried over magnesium sulfate. Evaporation of ether afforded 0.135 g. of the ketone **28** as a colorless liquid which was purified for analysis by preparative gas chromatography; infrared spectrum: 5.86 μ (carbonyl); n.m.r. spectrum: 9.04 (s), 9.12 (s), 9.13 τ (d, J = 6.0 c.p.s.) (methyl protons).

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 79.94; H, 11.18. Found: C, 79.63; H, 10.85.

The 2,4-dinitrophenylhydrazone was recrystallized in orange needles from ethanol; m.p. 121–122°.

Anal. Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.98; H, 6.71. Found: C, 59.88; H, 6.67.

6-*exo*-Acetoxy-*exo*-isocamphane (29).—To a solution of 0.135 g. (7.5×10^{-4} mole) of the ketone **28** in 10 ml. of chloroform was added 0.158 g. (8.7×10^{-4} mole) of monoperphthalic acid in 1 ml. of ether and the mixture stored at 0° for 16 hr., then at room temperature for 24 hr. The solvent was evaporated, the residue diluted with ether and washed with 5% sodium bicarbonate and water, dried over magnesium sulfate, and evaporated to afford 0.1172 g. of liquid consisting of 54% of the acetate **29** and 46% of the ketone **28**. The acetate **29** was isolated in pure form by preparative gas chromatography on column 1 at 137° and 38 ml./min. helium flow; infrared spectrum: 5.75, 8.0–8.1 μ (acetate); n.m.r. spectrum: 5.48 τ (q, J_1 = 3.5 c.p.s., J_2 = 7.1 c.p.s.) [1.0]; 8.10 τ (s) (OAc methyl protons); 9.08, 9.13 (s), 9.12 τ (d, J = 6.0 c.p.s.) (methyl protons).

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.78; H, 10.07.

6-*exo*-Hydroxy-*exo*-isocamphane Hydrogen Phthalate (29b).—A 656-mg. (0.0033 mole) sample of 6-*exo*-acetoxy-*exo*-isocamphane (**29**) dissolved in a solution of 1.00 g. (0.018 mole) of potassium hydroxide in 10 ml. of methanol and 0.6 ml. of water was stored at 27° for 19 hr. After the bulk of the methanol was removed under reduced pressure at 35–46°, the mixture was diluted with 15 ml. of water and extracted with 100 ml. of ether. The ethereal layer was washed 4 times with 15 ml. of water, dried over magnesium sulfate, and evaporated under reduced pressure to afford 425 mg. of the alcohol as a crystalline solid, infrared spectrum 2.9, 9.5, 9.7 μ (hydroxyl). A 420-mg. sample of the crude alcohol was treated with 428 mg. of phthalic anhydride in 10 ml. of dry pyridine at 70° for 4 hr., then was stored at room temperature for 16 hr. The mixture was diluted with 100 ml. of water and extracted two times with 100 ml. of chloroform. The chloroform layer was washed with 10 ml. of 10% hydrochloric acid, with water (4 × 20 ml.), dried over magnesium sulfate, and evaporated to afford 572 mg. of colorless crystals, m.p. 102–106°. Recrystallization from benzene–petroleum ether afforded 197 mg. of 6-*exo*-hydroxy-*exo*-isocamphane hydrogen phthalate (**29b**) as colorless needles, m.p. 123.6–124.5°. A second crop of **29b** weighed 0.1383 g., m.p. 121–123.8° (total yield 33% over-all from the acetate **29**). Further recrystallization from the same solvent did not alter the melting point, 123.6–124.5°; infrared spectrum: 6.80 (ester carbonyl), 6.93 μ (acid carbonyl); n.m.r. spectrum (5% in $CDCl_3$): −0.24 τ (s) [1.0] (acid proton); 2.0–2.8 τ (m) [4.0] (aromatic protons); 5.10 τ (m) [0.9] (C-6 proton); 9.06 (s), 9.13 (s), 9.12 τ (m) (methyl protons).

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.79; H, 7.59.

The melting point of the above hydrogen phthalate, m.p. 123.6–124.5°, was significantly different from that of an authentic specimen of 5-*exo*-hydroxy-*exo*-isocamphane, m.p. 111–112°.[28] The n.m.r. spectra of the two esters **29b** and **30b** were strikingly different; n.m.r. spectrum of 5-*exo*-hydroxy-*exo*-isocamphane (5% in $CDCl_3$): 2.0–2.8 τ (m) [4.0] (aromatic protons); 4.69 τ (m) [1.0] (C-5-proton); 8.94 (s), 9.11 (s), 9.18 τ (m) (methyl protons).

$\Delta^{5,6}$-*exo*-Isocamphene (26).—Essentially the method of Meinwald and Gassman[55] for the Schmidt reaction was employed. To a mixture of 7.77 g. (0.043 mole) of the acid **23**, 100 ml. of concentrated sulfuric acid, and 250 ml. of chloroform maintained at 45–50° was added with vigorous stirring over a period of 30 min. 10.0 g. (0.154 mole) of sodium azide. The mixture was stirred and heated 2 hr. longer at 45–55°, then cooled to 0–5° and made alkaline by dropwise addition of 80 g. of sodium hydroxide in 500 ml. of water. The organic and water layers were partitioned, the water layer washed with ether, and the combined organic layers dried over magnesium sulfate and evaporated to afford 4.27 g. (66%) of liquid amine **24**; infrared spectrum: 3.0–3.15, 6.1–6.5 μ (NH).

The methiodide of the amide **24** was prepared, without further characterization of the amine, according to the procedure of Cope.[56] To a mixture of 4.27 g. of the amine **27** in 50 ml. of methanol and 12.60 g. of sodium bicarbonate was added 21.00 g. of methyl iodide and this mixture stirred vigorously and heated at reflux for 72 hr. Additional 22.79-g. portions of methyl iodide were added at 24-hr. intervals (total of 66.58 g. of methyl iodide added, 72-hr. reaction time). The solvent was evaporated under reduced pressure and the residue extracted with hot chloroform. The extracts were filtered, evaporated, and the residue was recrystallized from ethanol to afford 5.68 g. (62%) of the methiodide **25** as colorless plates, m.p. 319–320°. The methiodide crystallized from ether–methanol to a constant m.p. 326–327° dec.; infrared spectrum: (coconitrile mull): absence of NH bands; n.m.r. spectrum (10% in $CDCl_3$): 6.00 τ (m, $J_1 \sim J_2 \sim$ 7.0 c.p.s.) [1.0] (C-6-proton); 6.61 τ (s) [8.6] [N-methyl protons); 8.79 τ (s), 9.02 (d, 6.0 c.p.s.), 9.08 τ (s) [9] (methyl protons).

Anal. Calcd. for $C_{13}H_{26}NI$: C, 48.31; H, 8.09; N, 4.33; I, 39.27. Found: C, 48.31; H, 8.02; N, 4.32; I, 39.80.

Essentially the procedure of Highet and Wildman[57] was employed for the Hoffman degradation. To a solution of 3.75 (0.0116 mole) of the methiodide **25** in 200 ml. of a 1:1 mixture of ethanol–water was added in 0.10-g. portions, over a period of 1 hr.

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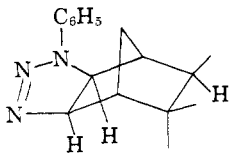
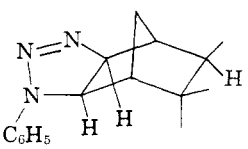
with occasional swirling, silver oxide prepared from 5.2 g. of silver nitrate. The precipitated silver iodide and excess silver oxide were removed by filtration and washed with water and ethanol. The solvent was removed under reduced pressure at 50–55° to afford 3.22 g. of yellow oil which solidified on standing. The mixture was heated at 120–155° over a period of 1 hr. and the distillate collected in a Dry Ice trap. The distillate and residue were combined, diluted with ether, and the ethereal layer washed with 5% hydrochloric acid and water, dried over magnesium sulfate, and evaporated cautiously at 20–25° and reduced pressure to afford 0.427 g. (27%) of the olefin **26** as colorless plates, m.p. 45–46° after sublimation; infrared spectrum (neat): 3.25, 6.05, 14.55 μ (*cis*-olefin); 6.25, 6.35, 6.8, 13.6 μ (characteristic bands); n.m.r. spectrum: 3.88 τ (t, J = 1.5 c.p.s.) [2.0] (C-5-, C-6-vinyl protons); 7.70 τ (m) [1.9] (C-1 and C-4 protons); 8.25 τ (d, J = 10 c.p.s.); 8.70 τ (d, J = 10 c.p.s.) [2.1] (C-7-bridgehead protons); 8.7–9.1 τ (m) (C-2-proton); 8.98 (s), 9.15 τ (s) (*gem*-dimethyl protons); 8.98 τ (m) (C-2-methyl protons).

Anal. Calcd. for $C_{10}H_{16}$: C, 88.1; H, 11.8. Found: C, 87.6; H, 11.3.

The phenyldihydrotriazole derivative was prepared by treatment of 25 mg. of the olefin **26**, m.p. 45–46°, with 100 mg. of freshly distilled phenyl azide, b.p. 49–50° (4 mm.), in 1 ml. of absolute ether. The mixture was stored 1 week at 0–5° when the dihydrotriazole separated in long prisms, m.p. 118–122°. A mixture m.p. of this material with a sample of the dihydrotriazole prepared from *dl-exo*-isocamphene,[28] m.p. 117–120.5°, was not depressed, m.p. 117–123°. (It is assumed that the dihydrotriazole derivative is a mixture of the two isomers **37a** and **37b**.)



37a



37b

Demethylation of *o*-Isobornylanisole (19).—The procedure outlined above for pyridine hydrochloride fusion of *o*-bornylanisole was followed. From 0.600 g. (0.002 mole) of *o*-isobornylanisole, m.p. 72–74.5°, fused with 20.0 g. of pyridine hydrochloride, there was isolated 0.500 g. (88%) of *o*-isobornylphenol (**19**) as colorless prisms from octane, m.p. 76–81°. Recrystallization from octane gave prisms, m.p. 85.5–86.0°. A mixture melting point with the *o*-isobornylphenol (**19**), m.p. 81.5–83.5°, prepared from camphor was not depressed, m.p. 83–84.2°. The n.m.r. and infrared spectrum of these two samples were identical.

Demethylation of 6-*exo*-*o*-Anisyl-*exo*-isocamphene (22).—The procedure for cleavage of *o*-bornylanisole was employed. From 2.96 g. (0.012 mole) of the ether **22** and 25 g. of pyridine hydrochloride there was isolated 2.5 g. (89%) of the phenol **4** as colorless prisms from petroleum ether; m.p. 73–75.5°. Two further recrystallizations from petroleum ether raised the melting point to 78.5–80°. A mixture melting point with the phenol **4**, m.p. 84–85°, isolated directly from the reaction of camphene and phenol by column chromatography was not depressed, m.p. 79.5–82.5°.

Demethylation of 6-*exo*-*p*-Anisyl-*exo*-isocamphane (36).—From 1.415 g. (0.0058 mole) of the methyl ether **36** and 10 g. (0.09 mole) of pyridine hydrochloride there was isolated 0.85 g. (63%) of the corresponding phenol **5** as colorless needles from petroleum ether; m.p. 89–90.5°. Recrystallization from petroleum ether raised the melting point to 101–103°. There was no depression of melting point upon admixture with the phenol **5** isolated by column chromatography of the camphene–phenol mixture.

Preparation of 2-*exo*-Hydroxymethyl-3,3-dimethylbicyclo[1.2.2]-hept-5-ene *p*-Toluenesulfonate (38).—2-*exo*-Hydroxymethyl-2-*endo*-3-*endo*-dimethylbicyclo[1.2.2]heptane (2.94 g., 0.019 mole), prepared from 4.50 g. (0.03 mole) of 3,3-dimethylbicyclo[1.2.2]hept-5-ene-2-*exo*-carboxylic acid according to the method of Alder and Roth,[58] was dissolved in a solution of 6.0 g. of *p*-toluenesulfonyl chloride in 20 ml. of anhydrous pyridine maintained at 0–10°. The mixture was stored overnight at 25°, diluted with 100 ml. of cold water, and the precipitated tosylate extracted with 200 ml. of absolute ether. The ethereal layer was washed with 2 100-ml. portions of water, with cold 10% hydrochloric acid (2 × 50 ml.), and 3 times with 50 ml. of cold water. The mixture was dried 5 hr. over magnesium sulfate and evaporated to yield 4.96 g. (84%) of the tosylate **38** as colorless plates from ethanol–water; m.p. 43.4–44.4°. The tosylate was dried for analysis without further recrystallization.

Anal. Calcd. for $C_{17}H_{22}SO_3$: C, 66.65; H, 7.24; S, 10.04. Found: C, 66.68; H, 7.14; S, 10.19.

Preparation of $\Delta^{5,6}$-*exo*-Isocamphene (26).—Essentially the method of Beckmann and Geiger[27] was employed for the reduction of the tosylate **38** except that ether was used as solvent. To a mixture of 4.0 g. (0.15 mole) of lithium aluminum hydride suspended in 200 ml. of anhydrous ether (freshly distilled over lithium aluminum hydride) was added 4.72 g. (0.015 mole) of the tosylate in 100 ml. of anhydrous ether and the mixture heated at reflux for 12.5 hr. Excess lithium aluminum hydride was destroyed by dropwise addition of 50 ml. of water to the cooled reaction mixture, followed by 250 ml. of 10% hydrochloric acid. The ethereal layer was partitioned, washed with water and 50 ml. of 10% sodium hydroxide and water until neutral. After drying over magnesium sulfate the solvent was removed under reduced pressure and the oily residue sublimed at 80–90° (756 mm.) to afford 1.12 g. of colorless oil (composition: 84.5% $\Delta^{5,6}$-*exo*-isocamphene and 16.5% of an unidentified alcohol). Elution with petroleum ether on 250 g. of Activity III Woelm alumina afforded 0.819 g. (17%) of the olefin **26** which was sublimed at 90–95° (756 mm.) in camphoraceous plates, m.p. 41–43°. Final purification was achieved by preparative gas chromatography on column 5 at 150° and 43 ml./min. helium flow and raised the melting point to 45–46°.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.26; H, 11.62.

Hydroboration of $\Delta^{5,6}$-*exo*-Isocamphene. Preparation of 5-*exo*-Acetoxy-*exo*-isocamphane (30) and 6-*exo*-Acetoxy-*exo*-isocamphane (29).—The general procedure of Brown and Rao[59] was followed for hydroboration of the olefin **26**. Diborane, generated from 3.8 g. (0.11 mole) of sodium borohydride in 100 ml. of diglyme and 22.8 g. (0.16 mole) of boron trifluoride etherate in 50 ml. of diglyme, was passed during a period of 30 min. into a solution of 0.920 g. (0.007 mole) of Δ^5-*exo*-isocamphene (**26**) in 100 ml. of tetrahydrofuran maintained at 0–5°. The mixture was warmed to 27° and stored for 1 hr. at this temperature, then was heated at 50–55° for 20 min.[1] To the cooled reaction mixture (0–5°) were added dropwise 20 ml. of water, 40 ml. of 3 *N* sodium hydroxide, and 40 ml. of 30% hydrogen peroxide and the mixture was stirred at room temperature for 1 hr. The mixture was heated at 50–55° for 20 min., cooled to room temperature, diluted with 200 ml. water, and extracted with 300 ml. of ether. The ethereal layer was washed 3 times with 75-ml. portions of water, dried over magnesium sulfate, and evaporated to afford 0.980 g. of colorless oil which could not be resolved by column chromatography or by gas chromatography. The oil was dissolved in 10 ml. of pyridine and 10 ml. of reagent grade acetic anhydride and stored overnight at room temperature. The mixture was poured into 100 ml. of water (0–5°) and the oily acetate layer washed with 50 ml. of water, with cold 10% hydrochloric acid (0–5°, 2 × 25 ml.), with 25 ml. of cold 10% sodium bicarbonate, and with water until neutral. The solution was dried over magnesium sulfate, the solvent evaporated, and the residue rectified from a modified Hickman still at 110° (12 mm.) bath temperature to afford 0.780 g. (59%) of the mixture of acetates **29** and **30**. Gas chromatographic analysis on column 5 at 144° and 75 ml./min. helium flow gave two peaks: 5-*exo*-acetoxy-*exo*-isocamphane (**30**, 47%, rel. ret. time 26.4 min.) and 6-*exo*-acetoxy-*exo*-isocamphane (**29**, 53%, rel. ret. time 28.3 min.). The two isomers were separated by preparative gas chromatography on the same column. A 250-mg. sample of the acetate mixture yielded 48 mg. of the acetate **30** and 64 mg. of the acetate **29**. The gas chromatography retention time of the acetate **30** and the acetate prepared from the hydrogen phthalate derivative[28] of 5-*exo*-hydroxy-*exo*-isocamphane were identical; acetate **30**: infrared spectrum (5% in CCl_4): 5.75 (carbonyl), 8.0–8.3 μ (acetate); n.m.r. spectrum: 4.99 τ (q, J_1 = 2.0 c.p.s., J_2 = 6.5 c.p.s.) [1.0]; 8.08 τ (s) [3.0] (CH_3–COO); 8.12–8.87 τ (m) [6.5] (methylene and C-2-methyne overlap); 8.96 (s), 9.1 (s), 9.15 τ (m), [9.4] (methyl protons and C-2-methyne overlap).

Anal. Calcd. for $C_{12}N_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.59; H, 10.13.

(58) K. Alder and W. Roth, *Chem. Ber.*, **90**, 1830 (1957).

(59) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6433 (1959).

The gas chromatography retention time, infrared spectrum, and n.m.r. spectrum of the acetate **29** prepared above and the acetate **29** obtained by degradation of the phenol **4** were identical.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.59; H, 10.21.

Condensation of *l*-Bornyl Acetate and Phenol.—To a rapidly stirred mixture of 50.0 g. (0.26 mole) of *l*-bornyl acetate, $[\alpha]^{26}D$ −38.3° (Aldrich Chemical Co.), and 24.0 g. (0.026 mole) of Baker Reagent Grade phenol was added 0.331 g. (0.002 mole) of freshly distilled boron trifluoride etherate and this mixture slowly heated to 100–110° over a period of 1 hr. The mixture was maintained at 100–110° under a nitrogen atmosphere for 6.5 hr., cooled to room temperature, and diluted with 300 ml. of ether. The ethereal solution was washed with water, 10% sodium bicarbonate, and water, dried over magnesium sulfate, and evaporated to yield 58.02 g. of viscous oily residue. Distillation through a 12 in. Vigreux column gave 5 fractions: 17.16 g. of a mixture of camphene and phenol, b.p. 74° (2.2 mm.); 0.97 g. of *l*-bornyl acetate, b.p. 74° (2.5 mm.), $[\alpha]^{26}D$ −36.6°; 2.57 g. of ether product, b.p. 170° (2.0 mm.); 12.17 g. (22%) of the mixture of 1:1 camphene–phenol adducts, b.p. 170–190° (1.2–1.5 mm.); and 1.33 g. of material b.p. 190–210° (1.0 mm.).

The 12.17 g. of product b.p. 170–190° was analyzed by gas chromatography on column 4 at 210° and 60 ml./min. flow rate and was shown to consist of 6 products: *o*-isobornylphenol (**2**, 26%), *p*-isobornylphenol (**3**, 12%), 6-*exo*-*o*-hydroxyphenyl-*exo*-isocamphane (**4**, 44%), 6-*exo*-*p*-hydroxyphenyl-*exo*-isocamphane (**5**, 13%), and the two unidentified phenols **34** (2.4%) and **35** (2.8%). The optical rotation of the crude mixture was 0.0° (*c* 1.03, ethanol).

The 12.17 g. of adduct was dissolved in 200 ml. of petroleum ether and separated by chromatography through 240 g. of Davison 100–200 mesh silica gel. Elution with 2.75 l. of petroleum ether and 2.25 l. of 0.2% ether in petroleum ether removed 0.21 g. of forerun. Elution with 1.25 l. of 0.5% ether in petroleum ether yielded 0.04 g. of ether product. Elution with 1.4 l. of 0.5% ether in petroleum ether yielded 0.06 g. of the two phenols **34** and **35** as a mixture. Elution with 1.4 l. of 1.0% ether in petroleum ether gave 0.03 g. of **34**, **35**, and **2** as a mixture. Further elution with 250 ml. of 5% ether in petroleum ether afforded 2.16 g. (3.9%) of the pure *dl*-*o*-isobornylphenol as colorless rhombical prisms from octane, m.p. 79–81°, $[\alpha]^{26}D$ 0.0° (*c* 3.01, ethanol). A mixture melting point of this material and the *dl*-*o*-isobornylphenol prepared from *dl*-camphor, m.p. 85.5–86.0°, was undepressed, m.p. 79–81°. The infrared spectrum (5% in CCl_4) of the two samples were essentially identical.

Elution with 250 ml. of 5% ether in petroleum ether removed 4.10 g. of **2** and **4** as a mixture. Further elution with 1.10 l. of the same solvent gave 2.07 g. (3.7%) of pure *dl*-6-*exo*-*o*-hydroxyphenyl-*exo*-isocamphane (**4**) as colorless rhombical prisms from petroleum ether; m.p. 74–76°, $[\alpha]^{26}D$ 0.0° (*c* 1.94, in ethanol). A mixture melting point of this sample with that of a sample of **4**, m.p. 79–80.8°, isolated from the reaction of *dl*-camphene and phenol, was undepressed; m.p. 79.5–81.5°.

Elution with 2.45 l. of 5% ether–petroleum ether and 1.75 l. of 10% ether–petroleum ether removed 4.31 g. of the two phenols **3** and **5** as a mixture. The two phenols were separated by fractional crystallization from petroleum ether as before. From the filtrate after six recrystallizations 0.210 g. (0.4%) of pure *dl*-*p*-isobornylphenol was isolated as fine colorless needles, m.p. 146–148°. A mixture melting point of this sample and a pure specimen of *dl*-*p*-isobornylphenol prepared from *dl*-camphor[11] was undepressed; m.p. 146–149°.

Most of the phenol **4** from the mother liquors of the first recrystallization, above, were removed by two subsequent crystallizations from petroleum ether. From the combined mother liquors there was isolated 0.69 g. (1.2%) of **5**, m.p. 93.5–95°. After five recrystallizations from petroleum ether the pure *dl*-*p*-*exo*-hydroxyphenyl-*exo*-isocamphane (**5**) was isolated as fine needles, m.p. 99–101°. The mixture melting point with a sample of **5** from the reaction of *dl*-camphene and phenol, m.p. 101–103°, was undepressed; m.p. 99–101°.

Reaction of Acetic Acid and Camphene.—A mixture of 26.63 g. (0.195 mole) of camphene, 24.00 g. (0.400 mole) of acetic acid, and 0.994 g. (0.007 mole) of boron trifluoride etherate was heated at 105° under a nitrogen atmosphere for 3 hr. The mixture was cooled to room temperature and diluted with 500 ml. of ice–water and 300 ml. of ether. The ethereal layer was partitioned, washed with 500 ml. of 10% sodium bicarbonate and water until neutral, and dried over magnesium sulfate. Evaporation of solvent yielded 33.37 g. of residual liquid. The liquid was analyzed by gas chromatography on column 5 at 43 ml./min. helium flow and 143° and was found to consist of: camphene (1.9%), tricyclene (0.2%), a mixture of unidentified olefins (1.4%), a mixture of unidentified acetates (3.2%, rel. ret. time ~15.4 min.), acetate A (10.2%, rel. ret. time 17.3 min.), bornyl acetate (15.4%, rel. ret. time 20.3 min.), isobornyl acetate (52.5%, rel. ret. time 21.2 min.), and two unidentified acetates: B (3.8%, rel. ret. time 23.6 min.) and C (5.5%, rel. ret. time 25.6 min.), and a mixture of two unresolved acetates D (6.2%, rel. ret. time 27.2 min.). The relative retention time of 6-*exo*-acetoxy-*exo*-isocamphane (**29**) analyzed on the same column was identical with the acetate mixture D (27.2 min.). However, as shown below, the n.m.r. spectrum of the mixture D was quite different from that of **29**.

The acetates were partially resolved by fractional distillation on an 18-in. spinning band column, but final separation of acetates A, C, and the mixture D and of bornyl and isobornyl acetate was made by preparative gas chromatography on the same column.

	Analyses for $C_{12}H_{20}O_2$			
	Calcd.		Found	
Acetate	C	H	C	H
A	73.43	10.27	72.99	9.96
Bornyl acetate	73.43	10.27	73.01	10.15
Isobornyl acetate	73.43	10.27	73.13	10.04
C	73.43	10.27	73.6	10.4

The n.m.r. spectra, gas chromatography retention time, and infrared spectra of the bornyl acetate and isobornyl acetate isolated above were identical with those of authentic specimens.[9]

The critical data from the n.m.r. spectra of acetates A, C, and the mixture D are listed in Table III. The n.m.r. spectra of these acetates are quite obviously different from that of 6-*exo*-acetoxy-*exo*-isocamphane (**29**). It is pertinent that the acetate mixture D did not show a signal in the 5.48 τ region suggesting the complete absence of acetate **29**.

TABLE III

N.M.R. SPECTRA

	H–COCOCH_3					
	–H–C–OAc–			Splitting	Methyl protons	
Acetate	Chem. shift, τ	Splitting pattern, c.p.s.	Chem. shift, τ	pattern, c.p.s.	Chem. shift, τ	Splitting pattern, c.p.s.
A	5.43	(q) J_1 = 3.0	8.08	s	9.01	s
		J_2 = 7.4			9.10	s
					9.28	d, J = 6.3
C	5.38	(q-broad)	8.02	s	9.08	s
					9.10	s
		J_1 = 3.0			9.09	s, J = 5.0
		J_2 = 7.0				
D	5.16	Multiplet	8.11	s	8.9–9.2	m
29	5.48	(q), J_1 = 3.5	8.10	s	9.08	s
		J_2 = 7.1			9.13	s
					9.12	d, J = 6.0

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