

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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RECEIVED APRIL 5, 1973

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.

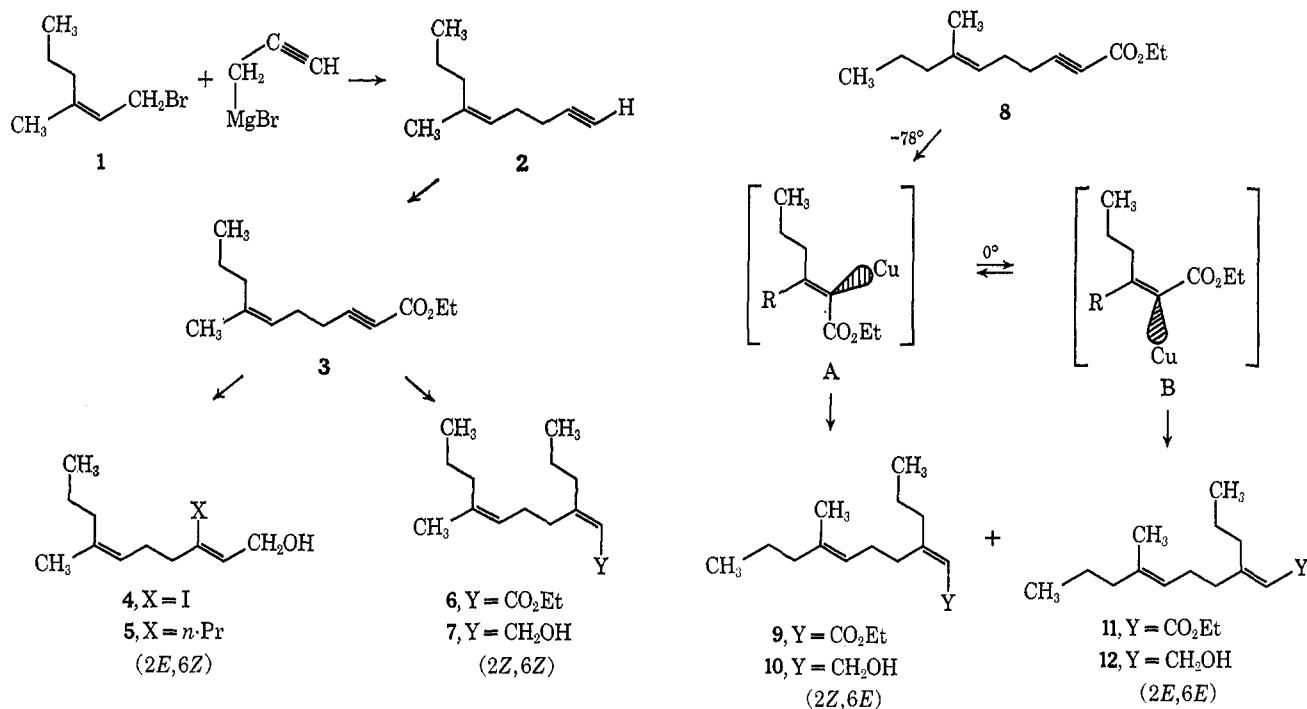
(4) An undetermined amount of the allene corresponding to 2 is found in this reaction, but may be conveniently removed by chromatography following the carbethoxylation reaction.

(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.



quenching with prechilled ethanol at -78° . Aluminum hydride reduction of ester 6 furnished the 2*Z*,6*Z* isomer 7 in 43% overall yield from 3.

The isomeric alcohols 5 and 7 are spectroscopically indistinguishable (nmr, ir, mass spectra); both show the allylic methyl resonance at δ 1.65. As the corresponding signal in the natural product is reported to be at δ 1.66, and that of the 2*Z*,6*E* isomer at 1.57, this confirms our previous suggestion that the natural material has the 6*Z* configuration.^{1a}

Inasmuch as the synthesis of the isomers 5 and 7 established the *Z* configuration at C-6, we felt that it was not profitable to undertake a stereoselective synthesis of the 2*E*,6*E* isomer 12. For the purpose of glpc comparison, however, we prepared this material as a mixture with the 2*Z*,6*E* isomer 10 by the convenient method described below.

Conjugate addition of lithium di-*n*-propylcuprate to the acetylenic ester 8 at -78° in THF gives exclusively the adduct with the stereochemistry shown in A.¹ Although this enolate is configurationally stable at -78° in THF,^{8a} it undergoes facile isomerization at 0° . The mixture of esters 9 and 11 was thus prepared by quenching the enolates A and B after equilibration at 0° for 0.5 hr. The alcohols 10 and 12 were obtained as a mixture after aluminum hydride reduction (overall yield of mixture 57% from 8).

Glpc analysis of the four isomers on OV-1 established their elution order as 2*Z*,6*Z*, 2*E*,6*Z*, 2*Z*,6*E*, and 2*E*,6*E* (7, 5, 10, and 12) with relative retention times of 0.91,

0.96, 1.00 and 1.04. On the basis of the report that the natural product cochromatographed with the second component in a mixture of all possible isomers prepared by a nonselective synthesis,^{2a} it was believed that the natural product had the 2*E*,6*Z* configuration.

Subsequent glpc comparisons of our synthetic isomers with the naturally occurring isomer on Carbowax 20M has shown that the natural material cochromatographs with the 2*Z*,6*Z* isomer (7).⁹ Comparison of our samples with the four-isomer mixture prepared by McDonough^{2a,9} indicates that the 2*Z*,6*Z* isomer does indeed elute as the second component; the first peak in the chromatogram of the mixture,^{2a} which was originally thought to be the 2*Z*,6*Z* isomer, is actually an unidentified impurity. The third peak consists of the mixed isomers (2*Z*,6*E* and 2*E*,6*Z*), which are not resolved on this phase, and the fourth peak is the 2*E*,6*E* isomer.

It is concluded that the natural material, obtained from the codling moth, is (2*Z*,6*Z*)-7-methyl-3-propyl-2,6-decadien-1-ol (7).

(9) These comparisons were carried out by Dr. L. M. McDonough, Agricultural Research Service, Yakima, Wash. Dr. McDonough's cooperation is gratefully acknowledged.

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RECEIVED APRIL 26, 1973