such as Na^+–K^+ will be published in a full paper along with a fuller description of this study.

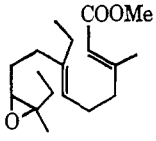
Acknowledgment. The support of the National Research Council of Canada (NRCC) and the Defense Research Board of Canada (DRB) is gratefully acknowledged.

D. M. Chen, K. Radley, L. W. Reeves*
Chemistry Department, University of Waterloo
Waterloo, Ontario, Canada
Received January 28, 1974

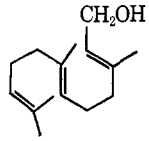
Stereoselective Epoxidations of Acyclic Allylic Alcohols by Transition Metal–Hydroperoxide Reagents. Synthesis of *dl*-C_{18} *Cecropia* Juvenile Hormone from Farnesol

Sir:

We report here a stereoselective synthesis of *dl*-C_{18} *Cecropia* juvenile hormone (**1**) from the readily available (*E*,*E*)-farnesol (**2**). A synthesis of **1** from farnesol



1

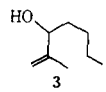


2

by a route involving nonstereoselective homologations has been reported previously.[1] Our approach depends crucially on the transition metal catalyzed epoxidation of olefinic alcohols by *tert*-butyl hydroperoxide.[2]

Having recently shown that transition metal catalyzed epoxidations of cyclic olefins by *tert*-butyl hydroperoxide are highly stereoselective,[2a] we have now found that these same reagents also effect stereoselective epoxidation of acyclic olefinic alcohols. Examination of the results in the table reveals that both the vanadium[3] and the molybdenum–*tert*-butyl hydroperoxide reagents are generally more selective in epoxidations of acyclic allylic alcohols than the previously reported peracid epoxidations[4–6] of these same substrates. The ratios of the diastereomeric epoxy alcohols reported in Table I using peracids were also determined in this study; these values correlate well with the reported literature values[4,5] using the same or similar peracids on the same olefinic substrates. Of special interest for the synthesis of hormone **1** is the observation that epoxidation of the allylic alcohols **3** and **7** with the $VO(acac)_2$–*t*-BuOOH reagent produces the erythro epoxy alcohols selectively. The erythro epoxy alcohol **4** on treatment with excess lithium dibutylcopper in ether at −26° for 2 hr was converted to vicinal diol **5** in 82% over-all yield.[7] Stereospecific deoxygenation of diol **5** was accomplished by the procedure of Eastwood and coworkers.[8] The diol was treated with *N*,*N*-dimethylformamide dimethyl acetal at 25° for 12 hr and the resulting dioxolane derivative

Table I. Stereochemistry of Epoxidations of Acyclic Allylic Alcohols

	Peracids[b]				*t*-BuOOH			
	NPBA		MCPBA		$VO(acac)_2$[d]		$Mo(CO)_6$[e]	
Olefin[a]	T[c]	E	T	E	T	E	T	E
	64	36	64	36	71	29	53	47
	9	91			<1	>99	2	98
 7	32	68	20	80	2	98	2	98
 3			38	62	4 (<1)[g]	96 (>99)[g]		
			62	38	90	10	97	3
	96	4	96	4	82	18	96	4
			80	20	94	6	85	15

[a] The olefinic alcohols were obtained from Chemical Samples Co. The pure (*E*)-3-penten-2-ol was separated from its (*Z*)-isomer by distillation (bp 56° (70 mm)) through a Perkin-Elmer NFA-200 autoannular still. All epoxidations were performed on 5 mmol of the olefin dissolved in 25 ml of solvent. The product mixtures were analyzed by glc on a 50 ft Carbowax K20M SCOT capillary column. [b] The *p*-nitroperbenzoic acid (NPBA) epoxidations were performed at 0° in ether and the *m*-chloroperbenzoic acid (MCPBA) cases at 0° in methylene chloride. [c] T = % threo; E = erythro. [d] The $VO(acac)_2$ reactions were run at room temperature in benzene with ~5 mg of catalyst and 7.5 mmol (1.5 equiv) of *t*-BuOOH (94%, Lucidol Division of Pennwalt Corp.). The *t*-BuOOH was dissolved in benzene and added slowly dropwise to the stirred reaction mixtures. [e] With the exception that the $Mo(CO)_6$ cases were run at reflux in benzene, the procedure was identical with that described for the $VO(acac)_2$ cases. [f] The threo and erythro epoxy alcohol diastereomers separated poorly (glc) in this case. Thus in order to confirm the assigned ratios and also the stereochemical assignments, the epoxy alcohol product mixtures were converted to mixtures of *threo*- and *erythro*-2,3-dihydroxyoctane by reaction with excess (8 equiv) lithium di-*n*-butylcuprate. The authentic 2,3-dihydroxyoctanes were prepared by osmylation of *cis*- and *trans*-2-octene, respectively. [g] The figures within the parentheses are the improved selectivities observed recently when the oxidation was carried out in toluene at 0° using 2 equiv of *t*-BuOOH. This result suggests that subambient temperatures ought to be explored whenever greater selectivity is desired in these epoxidations.

(1) E. E. van Tamelen and J. P. McCormick, *J. Amer. Chem. Soc.*, **92**, 737 (1970); see also R. J. Anderson, C. A. Henrick, and J. B. Siddall, *ibid.*, **92**, 735 (1970).

(2) (a) K. B. Sharpless and R. C. Michaelson, *J. Amer. Chem. Soc.*, **95**, 6136 (1973); (b) F. List and L. Kuhnen, *Erdoel Kohle*, **20**, 192 (1967); (c) M. N. Sheng and J. G. Zajacek, *J. Org. Chem.*, **35**, 1859 (1970).

(3) We would like to make an *important correction to our previous publication*[2a] on these oxidations. In the earlier work, epoxidation of 20 g of geraniol is carried out at reflux in benzene using the $VO(acac)_2$ catalyst. We have since found that most of the vanadium-catalyzed epoxidations of allylic alcohols proceed readily at room temperature, whereas the molybdenum systems do require heating. In contrast to the procedure described previously[2a] for the vanadium system, we recommend that the *tert*-butyl hydroperoxide (use 1.5 equiv instead of the 1.1 equiv recommended previously) be added slowly to the other reactants while stirring at room temperature; cooling is often necessary for large scale reactions. These milder conditions for the vanadium-catalyzed epoxidations should prove valuable when optimization of regio- and/or stereoselectivity is important (see also footnote *g* in table).

(4) M. L. Sassiver and J. English, *J. Amer. Chem. Soc.*, **82**, 4891 (1960).

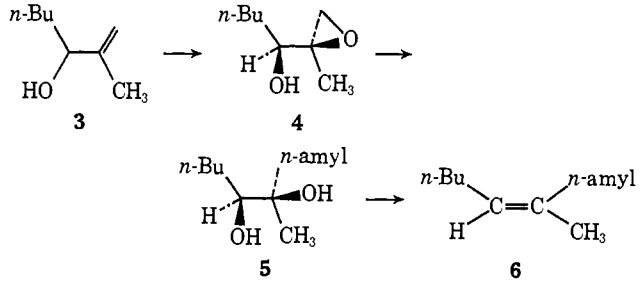
(5) J. L. Pierre, P. Chantemps, and P. Arnaud, *Bull. Soc. Chim. Fr.*, 1317 (1968).

(6) For an outstanding review on the stereochemical aspects of the synthesis of epoxides, see G. Berti, *Top. Stereochem.*, **7**, 83 (1973).

(7) R. W. Herr, D. M. Wieland, and D. R. Johnson, *J. Amer. Chem. Soc.*, **92**, 3813 (1970).

(8) F. W. Eastwood, K. J. Harrington, J. S. Josan, and J. L. Pura, *Tetrahedron Lett.*, 5223 (1970).

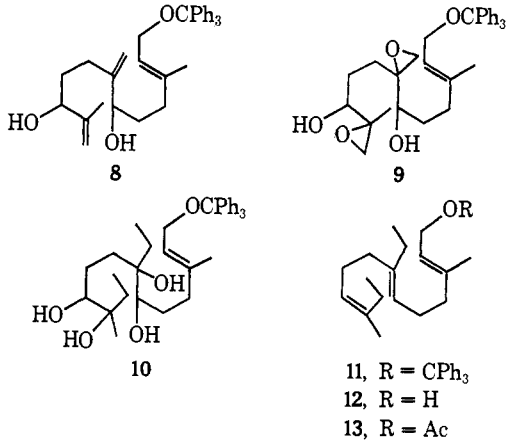
was heated in acetic anhydride at 130° for 2.5 hr to produce (*Z*)-6-methyl-5-undecene (**6**, 70% yield from **5**):



3 **4** **5** **6**

nmr (CCl_4, TMS) δ 1.65 (s, 3 H, $=CCH_3$), 5.03 (bt, 1 H, J = 7 Hz, =CH); >97% pure by glpc analysis.

The synthesis of hormone **1** begins with the known diol **8** (previously prepared from farnesol (**2**) by van Tamelen and McCormick[1]) and employs a series of reactions which parallel those described above for the stereoselective generation of olefin **6**. The bisallylic alcohol **8** was transformed to the bisepoxy alcohol **9** by reaction with vanadium acetylacetonate–*tert*-butyl hydroperoxide in benzene at 25° for 2 hr. After removal of the benzene, the crude product was subjected to the action of 8 equiv of ethereal lithium dimethylcopper at 0° for 12 hr. The tetraol trityl ether **10**, isolated by thin-layer chromatography (58% yield based on **8**), was homogeneous by silica gel tlc analysis using ethyl acetate as eluent (R_f = 0.60). Treatment of the tetraol **10** with excess *N*,*N*-dimethylformamide dimethyl acetal at 25° for 12 hr afforded the bisdioxolane derivative, which was subsequently heated at 130° with acetic anhydride to furnish the triene trityl ether **11** in 33% yield, homogeneous by tlc: nmr (100 MHz, $CDCl_3$, TMS) δ 0.94 and 0.86 (t, 3 H each), 1.46 (s, 3 H), 1.66 (s, 3 H), 3.61 (d, 2 H), 5.08 (bt, 2 H), 5.44 (bt, 1 H). Removal of the trityl group by 5% perchloric acid in tetrahydrofuran at 0° for 1.5 hr followed by chromatography on silica gel led to the desired bishomofarnesol **12** in essentially quantitative yield. Alcohol **12** exhibited appropriate spectral properties[9-11] and was identified, following acetylation, by tlc and glpc comparison with an authentic sample of acetate **13**.[12,13]

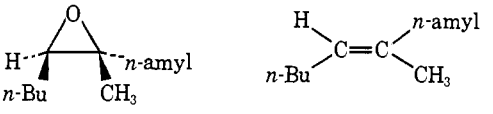


8 **9** **10**

11, R = CPh_3
12, R = H
13, R = Ac

This completes the formal synthesis of C_{18} juvenile hormone **1** since Corey has already converted alcohol **12** to the natural product.[9]

The stereochemical control and the flexibility inherent in this approach to the construction of trisubstituted olefins is further demonstrated by the following experiments. The vicinal diol **5** on successive treatment with *n*-butyllithium (2 equiv) and *p*-toluenesulfonyl chloride (1 equiv) at 25° for 2 hr was converted to epoxide **14** in 73% yield. The oxirane moiety in **14** was stereospecifically reduced to the corresponding olefin by the procedure of Cornforth[14,15] producing (*E*)-6-methyl-5-undecene (**15**) in 80% yield: nmr (CCl_4, TMS) δ 1.59 (s, 3 H, $=CCH_3$), 5.05 (bt, 1 H, J = 7 Hz, =CH).[16] Thus, taken together with the aforementioned results, these processes allow the synthesis of either olefinic isomer with high stereospecificity and in good yield.



14 **15**

Acknowledgment. This collaborative work grew out of an exchange of ideas between H. Y. and K. B. S. at the first U. S.–Japan Seminar on Natural Product Synthesis (NSF sponsored, Tokyo, 1972). One of us (K. B. S.) thanks the National Science Foundation (GP-30485X), Chevron Research Co., and Mobil Foundation for support of the research at M.I.T. J. D. C. is grateful to the National Science Foundation for a Graduate Fellowship (1973–1975).

(9) E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *J. Amer. Chem. Soc.*, **90**, 5618 (1968).
(10) J. A. Katzenellenbogen, Ph.D. Thesis, Harvard University, 1969.
(11) E. J. Corey and J. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 6636 (1970).
(12) We thank Dr. K. Kondo and associates for a generous comparison sample of the acetate **13**.
(13) Our product is contaminated with a maximum of 7% of unidentified impurities.
(14) J. W. Cornforth, R. H. Cornforth, and K. K. Mathes, *J. Chem. Soc.*, 112 (1959).
(15) The epoxide **14** was also converted to (*Z*)-olefin **6** by treatment with lithium diphenylphosphide followed by methyl iodide (30% yield): E. Vedejs and P. L. Fuchs, *J. Amer. Chem. Soc.*, **95**, 822 (1973).
(16) For stereochemical assignments of **6** and **13**, see G. D. Abrams, W. R. Bartlett, V. A. Fung, and W. S. Johnson, *Bioorg. Chem.*, **1**, 243 (1971).

Shin Tanaka, Hisashi Yamamoto, Hitosi Nozaki
Department of Chemistry, Kyoto University
Yoshida, Kyoto 606, Japan

K. B. Sharpless,* R. C. Michaelson, J. D. Cutting
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received March 25, 1974

Electrochemical Synthesis and Structure of a New Cyclic Barbiturate

Sir:

The synthesis of heterocyclic oligomers has been accomplished by a variety of conventional chemical methods as well as by photochemical and thermochemical techniques.[1] Of the various oxidative methods, however, the use of electrochemical techniques for the preparation of heterocyclic oligomers has been virtually ignored although Bobbit and coworkers[2-4]

(1) A. Albert and H. Yamamoto, *Advan. Heterocycl. Chem.*, **15**, 1 (1973).
(2) J. M. Bobbit, K. H. Weisgraber, A. S. Steinfeld, and S. G. Weiss, *J. Org. Chem.*, **35**, 2884 (1970).
(3) J. M. Bobbit, H. Yagi, S. Shibuyu, and J. T. Stock, *J. Org. Chem.*, **36**, 3006 (1971).
(4) J. M. Bobbit, J. F. Colarutolo, and S. J. Huang, *J. Electrochem. Soc.*, **120**, 773 (1973).