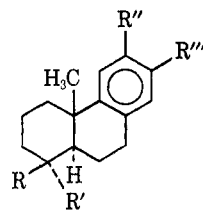


Reductive Backbone Rearrangements in Diterpene Acids¹

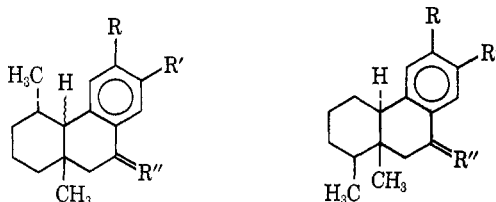
Summary: Reaction of dehydroabietic acid and podocarpic acid methyl ether derivatives with phosphoryl chloride affords 18-nor-5,10-freidoabietatrienes and podocarpatrienes, the result of decarboxylation, rearrangement, and reduction.

Sir: It was recently reported that reaction of either 12-methoxypodocarpa-8,11,13-trien-19-oic acid (1), abieta-8,11,13-trien-18-oic acid (2), or the corresponding acid chlorides and esters with phosphoryl chloride or polyphosphoric acid gave as major reaction products octahydrophenanthrenes 3 and 4, respectively, plus derived naphthalenes and phenanthrenes.² These structural assignments were based on the coincidence of melting points of the dimethylphenanthrene and its picrate derived from 3 with those of 4,10-dimethylphenanthrene³ and its picrate, combined with the observation that this phenanthrene had "... an nmr spectrum identical to those (that) recorded for 4,10-dimethylphenanthrene."² However, the chemical shifts of the aromatic methyl signals for 4,10-dimethylphenanthrene are reported as δ 2.72 and 3.14,³ while those of the dimethylphenanthrene described in ref 2 are δ 2.80 and δ 3.02. Consideration of the chemical shift data reported for other dimethylphenanthrenes,³ and the course of carbonium ion rearrangements in a similar system,⁴ indicates that more plausible structures for these reaction products are those of an 18- or 19-nor-5,10-freido-12-methoxypodocarpa-8,11,13-triene (5), derived from acid 1, and the corresponding abietatriene (6), derived from acid 2.

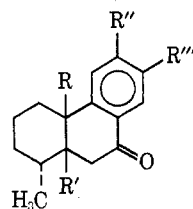
Repetition of the reactions of acids 1 and 2 with phosphoryl chloride gave the products described by Baguley, *et al.*,² and abieta-8,11,13-trien-19-oic acid (7)⁵ under these conditions afforded the same hydrocarbon as its 4 epimer (2). The methoxyoctahydrophenanthrene derived from acid 1 (*i.e.*, 3 or 5) was oxidized with chromic acid to the oily ketone:^{6,7} nmr (CHCl_3) δ 0.92 (s, 3 H), 0.92 (d, $J = 5$ Hz, 3 H), 2.08 (d, $J = 17$ Hz, 1 H), 2.58 (m, $w_{1/2}$ 14 Hz, 1 H), 2.90 (d, $J = 17$ Hz, 1 H), 3.55 (s, 3 H), 6.48 (m, 2 H), 7.55 (d, $J = 8$ Hz, 1 H); ir 5.99 μ ; uv $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 281 nm (log ϵ 4.17); M^+ (70 eV) 258. The presence of the benzylic proton as a broad multiplet is characteristic of an axial proton coupled to two adjacent protons,⁸ and is consistent with structure 8, but not with structure 9 in which this proton would appear as a doublet. It is assumed that the angular methyl group will migrate stereospecifically and the small coupling constant (5 Hz) for the secondary methyl indicates that this group is



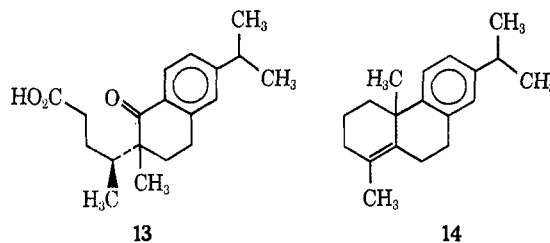
- 1, R = CO₂H; R' = CH₃; R'' = OCH₃; R''' = H
 2, R = CH₃; R' = CO₂H; R'' = H; R''' = (CH₃)₂CH
 7, R = CO₂H; R' = CH₃; R'' = H; R''' = (CH₃)₂CH



- 3, R = OCH₃; R' = H; R'' = H₂ 5, R = OCH₃; R' = H; R'' = H₂
 4, R = H; R' = (CH₃)₂CH; R'' = H₂ 6, R = H; R' = (CH₃)₂CH; R'' = H₂
 9, R = OCH₃; R' = H; R'' = O 8, R = OCH₃; R' = H; R'' = O
 12, R = H; R' = (CH₃)₂CH; R'' = O



- 10, R, R''' = H; R' = CH₃; R'' = OCH₃
 11, R = CH₃; R' = H; R'' = (CH₃)₂CH



equatorial.⁹ Although the stereochemistry depicted in 8 is that predicted on mechanistic grounds,⁴ a cis ketone, with a nonsteroidal conformation (10), would show the same spectral properties. The CD curve of the ketone from oxidation of 5 shows a simple negative Cotton effect, $\theta_{316} - 4620$, essentially antipodal to that of the 7 ketone derived from methyl *O*-methylpodocarpate,¹⁰ and in accordance with the predictions of the inverse octant rule.¹¹ The cis ketone 11,¹² with a nonsteroidal conformation, shows a multiple Cotton effect $\theta_{370} - 82$, $\theta_{353} - 132$, $\theta_{322} - 2700$, $\theta_{296} - 5800$ as should also a ketone of structure 10.

Oxidation of the hydrocarbon obtained from acids 2 and 7 gave the oily ketone 12: ir 5.94 μ ; uv $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 258 nm (log ϵ 4.20); M^+ (70 eV) 270. The nmr spectrum of 12 was identical with that of ketone 8, with the exception of the signals associated with the aromatic ring.

(1) Studies on Resin Acids. VIII. For part VII see J. W. Huffman, *J. Org. Chem.*, **37**, 17 (1972).

(2) B. C. Baguley, R. C. Cambie, W. R. Dive, and R. N. Seelye, *Aust. J. Chem.*, **25**, 1271 (1972).

(3) A. Regnault and P. Canonne, *Tetrahedron*, **25**, 2349 (1969).

(4) H. W. Whitlock and L. E. Overman, *J. Amer. Chem. Soc.*, **93**, 2247 (1971).

(5) J. W. Huffman, *J. Org. Chem.*, **35**, 3154 (1970).

(6) (a) E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.*, **80**, 211 (1958); (b) E. Wenkert and J. W. Chamberlin, *ibid.*, **81**, 688 (1959).

(7) All new compounds were characterized by ir, uv, and nmr spectroscopy. Their purity was monitored by glc and/or tlc and the molecular formula confirmed by mass spectrometry.

(8) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy," Holden-Day, San Francisco, Calif., 1964 pp 79-82.

(9) F. Johnson, N. A. Staskousky, and W. D. Gurowitz, *J. Amer. Chem. Soc.*, **87**, 3492 (1965).

(10) A. J. Bose, M. S. Manhas, and R. C. Cambie, *J. Org. Chem.*, **30**, 501 (1965).

(11) G. Sznatzke in G. Sznatzke, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Heyden and Sons, London, 1967, pp 208-223.

(12) J. W. Huffman, *J. Org. Chem.*, **35**, 478 (1970).

There was also obtained from this oxidation a keto acid (13), characterized as the methyl ester [nmr (CDCl₃) δ 0.96 (d, J = 6 Hz, 3 H), 1.08 (s, 3 H), 1.18 (d, J = 7 Hz, 6 H), 2.70 (t, J = 6 Hz, 2 H), 3.32 (s, 3 H), 6.60 (br s, 1 H), 6.70 (br d, J = 7 Hz, 1 H), 7.49 (d, J = 7 Hz, 1 H)]; ir 5.97, 5.84 μ ; uv $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 261 nm (log ϵ 4.14); M^+ (70 eV) 316], a substance readily derived from 6 by oxidation at C-10, followed by dehydration and further oxidation, but impossible to rationalize in terms of structure 4.

It is quite apparent that the structural assignments of Baguley, *et al.*,² are incorrect and that those compounds assigned structures 3 and 4 (structures 14 and 15 of ref 2) have in fact structures 5 and 6, and that the structures of all of the other compounds obtained from these reactions and reported by these authors should be revised accordingly.

The mechanistic path which gives rise to these compounds is probably essentially that suggested by the New Zealand group;² however, the initial carbonium ion formed at C-4 must rearrange in a stepwise fashion *via* intermediates similar to those suggested by Whitlock.⁴ In agreement with this hypothesis it was found that 18-norabieta-4,8,11,13-tetraene (14)¹² gave hydrocarbon 6 on reaction with phosphoryl chloride, although the reaction proceeds somewhat more slowly than with acids 2 and 7. It was also found that the methyl esters of acids 2 and 7 were smoothly converted to 6 with boron tribromide in methylene chloride at 5°. Although intermolecular hydride transfer reactions involving carbonium ion intermediates are known, they are not common under the relatively mild conditions of these reactions.¹³

Although the examples of the reductive rearrangement reactions cited above are all in the diterpene series, these should prove to be general reactions of appropriately constituted carbonium ions. A detailed investigation of the scope and limitations of these reactions is in progress.

Acknowledgments.—The spectropolarimeter and mass spectrometer used in this work were obtained through National Science Foundation Research Instrument Grants.

(13) (a) R. C. Fuson and L. L. Alexander, *J. Amer. Chem. Soc.*, **58**, 1745 (1936), and earlier papers in this series. (b) J. W. Huffman and J. J. Starnes, *J. Org. Chem.*, **37**, 487 (1972). (c) P. D. Bartlett and J. D. McCollum, *J. Amer. Chem. Soc.*, **78**, 1441 (1956), have reported the use of the triphenylmethylcarbonium ion as a hydride acceptor in the oxidation of alcohols under mild conditions. See also M. P. Doyle, D. J. DeBruyn, and D. J. Scholten, *J. Org. Chem.*, **38**, 625 (1973), and references therein.

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Synthesis of the Natural Isomer of a Tetrahomoterpene Alcohol Obtained From the Codling Moth

Summary: The synthesis of the four possible stereoisomers of 7-methyl-3-propyl-2,6-decadien-1-ol, a tetrahomoterpene isolated from the codling moth, has been

achieved, and spectroscopic and gas chromatographic comparison have established the natural material as the 2*Z*,6*Z* isomer.

Sir: We have recently described¹ the synthesis of (2*Z*,6*E*)-7-methyl-3-propyl-2,6-decadien-1-ol, a tetrahomoterpene alcohol reported² to be a pheromone of the codling moth (*Laspeyresia pomonella* L.). Spectroscopic and gas chromatographic comparison established that our synthetic material differed from the natural product; on the basis of nmr chemical shift data and relative retention times upon glpc, we suggested that the natural isomer had the 2*E*,6*Z* configuration. We now report the synthesis of the remaining three isomers of this compound, and the finding that the natural product has the 2*Z*,6*Z* configuration.

The synthesis of the 2*E*,6*Z* (5) and the 2*Z*,6*Z* (7) isomers proceeded from a common intermediate, the acetylenic ester 3.³ This ester was prepared by coupling the allylic bromide 1 with propargyl Grignard, followed by carbethoxylation of the lithio derivative of the acetylene 2⁴ with ethyl chloroformate.¹ Reduction of 3 with lithium aluminum hydride-sodium methoxide (2:1) in refluxing tetrahydrofuran (THF), and iodination of the intermediate alanate (0.5 hr, -78°) after consumption of the excess hydride with ethyl acetate, afforded the iodo alcohol 4.^{5,6} The iodo alcohol coupled cleanly with a fourfold excess of lithium di-*n*-propylcuprate in ether (4 hr, -78°)⁷ to give the 2*E*,6*Z*-decadienol 5 in 50% overall yield from 3.

The stereospecific *cis* addition of a propyl group and hydrogen to the carbon-carbon triple bond in 3 was effected by treatment with 2 equiv of lithium di-*n*-propylcuprate in THF (5 hr, -78°),⁸ followed by

(1) (a) S. B. Bowlus and J. A. Katzenellenbogen, *Tetrahedron Lett.*, 1277 (1973). (b) For another synthesis, see M. P. Cooke, *ibid.*, 1281 (1973).

(2) (a) L. M. McDonough, D. A. George, B. A. Butt, J. M. Ruth, and R. Hill, *Science*, **177**, 177 (1972). (b) The original stereochemical assignment of 2*Z*,6*E*^{2a} was based on the nmr chemical shift of the 7-methyl group and on the glpc elution order of a mixture of 7-methyl-3-propyl-2,6-decadien-1-ol isomers. From the results of this study it appears that the misassignment was due to the choice of inappropriate model systems for chemical shift comparison and the unsubstantiated composition and identity of the mixture of isomers. (c) More recent results (L. M. McDonough, personal communication) have established that both natural 3-propyl-7-methyl-2,6-decadien-1-ol and the mixture of four stereoisomers^{2a} are inactive as a pheromone in laboratory and field trials. The physiological significance of this substance is thus unknown. On the basis of electroantennogram studies, (8*E*,10*E*)-8,10-dodecadien-1-ol has been proposed to be a pheromone of the codling moth [W. Roelofs, A. Comeau, A. Hall, and G. Milicevic, *Science*, **174**, 297 (1971)]; synthetic material is equally attractive as the compound isolated from the codling moth [C. Descoins and C. A. Henrick, *Tetrahedron Lett.*, 2999 (1972)].

(3) Structural assignments for all new compounds were fully supported by nmr and ir spectroscopy, mass spectrometry, and combustion analysis and/or high resolution mass spectrometry.

(4) An undetermined amount of the allene corresponding to 2 is found in this reaction, but may be conveniently removed by chromatography following the carbethoxylation reaction.

(5) The reaction gives 10-15% 2-iodo alcohol, which may be removed by careful preparative thin layer chromatography.

(6) The reduction-iodination sequence has previously been applied to propargylic alcohols, to give selectively either the 2-iodo or the 3-iodo allylic alcohols: E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 4245 (1967); E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *ibid.*, **90**, 5618 (1968); E. J. Corey, K. Achiwa, and J. A. Katzenellenbogen, *ibid.*, **91**, 4318 (1969); E. J. Corey, H. A. Kirst, and J. A. Katzenellenbogen, *ibid.*, **92**, 6314 (1970); E. J. Corey, J. A. Katzenellenbogen, S. A. Roman, and N. W. Gilman, *Tetrahedron Lett.*, 1821 (1971). This application extends the scope of starting materials to propargylic esters.

(7) The coupling of iodo allylic alcohols with lithium dialkylcuprates is described in the references in ref 6.

(8) (a) E. J. Corey and J. A. Katzenellenbogen, *J. Amer. Chem. Soc.*, **91**, 1851 (1969); (b) J. B. Siddall, M. Biskup, and J. H. Fried, *ibid.*, **91**, 1853 (1969); (c) J. F. Normant, *Synthesis*, 63 (1972); (d) ref 1a.