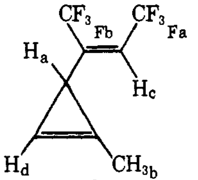
10 mg of π-allylpalladium chloride. The solution was stirred at 0° for 2 hr and the cream-colored precipitate which formed was collected by filtration. Nmr examination in benzene solution revealed two resonances at δ 1.71 and 3.08 in the ratio of 6:2 consistent with a ring-opened, polymeric structure.

Thermal Reaction of Methylcyclopropene with Acetylenes. Into a 5-ml serum-capped vial equipped with magnetic stirrer was placed 1 ml of $CFCl_3$. The solvent was degassed on the vacuum line, and *ca.* 1 g of hexafluorobutyne was distilled in followed by *ca.* 1 g of methylcyclopropene. The solution was warmed to −78° and then stirred for 3 hr at −30°. The nmr spectrum of the resulting solution was consistent with structure **8** for the adduct. The reaction occurs explosively if the neat compounds are allowed to warm toward room temperature: nmr ($CFCl_3$–TMS) δ 1.03 (broad singlet, H_a), 2.18 (doublet, J = 1.2 Hz, H_b), 5.54 (quartet, J = 9 Hz, H_c), 6.54 (broad singlet, H_d); ϕ^* = 57.4, quartet, J = 11 of doublets, J = 9 Hz, F_a; ϕ^* = 60.4, quartet, J = 11Hz, F_b. The reaction with dimethyl acetylenedicarboxylate proceeded analogously. The product is assigned the *cis* configuration by analogy with the hexafluorobutyne adduct: nmr ($CFCl_3$–TMS) δ 1.05 (broad, H_a), 2.18 (doublet, J = 1.5, H_b), 3.49, 3.55 (singlets, H_c), 5.7 (singlet, H_d), 6.51 (broad, H_e).



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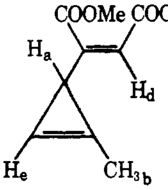


Acknowledgment. We wish to thank Drs. J. J. Mrowca and R. D. Cramer for valuable discussions.

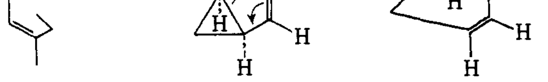
Communications to the Editor

New Stereospecific Synthetic Routes to Trisubstituted Olefins

Sir:

In connection with studies on the stereocontrolled synthesis of C_{17} and C_{18} Cecropia juvenile hormones,[1] a simple stereospecific synthesis of 5-methyl-*cis*-4-hepten-1-ol (**1**) was required.[2] This communication describes two methods for the assembly of olefinic alcohols such as **1** efficiently and with complete specificity.

The first approach is based on the thermal rearrangement defined by the class prototype, *cis*-2-methylvinylcyclopropane (**2**) → *cis*-1,4-hexadiene (**3**).[3–6] In this interesting transformation a stereorelationship about a three-membered ring is translated into a stereorelationship about a carbon–carbon double bond as shown, because the 1,5 hydrogen shift occurs with vinyl methylene oriented approximately s-cis to the cyclopropyl group. Figure 1 outlines the sequence of reactions utilized. *trans*-3-Methylpent-3-en-1-yne, prepared by dehydration of 3-methylpent-1-yn-3-ol using sulfuric acid–acetic anhydride, followed by distillation through a spinning-band column,[7,8] was hydroxymethylated by successive treatment in tetrahydrofuran with *n*-butyllithium (−78°, 30 min) and excess dry paraformaldehyde (−78° initially, then from −78 to 23° and at 23° for 2 hr)[9,10] to give the acetate **4**[11] after acetylation with acetic anhydride–pyridine. Selective hydrogenation of **4** using Lindlar catalyst[12] in benzene containing a small amount of quinoline, followed by saponification using 0.5 *N* methanolic sodium hydroxide, afforded the 2,3-*cis*-4,5-*trans*-dienol **5**[11] in high overall yield from the starting enyne. Addition to a solution of **5** in ether at reflux[10] of an excess of Simmons–Smith reagent[13,14] over a period of 1–2 hr resulted in selective formation of the cis-substituted cyclopropyl carbinol **6**[11] (90% yield). Addition of **6** to a vertical Pyrex column packed with Pyrex helices and maintained at 350° (with a slow current of nitrogen as carrier) yielded a condensate from which the pure aldehyde **7**[11] was readily obtained in 64% yield. No stereoisomeric products could be detected by vapor-phase chromatographic analysis. Reduction of the aldehyde **7** with ethanolic sodium borohydride at 0° produced the corresponding alcohol **1**[11] in 96% yield.



1 **2** **3**

A second synthesis of **1** (see Figure 2) proceeded from the tetrahydropyranyloxy aldehyde **8**,[11a] obtained in 98% yield from 1,4-butanediol monotetrahydropyranyl ether by oxidation with chromium trioxide–pyridine

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[1] See E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 6636 (1970).

[2] For a synthesis of the lower homolog, 4-methyl-*cis*-3-hexen-1-ol (from *p*-cresol) and its application to the synthesis of the C_{18} juvenile hormone, see E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *ibid.*, 90, 5618 (1968).

[3] W. R. Roth and J. König, *Justus Liebigs Ann. Chem.*, **688**, 28 (1965).

[4] R. J. Ellis and H. M. Frey, *Proc. Chem. Soc., London*, 221 (1964).

[5] G. Ohloff, *Tetrahedron Lett.*, 3795 (1965).

[6] M. J. Jorgenson and A. F. Thacher, *ibid.*, 4651 (1969).

[7] A. F. Thompson, Jr., N. A. Milas, and I. Rovno, *J. Amer. Chem. Soc.*, **63**, 752 (1941).

[8] M. Bertrand and H. Monti, *Tetrahedron Lett.*, 1069 (1968).

[9] A. Schaap, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays Bas*, **84**, 1200 (1965).

[10] Reaction conducted with exclusion of air.

[11] Satisfactory (a) spectroscopic and (b) analytical data were obtained for this intermediate, a colorless liquid.

[12] H. Lindlar and R. Dubuis, *Org. Syn.*, **46**, 89 (1966).

[13] H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

[14] Prepared by dropwise addition of methylene iodide to a stirred suspension of zinc–copper couple [E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964)] in ether at reflux.

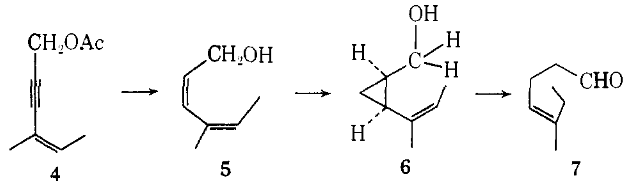

Figure 1.

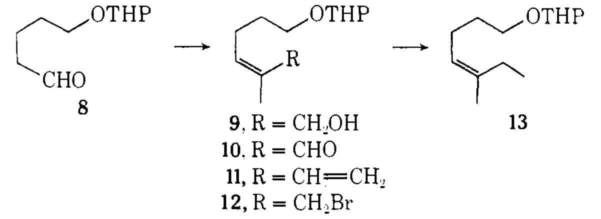

Figure 2.

complex.[15] Reaction of **8** with 1 equiv of ethylidinetriphenylphosphorane in tetrahydrofuran (from the phosphonium bromide and *n*-butyllithium at 0°) at $-78°$[10] produced the Wittig betaine which after *ca.* 5 min was treated dropwise over 20 min with 1 equiv of *n*-butyllithium. The resulting deep red solution of β-oxido phosphonium ylide[16] was allowed to warm to 0° and then treated with 2 equiv of dry paraformaldehyde. After 0.5 hr at 0° and 1 hr at 25°, the product was isolated by addition of water, extraction, and column chromatography on neutral alumina to give the pure alcohol **9**[11,16] in 60% yield. Oxidation of **9** with activated manganese dioxide in hexane afforded the aldehyde **10**[11] which was transformed into the conjugated diene **11**[11] (80% from **9**) by treatment[10] with methylenetriphenylphosphorane in tetrahydrofuran. Reduction of **11** with excess diimide (from 9 equiv of hydrazine and 7 equiv of 30% hydrogen peroxide in ethanol containing a trace of copper sulfate)[17] at 0° proceeded selectively to give after hydrolysis with 5 m*M* *p*-toluenesulfonic acid in methanol (30 min at 25°) 66% yield of the desired alcohol **1**, free of stereoisomeric impurities as determined by vapor-phase chromatographic analysis and identical in all respects with samples of **1** obtained by the process involving intermediates **4**–**7**.

The alcohol **9** could also be converted to **1** by an alternative route *via* the bromide **12**[11a] which was prepared in 98% yield by treating a solution of **9** and excess lithium bromide in dry ether at $-78°$ successively with *n*-butyllithium (1 equiv) and methanesulfonyl chloride (1.05 equiv), allowing the resulting suspension to warm to $-10°$ over 30 min, and then maintaining the reactants at $-10°$ for 30 min and 25° for 6 hr.[18] Reaction of **12** with trimethylironlithium[19] (6 equiv) in tetrahydrofuran–ether (4:1)[10] at $-78°$ for 20 hr followed by isolation of **13** and cleavage of the tetrahydropyranyl group in acidic methanol afforded after distillation the alcohol **1** in 77% yield and *ca.* 95% purity by vapor-phase chromatographic analysis.[20]

The unsaturated alcohol **1**, which is now easily available by the above-described synthetic routes, has been used successfully in the synthesis of the C_{17} and C_{18} Cecropia juvenile hormones, as is reported in the following communication.[1] These syntheses provide an independent confirmation, if needed, of the stereochemistry of **1**.[21]

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(15) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

(16) See E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 226, 3523 (1970).

(17) E. J. Corey, W. L. Mock, and D. J. Pasto, *Tetrahedron Lett.*, 347 (1961).

(18) (a) G. Stork, P. A. Grieco, and M. Gregson, *ibid.*, 1393 (1969); (b) E. J. Corey, H. A. Kirst, and J. A. Katzenellenbogen, *J. Amer. Chem. Soc.*, in press.

(19) E. J. Corey and G. H. Posner, *Tetrahedron Lett.*, 315 (1970).

(20) The iron reagent[19] is superior to dimethylcopperlithium [E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967)] in this case, since the latter reagent affords approximately a 1:1 mixture of **1** and the isomeric product resulting from allylic transposition in the cross-coupling reaction [see R. J. Anderson, C. A. Henrick, and J. B. Siddall, *ibid.*, **92**, 735 (1970)]. The utility of the iron reagent in such cases is also borne out in other experiments performed in these laboratories by H. Yamamoto.

(21) This work was assisted financially by a grant from the Hoffmann-La Roche Co. and a National Institutes of Health Fellowship to D. K. H.

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Simple, Stereospecific Syntheses of C_{17}- and C_{18}-Cecropia Juvenile Hormones (Racemic) from a Common Intermediate

Sir:

The extraordinary level of current chemical interest in insect juvenile hormones (JH) and the possibility of their application to the control of insect populations are reflected in the development of a wide range of synthetic approaches to the presently known JH of Cecropia. Perhaps of greatest interest are those routes which are stereospecific or highly stereoselective.[1–5] This communication records an unusually simple and efficient route which utilizes a *single* synthetic intermediate for the two known Cecropia juvenile hormones (C_{17} and C_{18} JH) and which is also *stereospecific.* This approach depends crucially on the recently developed method for stereospecific synthesis of trisubstituted olefins from β-oxido phosphonium ylides.[6,7]

Reaction of the phosphonium iodide **1**[8,9] (mp 178–179°) in dry tetrahydrofuran (THF) with 1 equiv of *n*-butyllithium at 0° for 30 min[10] afforded a solution of

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

(2) W. S. Johnson, T. Li, D. J. Faulkner, and S. F. Campbell, *ibid.*, **90**, 6225 (1968).

(3) R. Zurflüh, E. N. Wall, J. B. Siddall, and J. Edwards, *ibid.*, **90**, 6224 (1968).

(4) W. S. Johnson, T. J. Brocksom, P. Loew, D. H. Rich, L. Werthemann, R. A. Arnold, T. Li, and J. Faulkner, *ibid.*, **92**, 4463 (1970).

(5) For references to other syntheses, see E. E. van Tamelen and J. P. McCormick, *ibid.*, **92**, 737 (1970). For more general reviews, see (a) C. E. Berkoff, *Quart. Rev., Chem. Soc.*, **23**, 372 (1969); (b) B. M. Trost, *Accounts Chem. Res.*, **3**, 120 (1970).

(6) E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 226, 3523 (1970).

(7) E. J. Corey, J. I. Shulman, and H. Yamamoto, *Tetrahedron Lett.*, 447 (1970).

(8) Prepared from the corresponding unsaturated alcohol [E. J. Corey, H. Yamamoto, D. K. Herron, and K. Achiwa, *J. Amer. Chem. Soc.*, **92**, 6635 (1970)] in 75% yield by the sequence ROH → ROTs (tosyl chloride-pyridine at $-20°$ for 24 hr) → RI (sodium iodide in dry acetone at 25° for 18 hr) → $RP^+(C_6H_5)_3I^-$ (triphenylphosphine in benzene).

(9) Satisfactory (a) spectroscopic and (b) analytical data were obtained for this intermediate. Unless indicated otherwise, all intermediates were colorless oils.