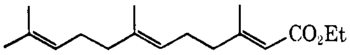
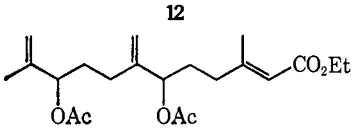
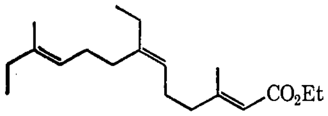
farnesoate (**12**) to the double allylic acetate **13**[7,13] in 23% yield. Methylation of **13** with ethereal[14] lithium dimethylcuprate (−10°, 0.5 hr) gave ethyl 3,11-dimethyl-7-ethyltrideca-2,6,10-trienoate in quantitative yield as a mixture of all-*trans* (14%), *trans,cis,cis* (8%), and *trans,cis,trans* **14** (76%). Thus *cis* olefins form stereoselectively from allylic acetates of type **1** when X is larger than the entering alkyl of reagent.



12



13



14

In general, lithium dialkylcuprate alkylation of **1**, Z = H, is highly stereoselective for the path A product which has alkyl groups X and Y in a *cis* relationship. Investigation of the scope[15] of this widely applicable olefin synthesis is continuing.

Acknowledgment. We thank L. Dunham and Virginia L. Spain for invaluable technical assistance.

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(13) No trace of the 7,8-double bond isomer is evident from nmr spectra of **13** or the corresponding diol.

(14) Methylation of **13** in tetrahydrofuran produces appreciable amounts of *trans,trans,cis*-**14**. The corresponding methyl ester has been converted to juvenile hormone by K. H. Dahm, B. M. Trost, and H. Röller, *J. Amer. Chem. Soc.*, **89**, 5292 (1967).

(15) The requirement for 2 equiv of alkyllithium when only 1 equiv is utilized could be obviated by use of mixed reagents,[3d] such as lithium butylvinylcuprate, which are being examined.

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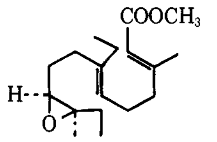
Received November 29, 1969

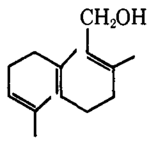
Synthesis of *Cecropia* Juvenile Hormone from *trans,trans*-Farnesol[1]

Sir:

As part of a continuing program concerned with the bioorganic chemistry of terpenoid terminal epoxides,[2] we have developed a convenient *Cecropia* juvenile hormone (I) total synthesis fundamentally different from those approaches previously described.[8–9] This route starts with the readily available *trans,trans*-farnesol (II), a possible biochemical precursor of the hormone, and features positionally selective oxidation, elimination, and methylation processes, all carried out in tandem in the 6,7 and 10,11 environments.



I



II

trans,trans-Farnesol acetate, on treatment (15 min, 0°) with $\sim$2 equiv of *m*-chloroperbenzoic acid in methylene dichloride, underwent exclusive oxidation at the nonallylic olefinic centers,[10] providing after saponification with aqueous–alcoholic potassium carbonate the 6,7:10,11-diepoxide III, which exhibited nmr peaks (CCl_4, 60 Mc) at δ 5.40, 4.03, 2.60, 1.67, and 1.23. Lithium diethylamide (5 equiv) in refluxing benzene during 1 hr induced in III a double, Hoffmann-like elimination[11] involving the epoxide moieties to give, of the possible trienetriols, only the desired bis(terminal methylene) case IVa, purified by silica gel chromatography. The nmr spectrum ($CDCl_3$, 60 Mc) possessed peaks at δ 5.44, 4.95, 4.13, 4.06, 1.70, and 1.66. In order to permit selectivity in the methylation phase, the trisallylic alcohol was transformed with trityl chloride–pyridine to the primary mono(trityl ether) IVb.

Conversion of IVb by means of tosyl chloride–lithium chloride (room temperature, 24 hr) to the unrearranged (nmr) bis(allyl chloride),[12] followed directly by the action of 5 equiv of lithium dimethylcopper at −5° for 1 hr,[13] led to formation of triene trityl ether Vb, isolated by column chromatography[14,15] (ether–hexane elution from silica gel). Nmr peaks (CCl_4,

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(1) First presented publicly in the Bachmann Memorial Lecture, Oct 31, 1969, at the University of Michigan, Ann Arbor.

(2) (a) E. E. van Tamelen and T. J. Curphey, *Tetrahedron Letters*, 121 (1962); (b) E. E. van Tamelen, *Accounts Chem. Res.*, **1**, 111 (1968), and references cited therein; (c) E. E. van Tamelen and J. P. McCormick, *J. Amer. Chem. Soc.*, **91**, 1847 (1969); (d) K. B. Sharpless and E. E. van Tamelen, *ibid.*, **91**, 1849 (1969).

(3) (a) H. Röller, K. H. Dahm, C. C. Sweeley, and B. M. Trost, *Angew. Chem. Int. Ed. Eng.*, **6**, 179 (1967); (b) K. H. Dahm, B. M. Trost, and H. Röller, *J. Amer. Chem. Soc.*, **89**, 5292 (1967); (c) K. H. Dahm, H. Röller, and B. M. Trost, *Life Sci.*, **7**, 129 (1968).

(4) E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *J. Amer. Chem. Soc.*, **90**, 5618 (1968).

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(7) K. Mori, B. Stalla-Bourdillion, M. Ohki, M. Matsui, and W. S. Bowers, *Tetrahedron*, **25**, 1667 (1969).

(8) H. Schulz and I. Sprung, *Angew. Chem. Int. Ed. Eng.*, **8**, 271 (1969).

(9) J. A. Findlay and W. D. MacKay, *J. Chem. Soc.*, *D*, 733 (1969).

(10) Selectivity of epoxidation is much less pronounced with farnesol itself.

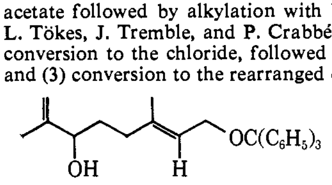
(11) Sharpless carried out (unpublished work, Stanford University) the base-induced 2-methylheptene-2 conversion to the 1-en-3-ol just prior to the appearance of the first in a series of notable publications on epoxide eliminations by Crandall and coworkers (J. K. Crandall and L. H. Chang, *J. Org. Chem.*, **32**, 435 (1967)).

(12) G. Stork, P. A. Grieco, and M. Gregson, *Tetrahedron Letters*, 1393 (1969).

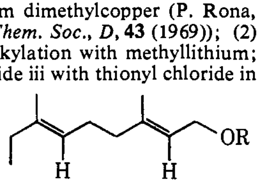
(13) E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967).

(14) Approximately 15% substitution without allylic isomerization was observed.

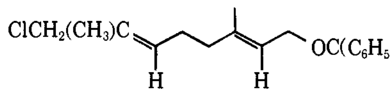
(15) Other methods of alkylation were investigated, all of which stereospecifically afforded only the *trans* isomer ii when applied to the model system i. These methods include: (1) conversion of i to the acetate followed by alkylation with lithium dimethylcopper (P. Rona, L. Tökes, J. Tremble, and P. Crabbé, *J. Chem. Soc.*, *D*, 43 (1969)); (2) conversion to the chloride, followed by alkylation with methyllithium; and (3) conversion to the rearranged chloride iii with thionyl chloride in ethyl ether, followed by alkylation with methyllithium. When either of the first two methods was tried on the diol IV, the seemingly exclusive product was the triene V with *trans,cis,trans* geometry. This novel stereospecific alkylation procedure deserves detailed study and should find utility in the controlled synthesis of trisubstituted olefins.



i



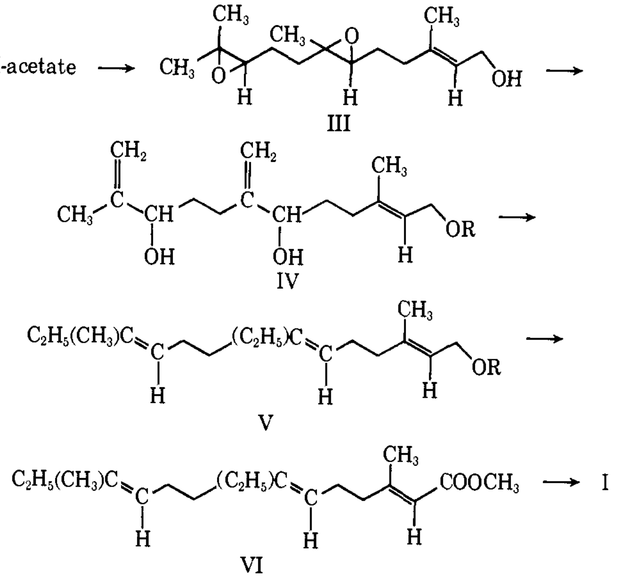
ii



iii

60 Mc) were observed at δ 7.20, 5.62–4.83, 3.35, 1.65, 1.58, 1.46, and 0.98. Geometrical isomers in hand at this point were not separated but carried through to the triene ester stage. To prepare for oxidation of the primary alcohol unit, the trityl group was removed from Vb by means of HCl–THF.

Manganese dioxide oxidation, first in hexane (of trienol Va to the corresponding trienal) and subsequently with cyanide[16] in methanol, generated the expected *trans* α,β-unsaturated ester system VI. Preparative glpc permitted separation of *t,c,c*:*t,c,t*:*t,t,c*:*t,t,t* geometrical isomers (1:2:1:1 ratio) and identification of the desired *trans,trans,cis* case was made by suitable glpc retention time and mass spectral comparison with authentic material. Formal completion of the synthesis depends on the well-established terpenoid terminal epoxidation process (N-bromosuccinimide–H_2O, followed by base),[2a] already utilized in the conversion of *trans,trans,cis*-triene ester VI to juvenile hormone I.[4]



a, R = H; b, R = $(C_6H_5)_3C$

In keeping with the general experience of others in the juvenile hormone area, we did not encounter crystalline materials in this synthesis. However, where possible and appropriate, assigned structures of intermediates were supported by ultimate analyses and by spectral means, including nmr, ir, and mass spectra. Yields of the various reactions were observed to be in general good, and in all cases (disregarding stereochemical aspects) above 50%.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant No. GP 7187X) for financial support. Also, the authors acknowledge the generous assistance of other workers in this field: Professors A. Meyer, Case Western Reserve University, and B. M. Trost, University of Wisconsin, who made helpful glpc comparisons with authentic samples; and Dr. J. Siddall, Zoecon Corporation, who provided both glpc information and authentic samples.

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(16) E. J. Corey, N. W. Gilman, and B. E. Ganem, *J. Amer. Chem. Soc.*, **90**, 5616 (1968).

(17) National Science Foundation Fellow, 1965–1969.

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Received November 29, 1969

The Molecular Structure of μ-Diazido-tetrakis(triphenylphosphine)dicopper(I)

Sir:

To date, X-ray structure determinations of transition metal complexes containing the azide ion[1,2] have shown the N_3^- groups to coordinate solely through one of the terminal nitrogen atoms[3] with the two N–N bond distances exhibiting a significant difference. For example, in the complex $[Co(NH_3)_5N_3]^{2+}$,[2] the two N–N distances are found to be 1.145 (7) and 1.208 (7) Å, the longer distance occurring between the middle nitrogen atom and the nitrogen atom attached to the metal ion. The ability of the azide group to bridge two transition metal ions through the terminal nitrogen atoms was first suggested by Snellgrove and King[4] for the electron transfer reaction between Cr^{2+} ion and *cis*-$Cr(H_2O)_4(N_3)_2^+$ and by Haim[5] for the corresponding reaction between Cr^{2+} ion and *cis*-$Co(NH_3)_4(N_3)_2^+$. These authors suggested that the activated complex possesses a symmetric doubly bridged structure. As part of our structural and photochemical[6] studies of azido complexes of group Ib metals we have determined the crystal and molecular structure of the complex μ-diazido-tetrakis(triphenylphosphine)dicopper(I), which represent the first example of a complex containing a diazo bridged structure.[7]

The complex was synthesized as described previously[7] and crystals suitable for a single-crystal X-ray study were grown from chloroform–hexane solution. On the basis of Weissenberg and precession photographs, the complex was found to crystallize in space group $P2_1/c$ of the monoclinic system with a unit cell of refined dimensions $a = 23.524$ (15), $b = 13.690$ (8), $c = 20.035$ (15) Å, $\beta = 106.3 \pm 0.1°$, and $V = 6193$ Å^3. An experimental density of 1.35 (1) g/cm^3 is in agreement with a calculated value of 1.36 g/cm^3 for four dimeric molecules of formula $Cu_2P_4N_6C_{72}H_{60}$ per unit cell.

A complete set of independent intensity data was collected by the θ–2θ scan technique using a Picker four-circle automatic diffractometer. Zr-filtered Mo Kα radiation and pulse height analysis were employed for the data collection. The intensities of 3200 reflections were measured, of which 2637 reflections were observed to be greater than σ. The intensity data were corrected for Lorentz and polarization effects, but not for absorption owing to the smallness of μ (8.74 cm^{-1}) and the uniformity of the crystal dimensions (0.41 × 0.38 × 0.31 mm). The structure was solved by standard Patterson and Fourier techniques and was refined by least-squares methods. In the refinement, the phenyl rings were treated as rigid groups described by three positional and three angular parameters. Each carbon atom was assigned its own isotropic thermal parameter, as were the nitrogen atoms of the azide groups. The Cu and P atoms were assumed to vibrate according to an anisotropic thermal model. This refinement of

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(1) Z. Dori, *Chem. Commun.*, 714 (1968).

(2) G. J. Palenik, *Acta Cryst.*, **17**, 360 (1964).

(3) The azide ion was also shown to bridge two metal ions through one of the terminal nitrogens: I. Agrell, *Acta Chem. Scand.*, **21**, 5 (1967).

(4) R. Snellgrove and E. L. King, *J. Amer. Chem. Soc.*, **84**, 4609 (1962).

(5) A. Haim, *ibid.*, **88**, 2324 (1966).

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