(1%, chloroform) (lit.[2] +109°); λ_{max}^{MeOH} 282.5 and 275 mμ (ε 1490 and 1270) [lit.[2] 269 mμ (ε 530)]. Hydrolysis by stirring the suspended diacetate in 70 ml of methanol with 37 ml of a 10% aqueous potassium hydroxide solution at 25° gave a clear solution overnight, which was acidified (pH = 6) and diluted with 65 ml of water. The methanol was removed under vacuum, the suspension was chilled, and the solids were recrystallized from ethanol to yield 4.5 g of crystals, mp 197–198°, in which a small impurity (2,4-dibromoestradiol, R_f 0.39) was still present. The material was dissolved in 90 ml of ethanol, basified with 0.8 g of potassium hydroxide in 3 ml of water, and diluted with 90 ml of water. Fractional precipitation by the cautious addition of 12.5 ml of 1 *N* hydrochloric acid in five equal increments with vigorous stirring gave five crops of material. Three of these, samples 2, 3, and 4, were recrystallized from ethanol to give 2.8 g (5.5%) of analytically pure 2-bromoestradiol (III): mp 197–198° (lit.[2] 156–157°); $[\alpha]^{25}\mathrm{D}$ +104° (1%, chloroform) (lit.[2] +132°).[15] Thin layer chromatography (silica gel-chloroform with 5% acetonitrile) showed a single spot (R_f 0.34); vapor phase chromatography exhibited a single peak. Ultraviolet absorptions were at λ_{max}^{MeOH} 287 mμ (ε 3440), shoulder at 292 mμ (ε 3230) [lit.[2] 281 mμ (ε 2320)].[15,16] The infrared spectrum (in Nujol) exhibited bands at 3620, 3590, and 3260 (OH) and 1600, 1560, and 1480 cm^{-1} (Ph). The nmr spectrum (in deuteriopyridine) was consistent with the assigned structure, showing no discernible splitting of the *para* protons and a pair of singlets at τ 2.39 and 2.97 and a singlet at 9.13 (18-CH$_3$).

Anal. Found: C, 61.30; H, 6.71; Br, 22.85 (for calculated values, see above).

Registry No.—II, 1630-83-7; III, 15833-07-5; IV, 15833-06-4; V, 15856-39-0.

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Total Synthesis of *dl*-Sabinene, *dl-trans*-Sabinene Hydrate, and Related Monoterpenes

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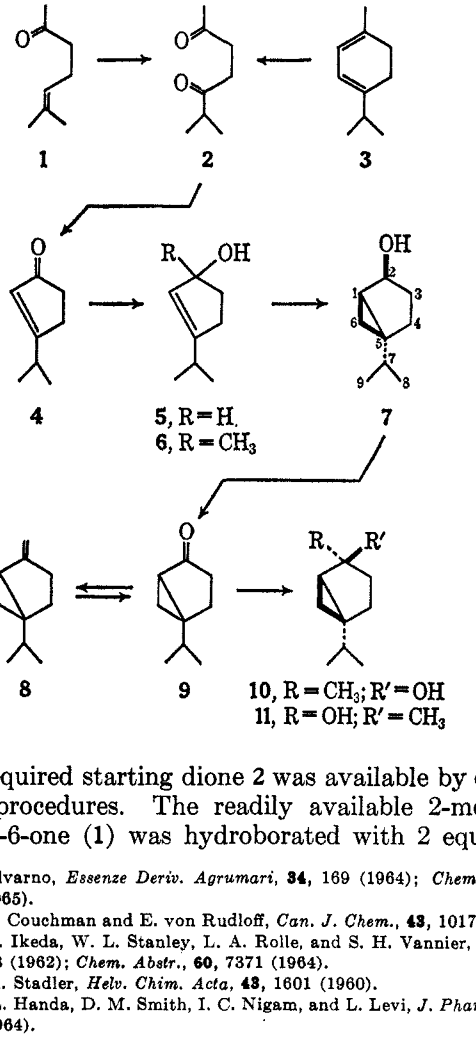
Despite the frequent occurrence of monoterpenes possessing the bicyclo[3.1.0]hexane ring system in essential oils, synthetic approaches to these substances have received little attention. As part of an over-all program directed toward the synthesis of mono- and sesquiterpenes, we investigated the construction of several representative bicyclo[3.1.0]hexanes of the sabinane group: sabinene (**8**),[1,2] sabina ketone (**9**),[3] and *cis*- and *trans*-sabinene hydrates (**10** and **11**).[4,5] Sabinene is reported to be present in a wide variety of essential oils including savin oil,[6] lavandin oil,[7] *Juniperus horizontalis* leaf oil,[8] and citrus oils[9] while sabina ketone is reportedly present in lavandin oil.[10] Although *cis*-sabinene hydrate has not been found in nature, the *trans* isomer represents a small but very important part of a number of mint oils.[5,11–13]

Although Eastman and coworkers[5] have reported the preparation of *cis*- and *trans*-sabinene hydrates from naturally occurring sabinene, no total syntheses of any of these materials has come to our attention.[13a] We wish to report here the total syntheses of racemic counterparts of the aforementioned members (**8–11**) of the sabinane group.

Our initial synthetic objective was *cis*-sabinene hydrate (**10**). Several reports, including an extensive investigation by Dauben and Berezin,[14] note that allylic and homoallylic alcohols react with the Simmons–Smith reagent[15] *via* participation of the hydroxyl function. This interaction results in a product having the alcohol function and the newly generated cyclopropyl ring in a *cis* relationship to one another. With this fact in mind, a synthetic scheme which is quite stereoselective can be visualized along lines outlined in Chart I.

CHART I



The required starting dione **2** was available by either of two procedures. The readily available 2-methyl-2-hepten-6-one (**1**) was hydroborated with 2 equiv of

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[1] J. L. Simonsen, "The Terpenes," Vol. II, 2nd ed, University Press, Cambridge, England, 1949, pp 16–23, and references therein.

[2] E. Guenther, "The Essential Oils," Vol. II, D. Van Nostrand Co., New York, N. Y., 1949, pp 64–65, and references therein.

[3] A. G. Short and J. Read, *J. Chem. Soc.*, 1415 (1939).

[4] O. Wallach, *Ann.*, **357**, 65 (1907); **360**, 82 (1908).

[5] J. W. Daly, F. C. Green, and R. H. Eastman, *J. Amer. Chem. Soc.*, **80**, 6330 (1958).

[6] A. B. Booth, *Amer. Perfumer Aromat.*, **69**, 45 (1957); *Chem. Abstr.*, **51**, 7658 (1957).

[7] I. Calvarno, *Essenze Deriv. Agrumari*, **34**, 169 (1964); *Chem. Abstr.*, **63**, 5443 (1965).

[8] F. M. Couchman and E. von Rudloff, *Can. J. Chem.*, **43**, 1017 (1965).

[9] R. M. Ikeda, W. L. Stanley, L. A. Rolle, and S. H. Vannier, *J. Food Sci.*, **27**, 593 (1962); *Chem. Abstr.*, **60**, 7371 (1964).

[10] P. A. Stadler, *Helv. Chim. Acta*, **43**, 1601 (1960).

[11] K. L. Handa, D. M. Smith, I. C. Nigam, and L. Levi, *J. Pharm. Sci.*, **53**, 1407 (1964).

[12] E. von Rudloff and F. W. Hefendehl, *Can. J. Chem.*, **44**, 2015 (1966).

[13] I. C. Nigam and L. Levi, *J. Agr. Food Chem.*, **11**, 276 (1963).

[13a] NOTE ADDED IN PROOF.—Since submission of this manuscript, a total synthesis of sabina ketone and sabinene by a different route has been reported: M. Marx, Ph.D. Thesis, Columbia University, New York, N. Y., 1966; *Dissertation Abstr.*, **27**, 4266-B (1967).

[14] W. G. Dauben and G. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963).

[15] H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

diborane in tetrahydrofuran and the resultant alkylborane was oxidized with alkaline hydrogen peroxide. Oxidation of the crude diol with chromic acid reagent[16] afforded dione **2** in 90% yield. Alternately, the ketone could be isolated in moderate yield by ozonation of α-terpinene (**3**) and subsequent reductive work-up.

Treatment of **2** with 2% aqueous sodium hydroxide in refluxing ethanol for 4.5 hr afforded cyclopentenone **4** (70%). Addition of ethereal methyllithium to ketone **4** produced the extremely unstable tertiary alcohol **6** which resisted attempts at purification: λ_{max}^{film} 2.95 μ; nmr signals at τ 4.79 (C=CH), 8.72 (HOCCH$_3$), 8.95 (doublet, J = 7 Hz, CHCH$_3$). The crude alcohol, when subjected to a Simmons–Smith reaction, decomposed rapidly and no bicyclic product (*e.g.*, **10** or **11**) could be isolated. On the other hand, reduction of cyclopentenone **4** with lithium aluminum hydride in ether at room temperature afforded the more stable secondary alcohol **5** (90%). This substance reacted rapidly with the zinc–copper couple and methylene iodide to afford demethyl-*cis*-sabinene hydrate (**7**) as a woody, camphoraceous-smelling oil. This bicyclic material was oxidized smoothly with chromic acid reagent to sabina ketone (**9**) in 90% yield. An authentic sample of the green, leafy-smelling sabina ketone, prepared by the oxidation of sabinene[17] (**8** → **9**) exhibited nmr and infrared spectral data as well as gas chromatographic retention time identical with those of the synthetic material.

Synthetic sabinene (**8**) was prepared by treatment of sabina ketone (**9**) with methylene triphenyl phosphorane in dimethyl sulfoxide. The crude oil was purified by filtration through a Florisil column and evaporative distillation. An authentic sabinene sample[17] exhibited spectral data and gas chromatographic retention time identical with those of the synthetically prepared material.

The final two objectives of the synthetic scheme were realized by treatment of sabina ketone (**9**) with ethereal methyllithium. This process afforded a mixture containing predominantly the two alcohols **10** and **11** in a ratio of about 8:1, respectively (90% yield). The use of methylmagnesium bromide[5] in place of methyllithium gave substantial increases in bicyclic ring decomposition. The two tertiary alcohols were separated by gas chromatography. Pure *cis*-sabinene hydrate, as described by Eastman,[18] exhibited spectra identical with those recorded for the major component of this mixture. In addition, pure *trans* isomer, as described by Eastman,[18] exhibited spectra identical with those prepared from the minty-smelling synthetic material. The gas chromatographic retention time of synthetic *trans*-sabinene hydrate was identical with those of a sample isolated from native spearmint and a sample generously donated by Dragoco Chemical Co.

Experimental Section[19]

2-Methyl-3,6-heptanedione (2). A. From 2-Methyl-2-hepten-6-one (1).—A solution of 50.4 g (0.4 mol) of **1** in 300 ml of tetrahydrofuran maintained at 0–5° was treated with 400 ml (0.4 mol) of 1 M diborane solution (Ventron Corp., Beverly, Mass.) over 1 hr.[19b] The resulting solution was stirred at 0–5° for 1 hr and at 25–27° for 3.5 hr, then cooled in an ice bath, and treated cautiously with 80 ml of water. With the temperature maintained at 0–5°, 200 ml of 3 N aqueous sodium hydroxide was added followed by 200 ml of 30% hydrogen peroxide over 30 min. The reaction was stirred at 0–5° for an additional 1 hr and at 25–27° overnight. Isolation[19f] afforded 82.8 g of crude diol (containing solvent) which was dissolved in 300 ml of acetone, cooled to 0–5°, and treated with 240 ml of Jones reagent[16] over 1 hr. The mixture was stirred an additional 1.75 hr prior to addition of 25 ml of isopropyl alcohol. Combined ether extracts were washed with several portions of saturated aqueous sodium bicarbonate which were back extracted and the total ether was washed with brine and dried. Solvent removal and subsequent distillation afforded 51.6 g (91%) of dione **2**, bp 68–72° (4.5 mm), which was shown to be 95% pure by glpc (150°). Material purified by redistillation and gas chromatography (150°) exhibited the following properties: bp 71–72° (5 mm); n^{25}D 1.4250 [lit.[20] bp 79–82° (9 mm); n^{20}D 1.4322]; λ_{max}^{film} 5.86, 8.60, 9.19, and 9.80 μ; nmr signals at τ 7.46 (5 H), 7.94 (3 H, COCH$_3$), and 8.95 (6 H, doublet, J = 7 Hz, CHCH$_3$).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.8; H, 10.2.

B. From α-Terpinene.—A stream of ozone–oxygen was bubbled through a solution of 17.17 g of a mixture of α- and γ-terpinene[21] [containing 11.5 g (0.085 mol) of α-terpinene] in 250 ml of methanol maintained at −78° over 5 hr. The cold ozonide solution was slowly added to a mixture of 140 g of sodium iodide and 72 ml of acetic acid in 200 ml of methanol and stirred overnight at room temperature. The resulting dark solution was decolorized with solid sodium bisulfite and neutralized with solid sodium bicarbonate. Isolation[19f] and distillation afforded 9.95 g (83% based on α-terpinene) of dione **2**, bp 70–72° (5.2 mm), which was shown to be 89% pure by glpc (150°).

3-Isopropyl-2-cyclopentenone (4).—A solution of 51.6 g (0.36 mol) of dione **2** in 580 ml of 2% aqueous sodium hydroxide and 180 ml of ethanol was refluxed under nitrogen[19b] for 4.5 hr. Isolation[19f] and subsequent distillation afforded 32.2 g (71%) of ketone **4**, bp 62–64° (2.75 mm) which showed greater than 95% purity by glpc (150°). Material purified by redistillation and glpc (150°) exhibited these properties: bp 73–74° (4.75 mm); n^{25}D 1.4774; λ_{max}^{film} 5.84, 6.20, 7.95, 8.50, 10.15, and 11.62 μ; λ_{max}^{EtOH} 228 mμ (ϵ 12,500); nmr signals at τ 4.25 (1 H, C=CH), 7.25–7.60 (3 H), 7.65–7.89 (2 H), and 8.85 (6 H, doublet, J = 7 Hz, CHCH$_3$) [lit.[22] for ketone **4**: bp 75–76° (3 mm); n^{15}D 1.4850; λ_{max}^{film} 5.85 and 6.19 μ; λ_{max}^{EtOH} 226.5 mμ (ϵ 13,750); nmr signals at τ 4.22 (1 H), 7.2–7.8 (4 H), and 8.83 (6 H)].

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.2; H, 9.8.

3-Isopropyl-2-cyclopentenol (5).—A solution of 32.2 g (0.26 mol) of ketone **4** in 100 ml of anhydrous ether was added over 15 min to a rapidly stirring, ice cold slurry of 5.0 g (0.13 mol) of lithium aluminum hydride in 500 ml of ether. The resulting mixture was stirred at room temperature for 2 hr and was decomposed by the cautious dropwise addition of 10 ml of water

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(16) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(17) Fluka Chemical Co. supplies sabinene which is only *ca.* 67% pure.

(18) Reference 2, footnote 1.

(19) (a) The prefix *dl* is omitted from the names of racemic substances. (b) The apparatus described by W. S. Johnson and W. P. Schneider [*Org. Syn.*, **30**, 18 (1950)] was used to maintain a nitrogen atmosphere. (c) Infrared spectra were determined on a Perkin-Elmer Model 137 spectrophotometer; ultraviolet spectra were determined in ethanol on a Perkin-Elmer Model 202 spectrophotometer; nmr spectra were determined in carbon tetrachloride [chemical shifts measured relative to tetramethylsilane (τ 10)] with a Varian Model HA-100 spectrometer by T. J. Flautt and associates of these laboratories; gas–liquid partition chromatography was accomplished with an Aerograph Model 202B using a flow rate of 100 cc/min on a 5 ft × 0.25 in. 20% FFAP on 60/80 Chromosorb P column at the temperature indicated. (d) Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. (e) Anhydrous tetrahydrofuran was obtained by distillation from lithium aluminum hydride; anhydrous dimethyl sulfoxide was obtained by distillation from calcium hydride. (f) The isolation procedure consisted of thorough extraction with ether, washing the combined extracts with brine solution, and drying over anhydrous magnesium sulfate. The solvent was removed from the filtered extracts under reduced pressure on a hot water bath.

(20) (a) C. G. Moore, *J. Chem. Soc.*, 234 (1951); (b) K. von Auwers and R. Hinterseber, *Ber.*, **48**, 1357 (1915).

(21) Prepared by potassium *t*-butoxide–dimethyl sulfoxide room temperature isomerization of γ-terpinene (prepared by lithium ammonia reduction of *p*-cymene).

(22) (a) L. Crombie and D. A. Mitchard, *J. Chem. Soc.*, 5640 (1964). (b) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, **29**, 2049 (1963).

and 8 ml of 10% aqueous sodium hydroxide. The reaction mixture was stirred overnight and filtered, and the solvent was removed at reduced pressure to afford 31.8 g (97%) of cyclopentenol **5**. Material purified by distillation exhibited these properties: bp 65–67° (3.5 mm); n^{25}D 1.4658; $\lambda_{\max}^{\text{film}}$ 3.00, 6.08, 9.71, 10.29, and 11.75 μ; nmr signals at τ 4.68 (1 H, C=CH), 5.36 (1 H, CHOH), 5.95 (1 H, OH), and 8.97 (6 H, doublet, J = 7 Hz, $CHCH_3$). Because the material was only moderately stable and decomposed on storage after several days, it was converted directly into bicyclic alcohol **7** without analysis.

Demethyl-*cis*-sabinene Hydrate (7).—An adaptation of the procedure of Dauben and Berezin[14] was employed. A nitrogen blanketed[19b] slurry of 7.84 g (0.12 mol) of zinc–copper couple[23] and a crystal of iodine in 60 ml of anhydrous ether was treated rapidly with 26.4 g (0.1 mol, 8 ml) of freshly distilled methylene iodide. The rapidly stirred mixture was heated at 40° for 0.5 hr. A solution of 6.42 g (0.05 mol) of pentenol **5** in 16 ml of ether was added dropwise at a rate sufficient to maintain gentle reflux without external heat (*ca.* 0.5 hr). Following addition, the reaction was refluxed for 1 hr, cooled, treated cautiously with excess saturated, aqueous ammonium chloride, and filtered. The solid was washed well with ether and the resulting filtrate was washed with two portions of 10% aqueous sodium carbonate. The combined aqueous layers were back extracted, and the combined ether layers were washed with brine and dried over magnesium sulfate. Solvent removal and subsequent distillation afforded three fractions: (1) 0.45 g, bp 25–40° (1 mm), containing 9% alcohol **7** by glpc (150°); (2) 0.34 g, bp 40–56° (1 mm), containing 75% alcohol **7**; (3) 4.62 g (66%) bp 56–57° (1 mm), containing 95% alcohol **7**. This material was purified by distillation, bp 60° (1 mm), and glpc (150°): n^{25}D 1.4655; $\lambda_{\max}^{\text{film}}$ 3.00, 9.49, and 9.75 μ; nmr signals at τ 5.55 (1 H, multiplet, CHOH), 7.90 (1 H, OH), 9.08 (3 H, doublet, J = 6 Hz, $CHCH_3$), 9.14 (3 H, doublet, J = 5 Hz, $CHCH_3$), 9.32 [1 H, triplet, J(C-6-*endo* H, C-1 H) = 4.5 Hz, J(C-6-*endo* H, C-6-*exo* H) = 4.5 Hz, C-6-*endo* H], and 9.69 [1 H, quartet, J(C-6-*exo* H, C-1 H) = 7.7 Hz, J(C-6-*endo* H, C-6-*exo* H) = 4.5 Hz, C-6-*exo* H].[24,25]

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.9; H, 11.6.

Sabina Ketone (9).—A solution of 4.62 g (0.033 mol) of alcohol **7** in 75 ml of acetone maintained at 0–5° was oxidized with 9 ml of Jones reagent[16] over a 15-min period. The resulting solution was stirred an additional 10 min at 0–5° and added to brine. Several ether extracts were washed with saturated aqueous sodium bicarbonate, the aqueous layers were back extracted, and the total ether was washed with brine and dried over magnesium sulfate. Removal of the solvent and distillation afforded 4.05 g (89%) of faint yellow sabina ketone, bp 67–70° (5 mm), n^{25}D 1.4654 (lit.[3] n^{25}D 1.4672), which showed 96% purity by glpc (150°). Pure material obtained by redistillation, bp 70° (5 mm), and glpc (150°) collection exhibited these spectral properties: $\lambda_{\max}^{\text{film}}$ 3.30, 5.79, 8.49, 9.79, 10.93, and 12.86 μ; nmr signals at τ 7.70–8.16 (3 H), 8.25–8.70 (2 H), and 8.73–9.20 (9 H). A pure sample of sabina ketone prepared by ozonation of naturally occurring sabinene[17] had an index of refraction of n^{25}D 1.4645 and an infrared spectrum superimposable with the synthetic material.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.4; H, 10.3.

Sabinene (8).—A slurry of 1.24 g (0.032 mol) of a 61% sodium hydride–mineral oil dispersion in 40 ml of dimethyl sulfoxide was heated at 70° under nitrogen[19b] for 1 hr. The resulting base solution was cooled to 0–5° and treated with a warm solution of 11.9 g (0.033 mol) of methyltriphenylphosphonium bromide in 40 ml of dimethyl sulfoxide. The semisolid mixture slowly warmed to 25–27° where solution took place. Stirring was continued for 20 min at 25–27°, and a solution of 1.30 g of 74% pure sabina ketone (0.007 mol) in 20 ml of dimethyl sulfoxide was added dropwise over 5 min. The resulting dark yellow solution was stirred at 25–27° for 3 hr, and added to water, and the product isolated with pentane. Several extracts were combined, washed with water and brine, and dried over magnesium sulfate. The solvent was removed by distillation and the total crude was passed through a chromatographic column containing 100 ml of Florisil. One 300-ml pentane fraction was collected and the pentane removed by distillation to afford 2.9 g of colorless, residual oil which on evaporative distillation afforded 880 mg (93% material balance) of colorless product, bp 60–70° (16 mm), which showed 79% purity by glpc (90°). A sample purified by glpc (90°) had the properties n^{25}D 1.4654 [lit.[26] bp 69° (30 mm), n^{20}D 1.4681]; $\lambda_{\max}^{\text{film}}$ 3.29, 6.04, 7.28, 7.37, 9.78, and 11.53 μ; nmr signals at τ 5.27, 5.46 (2 H, $C=CH_2$), 9.10 (3 H, doublet, J = 6 Hz, $CHCH_3$), 9.18 (3 H, doublet, J = 7 Hz, $CHCH_3$), and 9.34 and 9.40 (2 H, C-6 H's). A purified sample of natural sabinene[17] exhibited superimposable spectra with those reported above.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.0; H, 11.8.

***cis*- and *trans*-Sabinene Hydrate (10, 11).**—A solution of 2.94 g (0.021 mol) of sabina ketone (88% pure) in 16 ml of ether was added over 10 min to 37 ml of a 1.62 *M* solution of ethereal methyllithium and 26 ml of ether contained under a nitrogen atmosphere.[19b] The resulting mixture was refluxed for 1 hr, cooled, and poured onto excess ice. Isolation[19f] afforded 3.30 g (100% material balance) of faint green oil composed of solvent, an unknown [17% (10% present in starting material)], *trans*-sabinene hydrate (**11**, 13%), *cis*-sabinene hydrate (**10**, 71%), and sabina ketone (**9**, 1%). A run using 97% pure sabina ketone gave 11% *trans*- and 84% *cis*-sabinene hydrate. The crude products were chromatographed on 500 ml of Florisil with glpc (125°) monitoring of fractions. Subsequent combination and distillation afforded 680 mg of a mixture of unknown and isomeric alcohols **10** and **11** and 550 mg of pure *cis*-sabinene hydrate (**10**).

Pure *cis* isomer **10** exhibited the properties which follow: n^{25}D 1.4632; $\lambda_{\max}^{\text{film}}$ 3.00, 7.36, 8.85, 9.50, 10.12, 10.51, and 10.78 μ; nmr signals at τ 7.55 (1 H, OH), 8.70 (3 H, $HOCCH_3$), 9.08 (3 H, doublet, J = 6.8 Hz, $CHCH_3$), 9.12 (3 H, doublet, J = 6.5 Hz, $CHCH_3$), 9.34 [1 H, quartet, J(C-6-*endo* H, C-1 H) = 4.0 Hz, J(C-6-*endo* H, C-6-*exo* H) = 4.9 Hz, C-6-*endo* H], and 9.71 [1 H, quartet, J(C-6-*exo* H, C-1 H) = 8.0 Hz, J(C-6-*endo* H, C-6-*exo* H) = 4.9 Hz, C-6-*exo* H].[24,25] Pure *cis*-sabinene hydrate as described by Eastman[18] exhibited spectra identical with those described above.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.7; H, 11.8.

Pure *trans*-sabinene hydrate (**11**) exhibited these spectral properties: $\lambda_{\max}^{\text{CCl}_4}$ 2.80, 2.90, 7.23, 8.46, 9.46, 9.71, 10.03, 10.34, 10.86, and 10.99 μ; nmr signals at τ 8.70 (3 H, $HOCCH_3$), 9.03 (3 H, doublet, J = 7 Hz, $CHCH_3$), 9.10 (3 H, doublet, J = 7.5 Hz, $CHCH_3$), 9.62 [1 H, quartet, J(C-6-*exo* H, C-1 H) = 8.1 Hz, J(C-6-*endo* H, C-6-*exo* H) = 5.0 Hz, C-6-*exo* H], and 9.80 [1 H, triplet, J(C-6-*endo* H, C-1 H) = 5.0 Hz, J(C-6-*endo* H, C-6-*exo* H) = 5.0 Hz, C-6 H (*endo*)].[24,25] Pure *trans* isomer as described by Eastman[18] exhibited spectra identical with those described above. Glpc retention time (125°) of the synthetic **11** was identical with those of a sample obtained from native spearmint and to a sample obtained from Dragoco Chemical Co.

Registry No.—**2**, 13901-85-4; **4**, 1619-28-9; **5**, 15826-78-5; **7**, 15826-79-6; **8**, 15826-80-9; **9**, 513-20-2; **10**, 15826-82-1; **11**, 15826-83-2.

Acknowledgments.—The technical assistance of Mr. Kerry M. Fitzpatrick on part of this work is gratefully acknowledged.

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(23) R. D. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

(24) See W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967), for a discussion of nmr spectra of related bicyclic compounds.

(25) IUC nomenclature has been employed, see structure **7**.

(26) G. Ohloff, G. Uhde, A. F. Thomas, and E. sz. Kováts, *Tetrahedron*, **22**, 309 (1966).

The Reactions of Fluoroaromatic Nitriles with Sodium Pentafluorophenolate

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Sodium pentafluorophenolate (I) reacts with a series of substituted pentafluorobenzenes in dimethylacetamide (DMAC) yielding 4-substituted nonafluorodi-