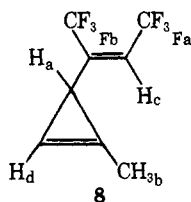


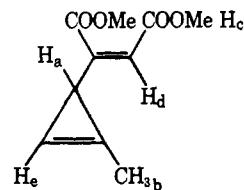
10 mg of  $\pi$ -allylpalladium chloride. The solution was stirred at 0° for 2 hr and the cream-colored precipitate which formed was collected by filtration. Nmr examination in benzene solution revealed two resonances at  $\delta$  1.71 and 3.08 in the ratio of 6:2 consistent with a ring-opened, polymeric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

**Thermal Reaction of Methylcyclopropene with Acetylenes.** Into a 5-ml serum-capped vial equipped with magnetic stirrer was placed 1 ml of  $\text{CFCl}_3$ . The solvent was degassed on the vacuum line, and ca. 1 g of hexafluorobutene was distilled in followed by ca.



1 g of methylcyclopropene. The solution was warmed to  $-78^\circ$  and then stirred for 3 hr at  $-30^\circ$ . 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 ( $\text{CFCl}_3$ -TMS)  $\delta$  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,  $H_d$ );  $\phi^* = 57.4$ , quartet,  $J = 11$  of doublets,  $J = 9$  Hz,  $F_a$ ;  $\phi^* = 60.4$ , quartet,  $J = 11$  Hz,  $F_b$ . The reaction with dimethyl acetylenedicarboxylate proceeded analogously. The product is assigned the *cis* configuration by analogy with the hexafluorobutene adduct: nmr ( $\text{CFCl}_3$ -TMS)  $\delta$  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,  $H_e$ ).

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

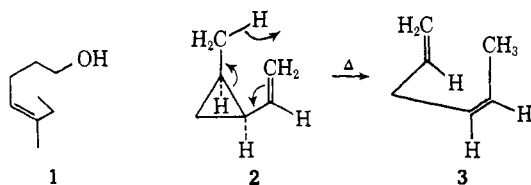
## Communications to the Editor

### 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,<sup>1</sup> a simple stereospecific synthesis of 5-methyl-*cis*-4-hepten-1-ol (**1**) was required.<sup>2</sup> 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**)  $\rightarrow$  *cis*-1,4-hexadiene (**3**).<sup>3-6</sup> In this in-



teresting 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,<sup>7,8</sup> was hydroxymethylated by successive treatment in tetrahydrofuran with *n*-butyllithium ( $-78^\circ$ , 30 min) and excess dry paraformaldehyde ( $-78^\circ$  initially, then from  $-78$  to  $23^\circ$  and at  $23^\circ$  for 2 hr)<sup>9,10</sup> to give the acetate **4**<sup>11</sup> after acetylation with acetic anhydride-pyridine. Selective hydrogenation of **4** using Lindlar catalyst<sup>12</sup> 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**<sup>11</sup> in high overall yield from the starting enyne. Addition to a solution of **5** in ether at reflux<sup>10</sup> of an excess of Simmons-Smith reagent<sup>13,14</sup> over a period of 1-2 hr resulted in selective formation of the *cis*-substituted cyclopropyl carbinol **6**<sup>11</sup> (90% yield). Addition of **6** to a vertical Pyrex column packed with Pyrex helices and maintained at  $350^\circ$  (with a slow current of nitrogen as carrier) yielded a condensate from which the pure aldehyde **7**<sup>11</sup> 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  $0^\circ$  produced the corresponding alcohol **1**<sup>11</sup> in 96% yield.

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

(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.

(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).

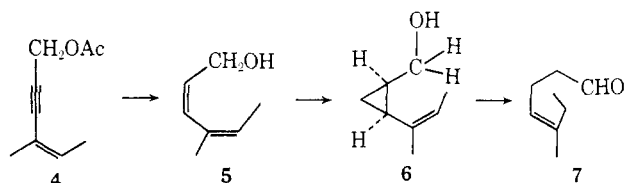


Figure 1.

complex.<sup>15</sup> Reaction of **8** with 1 equiv of ethylidene-triphenylphosphorane in tetrahydrofuran (from the phosphonium bromide and *n*-butyllithium at 0°) at -78°<sup>10</sup> 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  $\beta$ -oxido phosphonium ylide<sup>16</sup> 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**<sup>11,16</sup> in 60% yield. Oxidation of **9** with activated manganese dioxide in hexane afforded the aldehyde **10**<sup>11</sup> which was transformed into the conjugated diene **11**<sup>11</sup> (80% from **9**) by treatment<sup>10</sup> 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)<sup>17</sup> at 0° proceeded selectively to give after hydrolysis with 5 mM *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**<sup>11a</sup> 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.<sup>18</sup> Reaction of **12** with trimethylironlithium<sup>19</sup> (6 equiv) in tetrahydrofuran-ether (4:1)<sup>10</sup> 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.<sup>20</sup>

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<sub>17</sub> and C<sub>18</sub>

(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<sup>19</sup> 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.

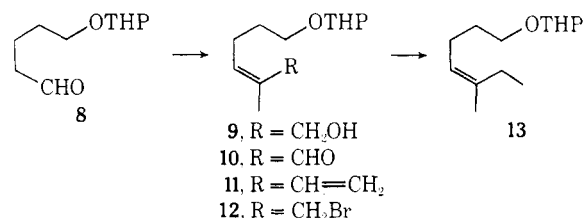


Figure 2.

Cecropia juvenile hormones, as is reported in the following communication.<sup>1</sup> These syntheses provide an independent confirmation, if needed, of the stereochemistry of **1**.<sup>21</sup>

(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.

\* Address correspondence to this author.

E. J. Corey,\* Hisashi Yamamoto, David K. Herron, Kazuo Achiwa  
Department of Chemistry, Harvard University  
Cambridge, Massachusetts 02138

Received August 5, 1970

### Simple, Stereospecific Syntheses of C<sub>17</sub>- and C<sub>18</sub>-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.<sup>1–5</sup> This communication records an unusually simple and efficient route which utilizes a *single* synthetic intermediate for the two known *Cecropia* juvenile hormones (C<sub>17</sub> and C<sub>18</sub> JH) and which is also *stereospecific*. This approach depends crucially on the recently developed method for stereospecific synthesis of trisubstituted olefins from  $\beta$ -oxido phosphonium ylides.<sup>6,7</sup>

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

(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. Wertheimann, 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  $\rightarrow$  ROTs (tosyl chloride-pyridine at -20° for 24 hr)  $\rightarrow$  RI (sodium iodide in dry acetone at 25° for 18 hr)  $\rightarrow$  RP<sup>+</sup>(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>I<sup>-</sup> (triphenylphosphine in benzene).

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