chlorate in 25 ml of anhydrous ether was treated with a solution of 0.0368 g (0.965 mmol) of lithium aluminum hydride in 10 ml of ether. The reaction was stirred 0.5 hr under nitrogen at room temperature, cooled in an ice bath, and hydrolyzed by dropwise addition of water. The crude reaction product was filtered, diluted with two 25-ml portions of ether, and dried over magnesium sulfate. Removal of ether afforded a viscous oil which was subjected to Kragen tube distillation (oil bath temperature 80–120° (8 mm)). The product was identified as 1,2,3-tri-*t*-butylcyclopropene (**8**) from the following data: infrared spectrum: $\nu_{max}^{CCl_4}$ (cm^{-1}) 2960 (s), 2900 (m), 2865 (m), 1835 (w), 1475 (m), 1465 (m), 1395 (m), 1365 (m), 1355 (w), and 1275 (w); mass spectrum: *m/e* 208, 207, and 151; nmr spectrum: 0.82 (9 H, s), 1.16 (18 H, s) 1.37, (1 H, s). An acceptable analysis could not be obtained for this compound.[15a]

Anal. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found: C, 85.66; H, 13.57.

Reaction of Cation 5d with *t*-Butyllithium. A suspension of 0.0962 g (0.314 mmol) of tri-*t*-butylcyclopropenyl perchlorate in 25 ml of anhydrous benzene was prepared under nitrogen and quenched by dropwise addition of 0.706 mmol of *t*-butyllithium. The resulting solution was stirred 0.5 hr and worked up as previously described. Kragen tube distillation of the crude product afforded 1,2,3-tri-*t*-butylcyclopropene (**8**) identical with an authentic sample prepared as described above from the reaction of **5d** with lithium aluminum hydride.

Acknowledgments. This investigation was generously supported by Public Health Service Research Grant No. GM-14579 from the National Institute of General Medical Sciences. The Varian A-60A nmr spectrometer and the Hitachi RMU-6D mass spectrometer employed in this work were purchased through a National Science Foundation Grant to Brown University. Finally, we wish to thank Professor A. S. Kende for a gift of the methyl ester of 1,2-dipropylcyclopropene-3-carboxylic acid.

The Syntheses of the (−)-α- and (+)-β-*cis*-Bergamotenes[1]

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Contribution from The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239. *Received February 14, 1969*

Abstract: Syntheses of (−)-α-*cis*-bergamotene (**2**) and (+)-β-*cis*-bergamotene (**3**) from (−)-β-pinene are described. The isomer **2** was shown to be identical with a sesquiterpene hydrocarbon isolated from oils of opopponax (*Commiphora erythraea* var. *glabrescens* Engler) and black pepper (*Piper nigrum* L.). The isomer **3** was found to be different from an isolate of Indian valerian oil (Valeriana wallichi) which has been assigned this structure.

The structure **1** has been proposed for a sesquiterpene hydrocarbon, which was isolated from bergamot oil by Sorm and coworkers, and given the name bergamotene.[2] This structural assignment was apparently based solely on the infrared spectrum[3] and has never been fully substantiated, although the nmr spectrum of the compound agrees with structure **1** and was used to suggest the *trans* stereochemistry of attachment of the side chain as shown.[4,5] This compound, now called α-*trans*-bergamotene in analogy to the structure of α-pinene, has been more recently detected in a number of other essential oils.[6] Muller and Jennings[7] reported its occurrence in black pepper accompanied by an unknown sesquiterpene hydrocarbon to which they assigned the α-*cis*-bergamotene structure **2**. The same compound was isolated from oil of opopanax by Wenninger.[8]

More recently, Bhattacharyya, *et al.*, isolated a hydrocarbon from Indian valerian oil, to which they assigned the β-*cis*-bergamotene structure **3**. While the chemical evidence cited[9] is in very good accord with the gross structure **3**, the *cis* stereochemistry was suggested on the basis of a comparison of the nmr spectrum with that of β-pinene. Even though the chemical shift of the quaternary methyl group in **3** fell midway between the values for the two quarternary methyl groups in β-pinene, the authors used this in conjunction with a conformational argument to favor the *cis* stereochemistry. However, comparison of this value with the reported chemical shifts of the quaternary methyl groups in copaene (**4**)[10] and mustakone (**5**),[11] suggested to us that, in fact, β-bergamotene possessed the *trans* structure. We felt that an unambiguous synthesis would be necessary to settle this question and that of the structure of α-*cis*-bergamotene. In this paper we describe the stereospecific synthesis of (−)-α-*cis*-bergamotene (**2**) and (+)-β-*cis*-bergamotene (**3**).

Synthesis of compounds of the *cis*-bergamotene structure would, in the most direct approach, involve substitution on the *cis*-quaternary methyl group in the pinane

(1) For a preliminary account of part of this work, see T. W. Gibson and W. F. Erman, *Tetrahedron Lett.*, 905 (1967).

(2) V. Herout, V. Ruzicka, M. Vrany, and F. Sorm, *Collect. Czech. Chem. Commun.*, **15**, 373 (1950).

(3) J. Pliva, M. Horak, V. Herout, and F. Sorm, "The Terpenes," Part I, Academic Press, Berlin, 1960, pp 193–194.

(4) E. sz. Kovats, *Helv. Chim. Acta*, 46, 2705 (1963).

(5) The stereochemistry of these systems is defined in relation to the four-membered ring, so that the more complex substituent (methylpentenyl in the bergamotenes themselves) is *cis* or *trans* to the three-carbon bridge.

(6) M. C. Nigam, K. L. Handa, I. C. Nigam, and L. Levi, *Can. J. Chem.*, 43, 3372 (1965); L. H. Zalkow, M. K. Park, and J. W. Ellis, *Perfumery Essent. Oil Record*, **55**, 507 (1963).

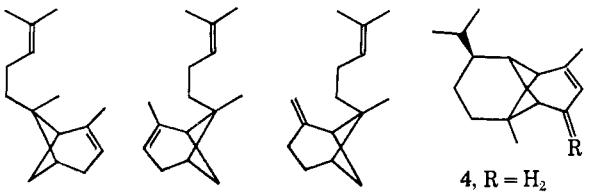
(7) C. J. Muller and W. G. Jennings, *J. Agr. Food Chem.*, **15**, 762 (1967).

(8) J. A. Wenninger, Division of Color and Cosmetics, Food and Drug Administration, private communication. We wish to thank Mr. Wenninger for his generosity in providing us with samples of α-*cis*-, α-*trans*-, and β-*trans*-bergamotenes.

(9) K. S. Kulkarni, S. K. Paknikar, A. S. Vaidya, G. R. Kelkar, R. B. Bates, and S. C. Bhattacharyya, *Tetrahedron Lett.*, 505 (1963); K. S. Kulkarni, S. K. Paknikar, and S. C. Bhattacharyya, *Tetrahedron*, **22**, 1917 (1966).

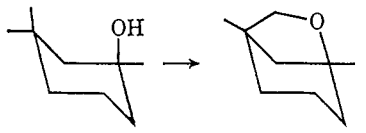
(10) P. de Mayo, R. E. Williams, G. Büchi, and S. H. Feairheller, *ibid.*, **21**, 619 (1965).

(11) V. H. Kapadia, B. A. Nagasampagi, V. G. Naik, and S. Dev, *ibid.*, **21**, 607 (1965).



1 2 3 4, R = H_2 5, R = O

nucleus. The Barton reaction[12] for substitution of unactivated carbon atoms has been applied widely, especially in the steroid field, and it was felt that it could be used profitably in this work. Reaction of the alcohol **6** with various reagents has been found to provide good yields of the bicyclic ether **7**,[13] so that we were prompted to examine the behavior of the closely related alcohol **8**.



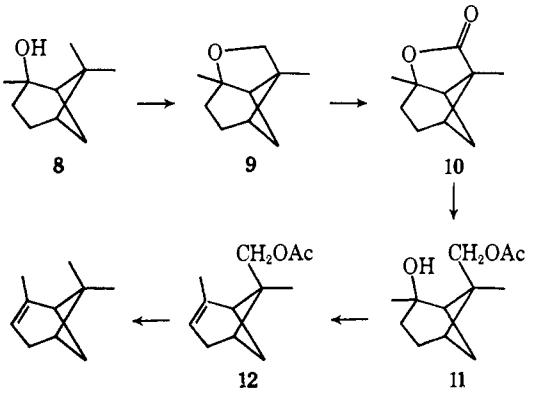
6 7

The alcohol **8**, synthesized by the reaction of (+)-nopinone (prepared from (−)-β-pinene) with methyllithium,[14] when treated with lead tetraacetate and iodine in cyclohexane during irradiation with a tungsten lamp,[15] afforded a single volatile product in high yield. This compound showed a band at 9.7 μ in the infrared spectrum, suggestive of the strained tetrahydrofuran ring,[16] with no evidence for the presence of other functional groups, and a parent molecular ion of mass 152. In the nmr spectrum, an AB quartet centered at τ 6.40 supported the presence of a dissymmetric methylene group adjacent to the ether oxygen, but only one peak appeared in the methyl region, a six-proton singlet at τ 8.73. No olefinic protons were indicated. An unambiguous proof for the structure **9** follows from these data and from conversion to α-pinene by the following series of steps.

Oxidation of **9** with chromium trioxide in acetic anhydride[17] afforded in good yield a γ-lactone, whose spectral data were consistent with the structure **10**. Reduction of **10** with lithium aluminum hydride, followed by acetylation, afforded the hydroxy acetate **11**, which could be readily dehydrated with phosphorus oxychloride at 0° in pyridine. In contrast to the dehydration of the methyl nopinols, which were reported to give a fair amount of rearrangement product,[18] **11** gave a mixture containing about 75% **12**, 20% isomer **23a**, and 5% ether **9**. The absence of rearrangement products here could be due to internal trapping of the intermediate carbonium ion by the adjacent acetoxy group, which could also explain the formation of **9**.

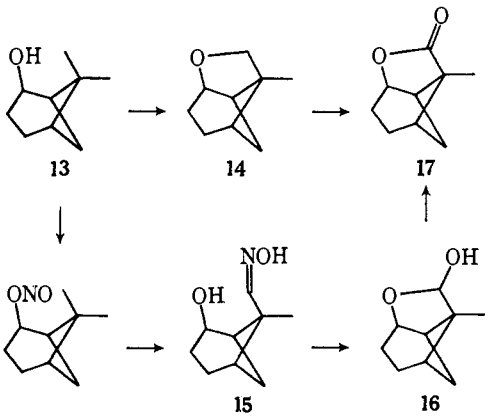
Reduction of **12** with lithium aluminum hydride followed by treatment with *p*-toluenesulfonyl chloride gave the tosylate, which afforded α-pinene as the only hydrocarbon product on reduction with lithium aluminum hydride in refluxing ether. Identification was made by comparison of the infrared and nmr spectra and glpc retention times with a purified sample of α-pinene.

The formation of **9** represents the first instance of the introduction of functionality into the *gem*-dimethyl group of the pinene nucleus, and should provide a simple means for the synthesis of a wide number of compounds of this class. This reaction is especially useful in the present synthetic plan because of the stereospecificity imposed on it by the structure of the pinane system. This ensures that only the *cis*-methyl group will be substituted and thus provide unambiguous means of determining whether the *cis*-stereochemistry of the bergamotenes **2** and **3** is correct. The use of mercuric oxide and bromine in refluxing pentane[13] was also found to be very effective in converting **8** to **9**, and was used in preparative reactions due to the simplicity of work-up.



8 9 10 12 11

Treatment of the secondary alcohol **13** with mercuric oxide and bromine provided the tricyclic ether **14** in 75% yield accompanied by a small amount of nopinone from oxidation of the alcohol. Photolysis[19] of the nitrite ester of **13** gave, after pyrolysis of the initially formed nitroso dimer, a crystalline hydroxyoxime whose spectral data were in good accord with structure **15**. Mild hydrolysis gave the hemiacetal **16**, which could be oxidized[20] to the lactone **17** identical with that obtained by oxidation of **14**.[17] The over-all yield of lactone from the nitrite photolysis route was superior to that from the shorter ether route due to the poor yield in the oxidation of the ether. This reaction did not proceed as well as



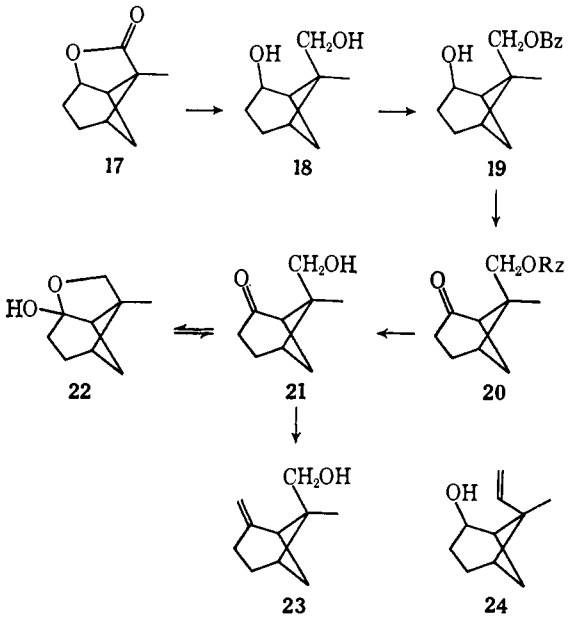
13 14 17 15 16

(12) O. L. Chapman, *Advan. Photochem.*, 1, 399 (1963).
(13) R. A. Sneen and N. P. Matheny, *J. Amer. Chem. Soc.*, 86, 5503 (1964).
(14) W. Hückel and E. Gelchscheimer, *Ann.*, 625, 12 (1959).
(15) K. Heusler and J. Kalvoda, *Angew. Chem. Intern. Ed. Engl.*, 3, 525 (1964).
(16) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1954, p 119.
(17) G. Cainelli, B. Kamber, J. Keller, M. Lj. Mihailovic, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, 44, 518 (1961).
(18) R. R. Sauers and J. M. Landesberg, *J. Org. Chem.*, 26, 964 (1961).
(19) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, *J. Amer. Chem. Soc.*, 82, 2640 (1960).
(20) R. G. Curtis, I. Heilbron, E. R. H. Jones, and G. F. Woods, *J. Chem. Soc.*, 457 (1953).

that of the ether **9**, apparently because of oxidation at the other α position.

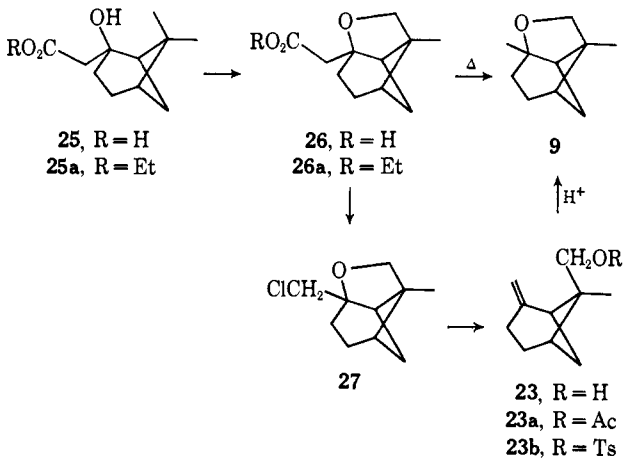
With the problem of effecting substitution into the desired position of the pinene molecule overcome, we turned our attention to the synthesis of β-*cis*-bergamotene. Our first approach began with the lithium aluminum hydride reduction of the lactone **17**, which afforded the diol **18**. Mild acetylation of **18** gave a difficultly separable mixture of mono- and diacetates, but benzoylation afforded the hydroxy benzoate **19** with little dibenzoate formation. Oxidation of **19** with Jones reagent[20] provided the keto benzoate **20**, which upon hydrolysis gave the ketol **21**. Attempts to convert **21** to the hydroxy olefin **23** by reaction with triphenylmethylenephosphorane in DMSO gave erratic results. Similar attempts with the keto benzoate **20** were also unsuccessful. Failure of **21** to react with the Wittig reagent may be due to a preference for the molecule to exist in the closed hemiketal form **22** in solution, as evidenced by the infrared and nmr spectra.

In an attempt to postpone the introduction of the methylene group until after elaboration of the side chain, the reaction of the hemiacetal **16** with various Wittig reagents was employed. Only triphenylmethylenephosphorane led to an isolable product, which gave satisfactory data for the structure **24**. No attempts were made to develop this approach further.



It was evident that, for a successful synthesis, the methylene group should be introduced during or before elaboration of the side chain. A method for doing this was suggested by Wallach's[21] conversion of the β-hydroxy acid **25**, prepared from nopinone by the Reformatsky reaction, to β-pinene by pyrolysis. We felt that pyrolysis of the ether acid **26**, which should be easily available from **25**, in the presence of base might afford the alcohol **23**. Treatment of the hydroxy ester **25a**[21] with mercuric oxide and bromine resulted in an 80% yield of **26a**, which could be readily hydrolyzed to **26**. Pyrolysis of **26** at 215–250° in the presence of quinoline afforded only a small amount of the tricyclic ether **9**. This result, while not directly useful in the synthetic plan, at least helped to confirm the structure of the ether acid **26**. It seemed likely that the alcohol **23** was being formed during the pyrolysis, but that the extreme conditions were causing cyclization to the ether. This thought prompted a further search for a milder method for generation of the alcohol **23** which would permit its isolation. The β-chloro ether **27** was prepared from **26** with Kochi's[22] modification of the Hunsdiecker reaction. Treatment of **27** with sodium in refluxing dimethoxyethane,[23] followed by destruction of the excess sodium with methanol, and basic work-up, produced the alcohol **23** in 48% yield. When the reaction was neutralized with acetic acid, only the ether **9** was obtained.

Examination of the nmr spectra of **23**, **23a**, and **23b** provides some evidence that the hydroxyl group in **23** is involved in a hydrogen bond with the olefinic group. The signal for the methylene group adjacent to the acetate in **23a** appears as a singlet, even though this group is adjacent to an asymmetric carbon atom. In the alcohol **23** and in the more bulky tosylate **23b**, the corresponding groups give rise to AB quartets. This would suggest that hydrogen bonding in **23** is at least strong enough to slow the rate of rotation about the single bond between the methylene carbon and the quaternary carbon to the point where the two protons are again in different over-all environments, thus giving rise to the expected AB quartet. Attempted glpc of **23** converted it to the ether **9** in varying amounts.



In order to obtain a more convenient functional group for attachment of the side chain, the alcohol was converted to the iodide **28**. This was carried out in high yield by displacement of the tosylate in **23b** by sodium iodide in acetone. When the Grignard reagent derived from **28** was hydrolyzed only the two monocyclic dienes **29** and **30** were obtained, with only a trace of β-pinene evident in the mixture. This event, while not completely unexpected,[24] did make it impossible to add the dimethylallyl side chain in one piece by the Grignard coupling method. A method for stepwise formation of this group had been developed with some success in the synthesis of α-santalol,[25] and was found to be even more efficient in the present instance. Displacement of the iodide in **28** by the acetylide anion to give the terminal acetylenic olefin **32** was easily effected in DMSO at 25°

(21) O. Wallach, *Ann.*, **357**, 49 (1907).

(22) J. Kochi, *J. Org. Chem.*, **30**, 3265 (1965).

(23) R. C. Blume, D. Plant, and W. P. O'Neill, *ibid.*, **30**, 1553 (1965).

(24) See E. A. Hill and J. A. Davidson, *J. Amer. Chem. Soc.*, **86**, 4663 (1964), for analogous behavior in other systems.

(25) R. G. Lewis, D. H. Gustafson, and W. F. Erman, *Tetrahedron Lett.*, 401 (1967).

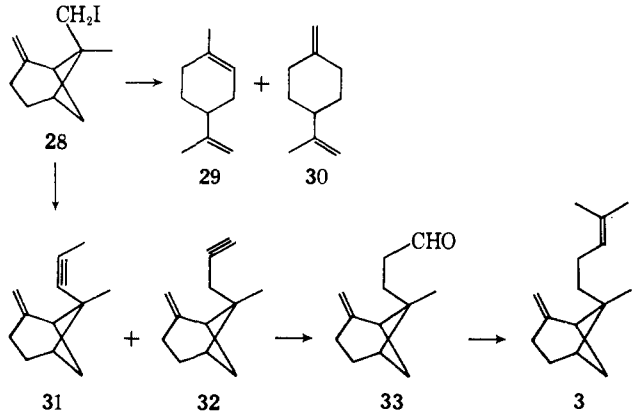
with the ethylenediamine complex of lithium acetylide. Small amounts of an isomer, apparently **31**, were formed. At higher temperature and longer reaction time **31** became the major product.[25] The aldehyde **33** was obtained in poor yield when **32** was treated with disiamylborane in THF,[26] and was converted directly to (+)-*β-cis*-bergamotene, **3**, upon reaction with triphenylisopropylidenephosphorane in THF.

As expected, this material was not identical with the compound isolated by Bhattacharyya[9] from Indian valerian oil. This was established most clearly by a comparison of the nmr spectrum of **3** with that published for the natural isomer.[9] The quaternary methyl group in the natural compound produces a signal at τ 9.05, while the corresponding signal in **3** is at τ 8.81. This latter value is consistent with the chemical shift values for the quaternary methyl groups for the whole series of compounds described in this paper, some of which are recorded in Table I. From the data in the

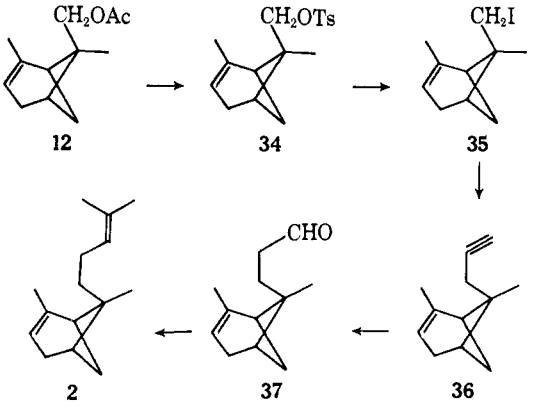
Table I. Chemical Shifts in Representative Substituted Pinanes

Compd	τ C_7-*endo*-H	τ Me
9	8.55	8.72
14	8.49	8.69
20	8.35	8.52
3	8.63	8.81
2	8.82	8.73
α-Pinene	8.84	8.73

table it will also be noted that all of these compounds show a characteristic doublet due to a single proton in the region of τ 8.6. This signal must be due to the *endo*-C_7 proton, which does not couple to the bridgehead protons due to the nearly 90° dihedral angle between them.[27] These results suggest that natural β-bergamotene has the *trans* stereochemistry. This can be proved unambiguously only by synthesis.



The synthesis of (−)-α-*cis*-bergamotene was carried out in a similar fashion from the readily available acetate **12**. Lithium aluminum hydride reduction of **12** followed by tosylation afforded the oily tosylate **34** which was converted to the iodide **35** with sodium iodide. Reaction with lithium acetylide gave the acetylenic olefin **36**, which provided the very unstable aldehyde **37** in very low yield when treated with disiamylborane. Immediate reaction of **37** with triphenylisopropylidenephosphorane gave (−)-α-*cis*-bergamotene (**2**). The infrared and nmr spectra of the synthetic **2** were identical in all major respects with a sample of **2** isolated from oil of opoponax by Wenninger.[8] The specific rotation of the natural sesquiterpene indicates that it also is of the same absolute stereochemistry as the synthetic, as shown in structure **2**.



Experimental Section

General. Melting points were determined on a micro hot stage and are corrected; boiling points are uncorrected. Infrared spectra were recorded on Perkin-Elmer 257 or 137 spectrophotometers as neat films or 5% solutions in CCl_4. Nuclear magnetic resonance spectra were obtained on a Varian Associates HA-100 spectrometer using TMS as an internal reference in $CDCl_3$. Nmr data are recorded in the order: chemical shift (integration, multiplicity where s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and coupling constant in hertz). Specific rotations were obtained using a Rudolph Model 70 polarimeter or a Jasco Model ORD/UV/CD-5 spectropolarimeter. Mass spectra were determined with an Atlas CH-4 spectrometer. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

trans-**2-Hydroxypinane (8).** This compound was prepared by ozonolysis[28] of (−)-β-pinene followed by addition of methyllithium to the nopinone formed.[14] It was found necessary to repeat the methyllithium addition in order to get good conversion to **8**, apparently because of enolate formation. The alcohol obtained was generally contaminated with 5 to 15% of nopinone.

6,9-Dimethyl-7-oxatricyclo[4.3.0.0^{3,9}]nonane (9). To a solution of 100.8 g of crude alcohol **8** in 1 l. of distilled pentane was added 200 g of yellow mercuric oxide.[13] The mixture was heated to reflux under N_2 and 20.0 ml of bromine added dropwise over about 2 hr. After an additional 2 hr at reflux, the mixture was cooled, filtered, and dried over a mixture of $MgSO_4$ and Na_2CO_3. After removal of the drying agent, percolation through 450 g of Al_2O_3 followed by vacuum distillation gave 69.0 g of **9**, bp 64° (10.5 mm), and 15 g of recovered nopinone. Material purified by glpc showed $n^{26}D$ 1.4702, $[\alpha]_{5461}$ +51.7° (*c* 3.0, EtOH), mol wt 152 (mass spectroscopy), major infrared absorptions at 9.7 and 11.8 μ and nmr signals at τ 8.72 (6 H, s), 8.55 (1 H, d, J = 9 Hz), 7.8–8.4 (7 H), and an AB quartet with doublets centered at 6.18 and 6.63 (2 H, J = 9.0 Hz).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.21; H, 10.49.

6,9-Dimethyl-8-oxo-7-oxatricyclo[4.3.0.0^{3,9}]nonane (10). A solution of 4.09 g of the ether **9** in 30 ml of acetic anhydride was heated to 100°, and a solution of 4.30 g of CrO_3 in 100 ml of acetic acid and 10 ml of H_2O was added dropwise over 1.5 hr.[17] After cooling and addition of 10 ml of ethanol to destroy excess oxidant the solution was poured onto crushed ice and extracted with ether and the ether extract washed with saturated Na_2CO_3 solution and dried over $MgSO_4$. Distillation of the residue after removal of the drying agent and solvent gave 1.047 g of nearly pure **9** and 2.414 g (72%) of lactone **10**, bp 84° (1.2 mm), $[\alpha]_{5461}$ +58.8° (*c* 2.16, EtOH), λ_{max} 5.64 μ (CCl_4), mol wt 166 (mass spectroscopy), and nmr

(26) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 3834 (1961).

(27) P. Teisseire, A. Galfré, M. Plattier, and B. Corbier, *Recherches* (Paris), No. 15, 52 (1966).

(28) J. Meinwald and P. G. Gassman, *J. Amer. Chem. Soc.*, **82**, 5445 (1960).

signals at τ 8.64 (3 H, s), 8.54 (3 H, s), 8.31 (1 H, d, J = 9.8 Hz), 8.09 (4 H, s), 7.77 (1 H, m), and 7.63 (2 H, s).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.12; H, 8.56.

trans-**2-Hydroxy-9-acetoxypinane (11).** A solution of 8.8 g of lactone **10** in ether was added dropwise to a slurry of 2.0 g of lithium aluminum hydride in ether and stirred at room temperature 1 hr. The excess reagent and complex was decomposed with sufficient saturated Na_2SO_4 solution, the ether layer decanted, the salts washed three times with ether, and the combined ether solutions dried over $MgSO_4$. Removal of drying agent and solvent gave 8.5 g of crude diol. A small amount recrystallized from hexane showed mp 82°, $[\alpha]_{5461}$ −53.7° (*c* 2.7, EtOH), λ_{max} 2.9, 9.1, and 9.7 μ, and nmr signals at τ 9.00 (1 H, d, J = 9.6 Hz), 8.72 (3 H, s), 8.70 (3 H, s), 7.95–8.6 (8 H), 7.80 (1 H, m), 7.02 (1 H, s, OH), and an AB quartet with doublets at 6.85 and 6.03 (2 H, J = 11 Hz). The downfield doublet was somewhat broadened relative to the upfield doublet, probably due to long-range coupling with the methyl group.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.62; H, 10.61.

A solution containing 4.10 g of pure diol and three drops of dry pyridine in 30 ml of acetic anhydride was allowed to stand overnight at room temperature, then poured into iced $NaHCO_3$ solution. The basic solution was extracted with ether and the ether solution washed with dilute HCl and saturated $NaHCO_3$ and dried over $MgSO_4$. Distillation of the residue after removal of drying agent and solvent gave 4.0 g (78%) of hydroxy acetate **11**, bp 102° (0.5 mm), n^{30}D 1.4784, $[\alpha]_{5461}$ +12.1° (*c* 6.10, EtOH), λ_{max} 2.85, 5.74, and 8.06 μ, and nmr signals at τ 8.93 (1 H, d, J = 9.5 Hz), 8.75 (6 H, s), 8.01 (3 H, s), 7.2–8.9 (8 H), and an AB quartet with doublets at 5.92 and 5.66 (2 H, J = 11 Hz).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.74; H, 9.38.

9-Acetoxy-α-pinene (12). To a solution of 6.4 g of **11** in 45 ml of dry pyridine at 0° was added 12 ml of phosphorus oxychloride *via* pipet and the resulting solution stored overnight at 0°. The cold mixture was poured into about 500 g of crushed ice and the resulting solution extracted four times with pentane. The pentane solution was washed with water, dilute HCl, saturated Na_2CO_3, and brine and dried over $MgSO_4$. Filtration and removal of solvent gave 3.5 g of crude oil showing three major peaks on glpc in the ratio of 5:75:20. The first (5%) peak was identified as the ether **9** by infrared spectrum and glpc retention time. The second (75%) peak was identified as the desired product **12**, bp 60° (0.5 mm), mol wt 194 (mass spectroscopy). $[\alpha]_{5461}$ −45.6° (*c* 2.06, EtOH), λ_{max} 5.74, 8.1, and 9.74, μ, n^{25}D 1.4676, and nmr signals at τ 8.78 (1 H, d, J = 8 Hz), 8.70 (3 H, s), 8.35 (3 H, d, J = 2 Hz), 8.01 (3 H, s), 7.5–8.1 (5 H), an AB quartet with doublets at 6.17 and 6.01 (2 H, J = 11 Hz), and 4.79 (1 H, m).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.25; H, 9.29.

The other minor product (20%) was identified as the β-pinene isomer **23a** by glpc and infrared comparison.

Conversion of 12 to α-Pinene. An ether solution of 0.542 g of crude acetates in which the ratio of **12** to **23a** was 73:27 was treated with 0.5 g of lithium aluminum hydride. After 1 hr the complex was decomposed with Na_2SO_4 solution, the ether layer decanted and dried over Na_2SO_4. Removal of drying agent and solvent gave 0.481 g of alcohol showing no carbonyl group absorption in the infrared. The crude alcohol was dissolved in 5.0 ml of dry pyridine; 0.555 g of recrystallized *p*-toluenesulfonyl chloride was added and the solution stored overnight at 0°. The mixture was poured into ice, and extracted with ether; the ether solution was washed with dilute HCl, saturated $NaHCO_3$, brine and dried over $MgSO_4$. Removal of drying agent and solvent gave 0.627 g of crude tosylate, showing no OH absorption in the infrared. This was added to 2.0 g of lithium aluminum hydride in ether, heated to reflux for 3 hr, and allowed to stand overnight at room temperature. After decomposition with Na_2SO_4 solution and drying over $MgSO_4$, the solvent was removed by distillation through a spinning-band column to give about 1 g of residue showing small OH absorption in the infrared. This material was separated into two fractions by glpc; the more volatile fraction on examination at lower temperature proved to be a mixture of two compounds in a ratio of about 50:1. The major peak was identified as α-pinene by comparison of retention time and infrared and nmr spectra with a pure specimen. The minor peak had the same retention time as β-pinene, but enough could not be obtained for an infrared comparison.

9-Methyl-7-oxatricyclo[4.3.0.0^{3,9}]nonane (14). To a stirred mixture of 21.0 g of *cis*-nopinol (**13**, prepared by lithium aluminum hydride reduction of nopinone[29]) and 44 g of yellow mercuric oxide in 500 ml of pentane under N_2 was added 29 g of Br_2.[13] During the addition and for 1 hr afterward the solvent was held at reflux. After cooling, the mixture was filtered, dried over $MgSO_4$ and Na_2CO_3, and stripped. Filtration of the resulting oil through a column of about 100 g of neutral alumina followed by distillation gave 12.0 g (58%) of ether **14**, bp 55–56° (6 mm), and 2.5 g of nopinone. The ether **14**, purified by preparative glpc, showed n^{27}D 1.4828, $[\alpha]_{5461}$ +82.5° (*c* 2.86, EtOH), λ_{max} 9.63 and 9.78 μ, mol wt 138 (mass spectroscopy), and nmr signals at τ 8.69 (3 H, s), 8.49 (1 H, d, J = 9.0 Hz), 8.20 (4 H, m), 7.8–8.2 (2 H), 7.63 (1 H, q, J = 5.6 Hz), an AB quartet with doublets centered at 6.63 and 6.15 (2 H, J = 9.0 Hz), and 5.44 (1 H, brd d, J = 6 Hz).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.29; H, 10.18.

9-Methyl-8-oxo-7-oxatricyclo[4.3.0.0^{3,9}]nonane (17). Oxidation of 9.9 g of the ether **14**, contaminated with a small amount of nopinone, was carried out as described for the ether **9** to give 12.5 g of crude product, which was hydrolyzed with excess KOH in aqueous methanol for 1 hr on a steam bath. After removal of methanol under vacuum, extraction with ether gave 2.6 g of neutral materials consisting of starting ether and nopinone. The aqueous phase was acidified with dilute HCl and extracted with ether and methylene chloride to give, after drying and distillation, 3.3 g (31%) of pure lactone, bp 83–84° (0.7 mm), $[\alpha]_{5461}$ +129° (*c* 2.61, EtOH), λ_{max} 5.65 μ, mol wt 152 (mass spectroscopy), and nmr signals at τ 8.68 (3 H, s), 8.40 (1 H, d, J = 9.6 Hz), 8.09 (4 H, brd s), 7.70 (2 H, m), 7.31 (1 H, q, J = 6 Hz), and 5.07 (1 H, brd d, J = 7.0 Hz).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.71; H, 7.99.

(2*R*,6*S*)-6-Methyl-6-oximinomethylbicyclo[3.1.1]heptan-2-ol (15). To a solution of 15.4 g of *cis*-nopinol in 200 ml of dry pyridine at 0° was added 11.0 g of NOCl by flask to flask distillation. After an additional 1 hr at 0°, the mixture was allowed to warm to room temperature and poured into 1.5 l. water and the aqueous phase extracted with ether. The ether phase was washed with water, cold diluted HCl, and again with water. After drying over $MgSO_4$, filtration and removal of solvent gave 18.6 g of crude nitrite ester, which was immediately dissolved in 450 ml of cyclohexane and irradiated with a 450-W mercury lamp for a total of 6 hr through Vycor glassware.[19] A total of 14.2 g of nitroso dimer, which precipitated during the irradiation, was collected by filtration, dissolved in 400 ml of isopropyl alcohol, and the resulting solution heated to reflux for 36 hr. Removal of solvent gave 10.5 g (57%) of hydroxyoxime **15**, which crystallized on standing. Recrystallization from pentane–ether gave material with mp 121–122°, $\lambda_{max}^{CH_2Cl_2}$ 3.05 9.33, 9.78, and 10.28 μ, and nmr signals at τ 8.65 (3 H, s), 8.6 (1 H), 8.22 (3 H, m), 7.5–7.9 (5 H), 5.92 (1 H, m), and 2.63 (1 H, s).

Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.94; N, 8.28. Found: C, 63.95; H, 8.96; N, 8.16.

9-Methyl-8-hydroxy-7-oxatricyclo[4.3.0.0^{3,9}]nonane (16). A solution of 9.5 g of hydroxyoxime **15** was dissolved in 570 ml of 80% acetone–water containing 2% concentrated HCl and stirred overnight at room temperature. The solution was poured into water and extracted with ether and the ether solution washed with saturated $NaHCO_3$ and saturated NaCl, dried over $MgSO_4$, filtered, and stripped to give 5.0 g of hemiacetal. Continuous extraction of the aqueous phase gave an additional 2.6 g (87% total yield). Attempted distillation of this material led to extensive decomposition, but glpc was found effective for purification. Pure material showed λ_{max} 2.90 μ (no C=O band) and nmr signals at τ 8.75 (3 H, s), 8.85 (1 H, d, J = 10.4 Hz), 5.19 (1 H, bd d, J = 6 Hz), and 4.87 (1 H, s). The material decomposed rapidly on storage and was not analyzed further. Formation of a 2,4-DNP derivative, mp 177–178°, was carried out in H_3PO_4–ethanol solution.

Anal. Calcd for $C_{15}H_{18}N_4O_5$: C, 53.88; H, 5.43; N, 16.76. Found: C, 53.99; H, 5.51; N, 17.29.

Oxidation of 0.409 g of hemiacetal with CrO_3 in acetone[20] gave 0.350 g of lactone **17**, identical in retention time and infrared spectrum with that obtained by direct oxidation of ether **14**.

9-Hydroxy-*cis*-nopinol (18). To a slurry of about 0.2 g of lithium aluminum hydride in ether was added 0.360 g of lactone **17** in ether. Normal work-up gave 0.277 g (75%) of sublimed diol, mp 131–132°, λ_{max} 2.95 μ, and nmr signals at τ 9.07 (1 H, d, J =

(29) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, 77, 3054 (1955).

9.0 Hz), 8.70 (3 H, s), 7.6–8.5 (7 H), an AB quartet with doublets centered at 6.77 and 6.03 (2 H, J = 11 Hz), and 5.69 (1 H, d of t, J = 9.0 and 3.0 Hz).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.41; H, 10.45.

9-Benzoyloxy-*cis*-nopinol (19). To a solution of 2.064 g of diol **18** in 10 ml of ether and 5 ml of pyridine cooled to 0° was added 1.841 g of freshly distilled benzoyl chloride dissolved ine ther. The mixture was allowed to come to room temperature slowly and then stand for 6 hr. After dilution with ether, the solution was extracted with water, diluted HCl, saturated $NaHCO_3$, and saturated NaCl, dried over $MgSO_4$, and stripped to give 3.35 g of oil. Chromatography of 0.261 g of this oil through 10 g of silica gel gave 0.034 g of crystalline dibenzoate, eluted with 5% ether in pentane, and 0.192 g of hydroxybenzoate **19,** eluted with 20% ether in pentane. This material, which could not be induced to crystallize, was short-path distilled to give material with λ_{max} 2.85 and 5.82 μ, and nmr signals at τ 8.97 (1 H, d, J = 8.0 Hz), 8.63 (3 H, s), 7.6–8.4 (8 H), 7.50 (1 H, s, OH), 5.70 (1 H, m), an AB quartet with doublets at 5.63 and 5.39 (2 H, J = 11.4 Hz), and 1.9–2.7 (5 H).

9-Benzoyloxynopinone (20). A solution of 3.065 g of crude hydroxybenzoate **19** in 100 ml of acetone was oxidized by titration with Jones reagent.[20] Normal work-up gave 2.767 g of oil which was chromatographed on 57 g of silica gel. Elution with 5% ether in pentane gave 0.584 g of crystalline dibenzoate, mp 68–69°. Elution with 20% ether in pentane gave 2.141 g of keto benzoate **20,** which could not be made to crystallize. Short-path distillation gave material with bp 170° (0.13 mm), λ_{max} 5.81 μ, $[\alpha]_{5461}$ −28.4° (*c* 1.90, EtOH), and nmr signals at τ 8.52 (3 H, s), 8.35 (1 H, J = 9.6 Hz), 7.92 (2 H, br), 7.2–7.6 (5 H), an AB quartet with doublets at 6.01 and 5.85 (2 H, J = 11.5 Hz), and 1.9–2.6 (5 H).

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.37; H, 7.16.

9-Hydroxynopinone (21). A solution of 1.66 g of keto benzoate **20** in methanolic KOH was heated at reflux for 3 hr, allowed to stand overnight at room temperature, poured into water, and extracted with ether to give 0.489 g of neutral product. Chromatography on 10 g of silica gel gave 0.404 g of pure ketol **21.** Acidification of the aqueous solution followed by extraction with ether gave a mixture of benzoic acid and ketol, from which 0.705 g (87%) of benzoic acid was obtained by crystallization and silica gel chromatography, and 0.244 g of ketol was obtained by chromatography. Subsequent preparations utilized continuous extraction of the alkaline solution to give essentially quantitative recovery of ketol. Short-path distillation gave material with λ_{max} 2.9 and 5.84 μ (the low intensity of the carbonyl band at 5.84 μ suggested the presence in solution of both the ketol form **21** and the hemiacetal form **22**), and nmr signals at τ 8.74 and 8.60 (3 H, 2s, due to both forms **21** and **22** in about equal amounts), 8.41 (1 H, d, J = 9.6 Hz), 7.8–8.3 (4 H), 7.3–7.7 (3 H), 6.66 (s), and 6.31 and 6.79 (doublets of AB quartet, J = 9 Hz). The latter three signals are due to the two protons adjacent to the hydroxyl group in the ketol form and the corresponding methylene group in the hemiacetal, respectively.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.18; H, 9.21.

9-Methylene-*cis*-nopinol (24). To a solution of 0.288 g of NaH in 10 ml of dry DMSO, which had been kept at 50° for 4 hr under argon to form the sodium salt of DMSO, was added 4.29 g of triphenylmethylphosphonium bromide. After 0.5 hr at room temperature, 0.841 g of the hemiacetal **16** in a small amount of DMSO was added, and the mixture stirred overnight at room temperature, followed by 24 hr at 60°. The mixture was poured into ice water, extracted four times with pentane, and dried over $MgSO_4$. Removal of solvent and drying agent gave 1.64 g of oil from which some triphenylphosphine oxide separated on attempted distillation. Short-path distillation of a small amount of the oil gave some crystalline material which was sublimed to give the olefinic alcohol **24,** mp 72–73°, λ_{max} 2.9, 6.10, 9.4, 9.9, 10.0, and 11.0 μ, $[\alpha]_{5461}$ +65.0° (*c* 1.74, EtOH), and nmr signals at τ 9.22 (1 H, d, J = 8.0 Hz), 8.69 (3 H, s), 7.5–8.5 (9 H), 5.94 (1 H, m), 5.07 (1 H, q, J = 18 and 1.5 Hz), 5.07 (q, J = ~10 and 1.5 Hz), and 3.70 (1 H, doublet of doublets, J = 18 and 10.4 Hz).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.16; H, 10.34.

6-Carboethoxymethyl-9-methyl-7-oxatricyclo[4.3.0.0^{3,9}]nonane (26a). To a mixture of 20.2 g of the hydroxy ester **25a**[21] and 33 g of yellow HgO in 500 ml of pentane was added 22 g of Br_2. During addition the pentane was kept at reflux and a stream of Ar was passed through the system to remove HBr. After addition, reflux was continued for 1 hr, and the mixture was cooled, filtered, and dried over $MgSO_4$. Removal of drying agent and solvent gave 20.4 g of dark oil, which was filtered through 150 g of Al_2O_3 twice to give 16.0 g of the ether ester **26a** (80%), which appeared to be pure by glpc. Attempted distillation led to decomposition, so purification was carried out by glpc followed by short-path distillation to give material with bp 88° (0.2 mm), $n^{26}D$ 1.4755, $[\alpha]_{5461}$ +50.5° (*c* 2.04, EtOH), λ_{max} 5.78 and 9.7 μ, and nmr signals at τ 8.76 (3 H, t, J = 7.1 Hz), 8.74 (3 H s), 8.51 (1 H, d, J = 9.0 Hz), 7.9–8.4 (6 H), 7.75 (1 H, q, J = 4.5 Hz), 7.44 (2 H, s), an AB quartet with doublets at 6.66 and 6.21 (2 H, J = 8.6 Hz), and 5.90 (2 H, q, J = 7.0 Hz).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.65; H, 8.99.

Hydrolysis of 15.5 g of the ester **26a** with 8.4 g of KOH in aqueous methanol afforded 13.5 g of acid **26,** λ_{max} 3.0–3.7 and 5.83 μ, $[\alpha]_{5461}$ +24.3° (*c* 1.36, EtOH), and nmr signals at τ 8.71 (3 H, s), 8.50 (1 H, d, J = 8.6 Hz), 7.7–8.4 (8 H), 7.37 (2 H, s), and an AB quartet with doublets at 6.59 and 6.14 (2 H, J = 9.0 Hz). This compound could not be induced to crystallize from any of the common solvents, and was only partially purified by short-path distillation in a sublimation tube.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 66.41; H, 8.27.

Pyrolysis of 26. A solution of 1.073 g of **26** in 15 ml of quinoline was heated in an oil bath for 3.5 hr, during which time the temperature rose from 200 to 250°. At 215° a small amount of material began to collect in the condenser and gas was given off slowly. The system was washed with ether and the ether solution washed three times with 3% HCl, twice with saturated Na_2CO_3, and once with brine and dried over $MgSO_4$. Removal of drying agent and solvent gave 0.624 g of oil, which showed no absorption for terminal olefin or hydroxyl in the infrared spectrum. Glpc analysis showed only the cyclic ether **9**, identified by retention time and infrared spectrum, and a material originally present as an impurity in the quinoline.

6-Chloromethyl-9-methyl-7-oxatricyclo[4.3.0.0^{3,9}]nonane (27). To a solution of 12.93 g of the acid **26** in 250 ml of benzene was added 44 g of $Pb(OAc)_4$. This mixture was stirred until homogeneous, when 4.31 g of NaCl was added. After repeated evacuation of the system and introduction of an Ar atmosphere, the mixture was heated to 80° overnight.[22] As the reaction proceeded, CO_2 was given off and the color became lighter as Pb^{2+} salts precipitated. The solution was decanted from the gummy salts, washed with dilute $HClO_4$, saturated Na_2CO_3, and saturated NaCl, dried over $MgSO_4$, filtered, the benzene removed under vacuum, and the residue chromatographed on 50 g of Al_2O_3. Elution with 10% ether in pentane gave 5.50 g of pure chloro ether **27.** An additional 0.636 g was obtained on rechromatography of the later fractions, total yield 50%. Purification by glpc gave material washed with bp 65° (1.3 m), $n^{26}D$ 1.4969, $[\alpha]_{5461}$ +46.2° (*c* 2.17, EtOH), λ_{max} 9.75 μ, mol wt 186 (mass spectroscopy with characteristic pattern for a monochloro compound), and nmr signals at τ 8.72 (3 H, s), 8.52 (1 H, d, J = 8.5 Hz), 7.7–8.4 (7 H), 6.47 (2 H, s), and an AB quartet with doublets at 6.59 and 6.12 (2 H, J = 9.0 Hz).

Anal. Calcd for $C_{10}H_{15}ClO$: C, 64.33; H, 8.09; Cl, 19.10. Found: C, 64.32; H, 7.89; Cl, 19.18.

9-Hydroxy-β-pinene (23). A. From the Chloro Ether 27. To a solution of 14.4 g of the chloro ether **27** in 150 ml of dry monoglyme was added 4.6 g of sodium and the solution refluxed overnight. After cooling, the excess sodium was decomposed by the addition of methanol; the solution was diluted with water and extracted thoroughly with ether. The ether solution was washed with water, dried over $MgSO_4$, filtered, and stripped. Distillation of the residue gave 5.6 g (48%) of pure alcohol, bp 55° (0.5 mm), $[\alpha]_{5461}$ +44.4° (*c* 1.80, EtOH), λ_{max} 2.90, 3.22, 6.07, 9.8, and 11.36 μ, mol wt 152 (mass spectroscopy), and nmr signals at τ 8.70 (3 H, s), 8.59 (1 H, d, J = 9.0 Hz), 7.3–8.3 (8 H), an AB quartet with doublets at 6.76 and 6.57 (2 H, J = 11 Hz), and 5.40 (2 H, m).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.23; H, 10.27.

B. From the Ketol 21. To a solution of DMSO carbanion prepared from 0.40 g of NaH in 10 ml of DMSO at 60° was added 2.80 g of triphenylmethylphosphonium bromide at 0°. After warming to room temperature and stirring for 0.5 hr, 0.608 g of ketol **21** was added, and the mixture warmed to 60° for 16 hr. The mixture was poured into ice water and extracted with pentane. The pentane solution was washed with water and brine, dried over $MgSO_4$, filtered and the solvent removed to give 0.587 g of olefinic alcohol **23**, showing identical properties with that obtained *via*

method A above. Subsequent attempts at this reaction were unsuccessful.

9-Acetoxy-β-pinene (23a). A solution of 2.5 g of crude alcohol **23** and 5 ml of pyridine in 5 ml of acetic anhydride was stirred overnight at room temperature. The mixture was poured into saturated $NaHCO_3$ solution under ether and stirred for 2 hr. The ether phase was separated, washed twice with 3% HCl, water, and brine, and dried over $MgSO_4$. After removal of drying agent and solvent, distillation gave 1.6 g of oil, bp 72–74° (1.2 mm), giving rise to two peaks on glpc in a ratio of 1:4. The minor peak was identified as the ether **9**, while the major peak gave data consistent with the desired acetate **23a**. Glpc pure material showed $[\alpha]_{5461}$ +5.6° (*c* 5.37, EtOH), $n^{26}D$ 1.4785, λ_{max} 3.22, 5.71, 6.08, 8.1, 9.7, and 11.3 μ, mol wt 194 (mass spectroscopy), and nmr signals at τ 8.72 (3 H, s), 8.54 (1 H, d, *J* = 9.5 Hz), 8.01 (3 H, s), 7.3–8.3 (7 H), 6.21 (2 H, s), and 5.38 (2 H, m).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.22; H, 9.26.

9-*p*-Toluenesulfonyloxy-β-pinene (23b). To a solution of 5.20 g of 9-hydroxy-β-pinene (**23**) in 90 ml of dry pyridine at 0° was added 6.55 g of *p*-toluenesulfonyl chloride and the solution put in a 0° refrigerator overnight. The mixture was poured onto ice and extracted with ether; the ether was washed with dilute HCl and saturated $NaHCO_3$, dried over $MgSO_4$, filtered, and stripped. Crystallization of the residue from ether–pentane gave 7.42 g of pure tosylate (71%), mp 115°, λ_{max} 3.22, 6.10, 6.27, 7.33, 8.51, 10.4, and 11.3 μ, and nmr signals at τ 8.79 (3 H, s), 8.61 (1 H, d, *J* = 9.2 Hz), 7.4–8.4 (7 H), 7.60 (3 H, s), an AB quartet with doublets at 6.46 and 6.20 (2 H, *J* = 9.6 Hz), 5.50 (2 H, bd), and an AA′BB′ quartet with doublets at 2.74 and 2.39 (4 H, *J* = 8.5 Hz).

Anal. Calcd for $C_{17}H_{22}SO_3$: C, 66.65; H, 7.24; S, 10.44. Found: C, 66.58; H, 7.27; S, 10.48.

9-Iodo-β-pinene (28). A solution of 4.20 g of the pure tosylate and 5.60 g of NaI in 50 ml of purified acetone was refluxed for 18 hr. After cooling in an ice bath and filtration of the sodium tosylate, the acetone was removed under vacuum and the oily residue taken up in ether. The ether solution was washed with a dilute $Na_2S_2O_3$ solution and dried over $MgSO_4$. Distillation of the residue after filtration and removal of ether gave 3.20 g (89%) of the iodide **28**, bp 66° (0.4 mm), $n^{27}D$ 1.5625, $[\alpha]_{5461}$ +76.8° (*c* 1.63, EtOH), λ_{max} 6.08 and 11.37 μ and nmr signals at τ 8.66 (3H, s), 8.68 (1H, d, *J* = 9.5 Hz), 7.3–8.3 (7 H), an AB quartet with doublets at 7.13 and 6.96 (2 H, *J* = 9.5 Hz), and 5.35 (2 H, brd).

Anal. Calcd for $C_{10}H_{15}I$: C, 45.84; H, 5.77; I, 48.39. Found: C, 45.93; H, 5.84; I, 48.50.

Formation of Grignard Reagent from 28. To 0.060 g of sublimed Mg in THF at 50° was added 0.308 g of iodide **28**. The mixture was stirred for 3 hr, quenched with water, filtered, diluted with ether, washed with water, and dried over $MgSO_4$. The solvent was removed by distillation through an 18-in. spinning-band column, and the residue distilled in a Hickman still to give 0.187 g of colorless oil, bp 60–90° (~30 mm). Glpc analysis showed two constituents in a 56:44 ratio, which were identified as the olefins **30** and **29**, respectively, by means of comparison of their retention times and infrared spectra with those of authentic samples.[30] Only a trace of β-pinene was detectable in the chromatogram. Formation of the Grignard reagent in ether at room temperature followed by the same work-up gave the same two products in a ratio of 75:25.

9-Ethynyl-β-pinene (32). A solution of 2.475 g of the iodide **28** and 1.72 g of the ethylenediamine complex of lithium acetylide in 50 ml of DMSO was stirred at room temperature under Ar for 20 hr. The solution was poured into water, neutralized with NH_4Cl solution, and extracted with pentane. The pentane solution was washed with saturated NaCl solution, dried over Na_2SO_4, filtered, and stripped. Short-path distillation of the residue gave 1.067 g (71%), bp ~50° (0.5 mm), which showed two peaks on glpc in the ratio of 4:1 (planimeter). The major peak, assigned structure **32**, showed $n^{25}D$ 1.4975, $[\alpha]_{5461}$ +41° (*c* 1.95, EtOH), mol wt 160 (mass spectroscopy), λ_{max} 2.98, 3.22, 4.70, 6.08, and 11.35 μ, and nmr signals at τ 8.66 (3 H, s), 8.57 (1 H, d, *J* = 9.6 Hz), 7.6–8.3 (8 H), 7.46 (2 H, t, *J* = 5.2 Hz), 5.43 (1 H, m), and 5.35 (1 H, m).

Anal. Calcd for $C_{12}H_{26}$: C, 89.94; H, 10.06. Found: C, 89.78; H, 9.97.

The minor constituent is assigned structure **31** on the basis of its infrared spectrum, λ_{max} 3.22, 6.08, and 11.4 μ, and nmr signals at τ 8.65 (1 H, d, *J* = 9.6 Hz), 8.54 (3 H, s), 8.24 (3 H, s), 7.5–8.5 (5 H), 7.40 (1 H, q, *J* = 5.4 Hz), and 5.41 (2 H, m). When the displacement reaction was carried out at 50° in DMSO, the internal isomer **31** represented about 80% of the product, apparently because of isomerization of **32** under the strongly basic conditions.

9-Carboxaldehydomethyl-β-pinene (33). To a solution of 0.303 g of the crude mixture of acetylenic olefins in 20 ml of THF, cooled in an ice bath, was added 2.0 ml of 1 M disiamylborane by syringe.[26] The solution was then stirred 4 hr at room temperature, decomposed with 2 ml of 3 *N* NaOH and 2 ml of 30% H_2O_2, poured into water and the water solution extracted with pentane. The pentane extract was washed with water, dried over Na_2SO_4, filtered, and stripped to give 0.320 g of crude product. Glpc analysis indicated the presence of a number of compounds, the major peak of which (~30%) was shown to be the desired aldehyde **33**. Material collected by glpc showed bp 90–95° (0.6 mm), λ_{max} 3.23, 3.68, 5.76, 6.08, and 11.4 μ, mol wt 178 (mass spectroscopy), and nmr signals at τ 8.81 (3 H, s), 8.57 (1 H, d, *J* = 9.0 Hz), 7.6–8.4 (1 H), 7.49 (2 H, t, *J* = 5.2 Hz), 5.44 (1 H, m), 5.36 (1 H, m), and 0.30 (1 H, t, *J* = 1.5 Hz).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.15; H, 10.13.

(+)-β-*cis*-Bergamotene (3). Triphenylisopropylidenephosphorane was generated from 1.93 g of triphenylisopropylphosphonium bromide in 50 ml of THF by the addition of 1 equiv of butyllithium. After 2 hr at room temperature the crude product from the reaction of 0.305 g of the acetylene mixture with disiamylborane, followed by oxidation, was added and the mixture heated to 60° overnight. After cooling, the mixture was poured into water, extracted with pentane, and the pentane washed with water, dried over $MgSO_4$, filtered, and stripped to give 0.235 g of crude product. This material was filtered through 6 g of Al_2O_3 to give 0.099 g of hydrocarbons, consisting of ~90% (+)-β-*cis*-bergamotene (**3**) and 10% of the starting acetylenes. Purification gave material with bp ~105° (0.5 mm), $[\alpha]^{25}D$ +40.2° (*c* 1.74, $CHCl_3$), λ_{max} 3.22, 6.06, 11.43, and 11.95 μ, mol wt 204 (mass spectroscopy), and nmr signals at τ 8.81 (3 H, s), 8.63 (1 H, d, *J* = 9.5 Hz), 8.47 (3 H, s), 8.39 (3 H, s), 7.7–8.3 (9 H), 7.56 (2 H, t, *J* = 5 Hz), 5.50 (1 H, m), 5.42 (1 H, m), and 4.99 (1 H, brd t, *J* = 8.0 Hz).

Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 87.93; H, 11.16.

9-Iodo-α-pinene (35). The tosylate **34** was prepared from 3.25 g of the acetate **12** as described for the conversion of **12** to α-pinene. The crude tosylate, 4.6 g, was dissolved in 75 ml of acetone with 6.8 g of NaI and the solution refluxed overnight. The mixture was cooled to room temperature, filtered, and the solvent removed *in vacuo*. The residue was dissolved in ether, washed with sodium thiosulfate solution, water, and brine, and dried over $MgSO_4$. After removal of drying agent and solvent, distillation gave 0.44 g of cyclic ether **9** and 1.70 g of iodide **35**, bp 58–61° (0.6 mm). This represents a 39% yield from **12**. The material could not be purified by glpc due to excessive decomposition, but the distilled material showed $\lambda_{max}^{CCl_4}$ 7.25, 8.28, and 8.42 μ. The mass spectrum showed no peaks above *m/e* 134, corresponding to loss of HI from $C_{10}H_{15}I$, probably in the inlet system. The nmr spectrum showed signals at τ 8.94 (1 H, d, *J* = 8.0 Hz), 8.60 (3 H, s), 8.22 (3 H, d, *J* = 2.0 Hz), 7.77 (5 H), an AB quartet with doublets at 6.87 and 6.60 (2 H, *J* = 9.0 Hz), and 4.71 (1 H, m).

9-Ethynyl-α-pinene (36). A solution of 1.55 g of iodopinene **35** in DMSO was added to a stirred mixture of 1.20 g of lithium acetylide ethylenediamine complex in 30 ml of DMSO at 0° under an Ar atmosphere. The mixture was allowed to warm to room temperature and stirred overnight. The mixture was poured into ice water, and the resulting solution extracted with pentane. The pentane solution was washed with water and dried over Na_2SO_4. Distillation of the residue after filtration and removal of solvent gave 0.703 g (74%) of colorless oil, bp 67–70° (2.0 mm), which showed two peaks on glpc in the ratio of 32:68. The minor peak gave spectral data indicating a nearly equimolar mixture of the ether **9** and another compound, probably the internal acetylene isomer corresponding to **31**. No further work was done to characterize this compound. The major peak gave satisfactory data for the acetylenic olefin **36**, λ_{max} 3.05, 4.74, and 12.6 μ, mol wt 160 (mass spectroscopy) and nmr signals at τ 8.81 (1 H, d, *J* = 8.0 Hz), 8.60 (3 H, s), 8.30 (3 H, d, *J* = 1.8 Hz), 8.15 (1 H, t, *J* = 2.6 Hz), 7.81 (7 H), and 4.77 (1 H, m).

(−)-α-*cis*-Bergamotene (2). To a solution of 0.373 g of 2-methyl-2-butene in 50 ml of THF was added 1.20 ml of diborane (1.06 *M* in THF) *via* syringe. The solution was stirred at room temperature for 1 hr, then a THF solution containing 0.147 g of acetylenic olefin **36** added dropwise *via* syringe and then allowed to stir overnight at room temperature under Ar. The solution was cooled in an ice

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bath and treated with 3.2 ml of 3 *N* NaOH and 3.2 ml of 30% H_2O_2. After 2 hr at room temperature, the reaction mixture was poured into 500 ml of H_2O, the aqueous solution extracted with ether, and the ether extract washed with water and dried over Na_2SO_4. The infrared spectrum of the residue remaining after removal of solvent and drying agent showed that very little of the aldehyde **37** had been formed and that only traces of starting material remained. Attempts to isolate the aldehyde by glpc were unsuccessful. The crude product obtained above was added to a THF solution of the ylide prepared from 2.06 g of triphenylisopropylphosphonium bromide and butyllithium. After 24 hr at room temperature the mixture was poured into 500 ml of H_2O and the aqueous phase extracted with pentane. The pentane solution was washed with water, dried over $MgSO_4$, and filtered and the solvent removed *in vacuo*. The residue was adsorbed on 30 g of alumina. Elution with pentane gave 21.0 mg of crude hydrocarbons, containing some starting acetylenic olefin and the desired (−)-α-*cis*-bergamotene. Purification by glpc gave 8.5 mg of pure material, $\lambda_{max}^{CCl_4}$ 6.05, mol wt 204 (mass spectroscopy), $[\alpha]_{5461}$ −39.4° (*c* 0.48, $CHCl_3$), and nmr signals at τ 8.82 (1 H, d, *J* = 8 Hz), 8.73 (3 H, s), 8.43 (3 H, s), 8.36 (3 H, s), 8.32 (3 H, d, *J* = 2 Hz), 7.82 (5 H), 4.99 (1 H, brd t, *J* = 7 Hz), and 4.85 (1 H, m). The infrared and nmr spectra of this material were identical with those of a sample isolated from oil of opoponax,[8] which showed $[\alpha]_{5461}$ −45° (*c* 0.038, $CHCl_3$).

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The Synthesis of 1,2,2-Tris(difluoramino)alkanes[1a]

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Abstract: Enol esters are converted to 1,2,2-tris(difluoramino)alkanes when treated successively with tetrafluorohydrazine and difluoramine–sulfuric acid. Some of the limitations of this reaction are described. The tris(difluoramino)alkanes are stable compounds; their chemistry resembles that of olefin–tetrafluorohydrazine adducts.

The synthesis of poly(difluoramino) compounds of specific configurations presents some special problems. Essentially, there are two general methods available. The addition of tetrafluorohydrazine to an olefin double bond[2] and the conversion of carbonyl groups[3] or their equivalent[4] to *gem*-difluoramines using difluoramine in strong acids. Attempts to combine these reactions with α,β-unsaturated ketones have been frustrated by the instability of the olefin–N_2F_4 adduct[2] and by the tendency of difluoramine to add to the olefinic double bond.[4] For example, difluoramine reacts with methyl vinyl ketone in the presence of sulfuric acid to yield 1,3,3-tris(difluoramino)butane.[3,5] The α-alkyl-α-difluoraminocarbonyl compounds encountered in this study were unstable in strong acid; fragmentation, as discussed below, was observed.

$$CH_3\overset{O}{\overset{\|}{C}}CH{=}CH_2 \xrightarrow[H_2SO_4]{HNF_2} CH_3C(NF_2)_2CH_2CH_2NF_2$$

In searching for useful intermediates for combining the N_2F_4 and HNF_2 reactions, it appeared that enol derivatives would offer a useful and potentially convenient route for the conversion of a ketone function to a tris(difluoramino) function. Enol esters react readily with tetrafluorohydrazine[2] and it has now been established that the resulting adducts are cleaved by difluoramine in strong acids to yield the desired derivatives.

$$\diagdown C{=}C(\mathrm{OR})\diagup + N_2F_4 \longrightarrow \diagdown \underset{NF_2}{C}-\underset{NF_2}{C}(\mathrm{OR})\diagup + HNF_2 \xrightarrow{H^+} \diagdown \underset{NF_2}{C}-\underset{NF_2}{C}(NF_2)\diagup$$

Results

Both enol phosphates and enol acetates have been employed in this sequence. Both have virtues and drawbacks. When the requisite α-halo ketone is available, the enol phosphate is useful because the double bond is located unequivocally between the carbonyl carbon and carbon originally bearing halogen. However, in many instances it is not convenient to prepare and purify the desired monohalo ketone. Enol acetates are easier to prepare, but unless a symmetrical ketone is employed mixtures result. Decision in individual instances must be made on the basis of these considerations.

The reaction of the α,β-bis(difluoramino)alkyl acetates or phosphates with difluoramine in fuming sulfuric acid or fluorosulfonic acid was very sensitive to the structure of the ester and to the reaction conditions. It was generally found necessary to carry out these reactions in the presence of methylene chloride to extract the tris(difluoramine) from the reaction zone.

Some of the representative tris(difluoramines) prepared are listed in Table I. In general, the intermediate N_2F_4 adducts were not purified but were used directly. In all cases they were characterized by nmr analyses. The low molecular weight tris(difluoramines) are extremely sensitive compounds, and explode readily when initiated by friction or impact. Extreme care was necessary in their handling. Great difficulty was

(1) (a) This research was carried out under Army Ordnance Contract No. DA-01-021-ORD-11909. (b) Deceased. (c) Address inquiries to this author.

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(5) Addition to HNF_2 to α,β-unsaturated ketones[3] appears to be a general route to 1,3,3-tris(difluoramino)alkanes. Cyclohexenone and cyclopentenone were converted to 1,1,3-tris(difluoramino)cyclohexane and 1,1,3-tris(difluoramino)cyclopentane, respectively; an example is given in the Experimental Section.