photochemically. The dianion $I^{2-}$ is not accessible electrochemically so we have no way of estimating the disproportionation equilibrium constant in order to calculate the $I^{2-}$ concentration, nor do we have any information on the frequency of the $\pi^* \rightarrow \sigma^*$ transition involved so this mechanism cannot be ruled out. The difficulty in producing dianions of the biphenyl-like systems, however, makes it unlikely that appreciable concentrations of $I^{2-}$ are present.

## Experimental Section

**Materials.** Dibenzonorcaradiene was prepared as previously indicated. DMF was dried by distillation from calcium hydride. Tetrahydrofuran and 1,2-dimethoxyethane were purified by first refluxing and then distilling from calcium hydride. These solvents were then stored over Na–K alloy before use.

**Equipment.** Esr spectra were recorded on a Varian E-3 spectrometer equipped for variable-temperature experiments.

Cyclic voltammograms were run on a Princeton Applied Research Model 170 instrument. The cell was purged of air with argon.

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**Registry No.**—I, 949-41-7; I·⁻, 34468-58-1; III·⁻, 53166-03-3.

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# A New Synthesis of Cyclohexadienes

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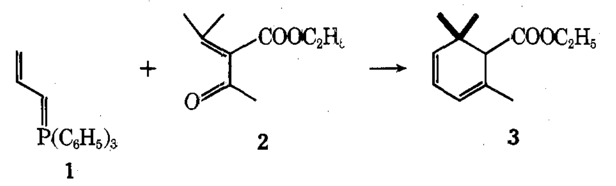
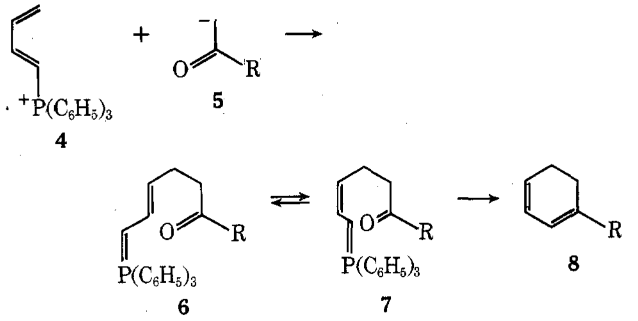
The two bicyclic cyclohexadienes 13 and 17–18 were synthesized by condensation of the two ketones 12 and 16 with 1-butadienyltriphenylphosphonium bromide prepared *in situ* from 2-butenylenetriphenylphosphonium bromide (9) or 4-bromo-2-butenyltriphenylphosphonium bromide (10) and potassium *tert*-butoxide in ether. Efforts to combine ketone 16 with the butadienylphosphonate 25 failed. Phosphonate 25 was prepared by a new method. Alkylation of diethyl ethylphosphonate (23) with propargyl bromide afforded the acetylene 24 which was isomerized to the more stable diene 25 with potassium *tert*-butoxide.

In conjunction with work on the synthesis of damascenones it was found that allyltriphenylphosphorane (1) combines with the highly electron deficient $\alpha,\beta$-unsaturated ketone 2 to produce the cyclohexadiene 3.[1] Subsequent work demonstrated the method to be useful with simple $\alpha,\beta$-unsaturated ketones[2,3] lacking an electron-withdrawing substituent and with more highly substituted phosphoranes.[4] It served also in strikingly simple preparations of cyclohexadienes containing bridgehead double bonds.[5] In this synthesis the cyclohexadiene is constructed from two structural units each containing three carbon atoms.

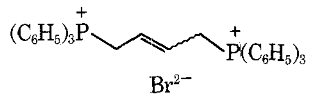


Cyclohexadienes in principle should also be available from starting materials supplying two and four carbon atoms, respectively. More specifically, an enolate 5 should add to the terminal double bond of a butadienylphosphonium salt 4 to produce stereoisomeric ylides 6 and 7. If these are in equilibrium the Z isomer 7 should undergo an intramolecular olefin synthesis to afford cyclohexadiene 8. A search of the literature produced little on the chemistry of butadienylphosphonium salts but nucleophilic additions to vinylphosphonium salts, their lower vinylogs, have been explored thoroughly.[6,7]

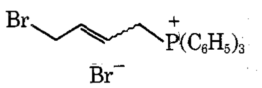


Slurries of the diphosphonium salt 9[8] or the bromophosphonium salt 10,[9] both of undefined stereochemistry, in ether on treatment with potassium *tert*-butoxide yielded brown solutions presumably containing 1-butadienyltriphenylphosphonium bromide. Addition of dihydrocarvone (12) or hydroxytetrahydrocarvone (16) in *tert*-butyl alcohol solutions produced the anticipated cyclohexadienes 13 and 17–18. The former appeared to be a single diastereomer and in analogy to the products formed in Robinson-annelations[10] structure 13 was assigned. Addition of the most stable enolate 11 to the phosphonium salt 4 should give a ketone in the chair conformation containing the new substituent in axial orientation. Annelation to hydroxytetrahydrocarvone (16) led to a 4:1 mixture of products assumed to be epimers 17 and 18, respectively. Hydrolysis of the reaction mixtures shortly after the addition of the ketones 12 and 16 led to substitution products 14 and 19 with

($E$)-crotyl side chains undoubtedly derived from the ($E$)-phosphoranes **6** by hydrolysis to olefins and triphenylphosphine oxide. The three cyclohexadienes **13**, **17**, and **18** proved to be air sensitive but the products **15** and **20** resulting from selective catalytic hydrogenation of the cis-disubstituted double bonds were stable.



**9**



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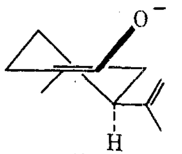

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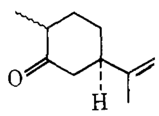

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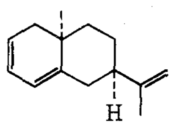
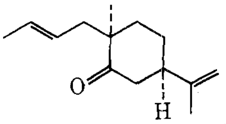


**13**



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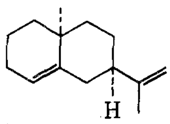

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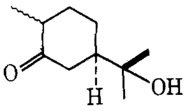
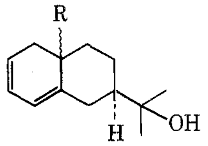
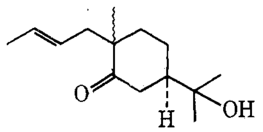


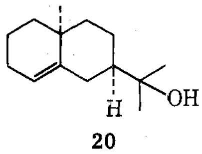
**16**



**17**, R = α-$CH_3$
**18**, R = β-$CH_3$

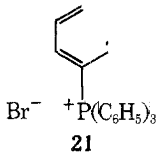


**19**

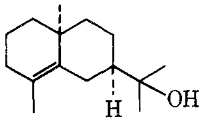


**20**

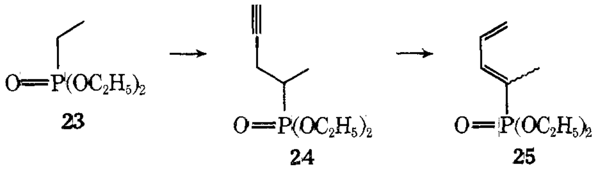
In an attempted synthesis of 10-*epi*-γ-eudesmol (**22**)[11,12] we tried to replace the unknown and seemingly inaccessible phosphonium salt **21** with the corresponding phosphonate **25**. However, efforts to condense **25** with the hydroxy ketone **16** failed, displaying again the inability of nonstabilized phosphonate anions to undergo the Horner–Emmons olefin synthesis.



**21**



**22**



**23** **24** **25**

Since 1,3-butadiene-1-phosphonates are difficult to synthesize,[13] but have found uses,[14] we describe a new and facile method for their preparation. Alkylation of the lithium salt prepared *in situ* from diethyl ethylphosphonate **23** and *n*-butyllithium in tetrahydrofuran with propargyl bromide afforded the alkynyl phosphonate **24**. Isomerization to diethyl 1,3-pentadiene-4-phosphonate (**25**) was accomplished in 82% yield with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol.

## Experimental Section

Microanalyses were performed in the laboratory of Dr. F. Gautschi, Firmenich et Cie., Geneva. Boiling points and melting points are uncorrected. Gas–liquid chromatography was performed on a F&M 720 instrument, using silicone rubber gum SE-30 and Carbowax 20M columns. Silicic acid "Mallinckrodt" 100 mesh and silica gel "Merck" 0.05–0.2 mm was used for column chromatography. The following spectrometers were used: nmr, Varian T-60; ir, Perkin-Elmer Model 247; uv, Cary Model 14′; mass spectra, Hitachi RMU 6D. All experiments were carried out under nitrogen.

**Annelation of Dihydrocarvone (12).** To a slurry of 7.4 g (10 mmol) of phosphonium salt **9**[8] in 100 ml of dry ether was added, at −20°, 4.5 g (40 mmol) of potassium *tert*-butoxide. The resulting brown mixture was stirred for 10 min, followed by dropwise addition of a solution of 1.5 g (10 mmol) of dihydrocarvone (**12**) in 6 ml of dry *tert*-butyl alcohol and 60 ml of dry ether. The mixture was kept for 1 hr at −20° and was then allowed to warm up to room temperature. After stirring for 3 hr at room temperature, the mixture was heated under reflux for 4 hr. The reaction mixture was poured into cold water, extracted with hexane, washed with water, dried ($Na_2SO_4$), and evaporated. The remaining oil (6.2 g) was chromatographed on 70 g of silicic acid. Elution with hexane gave 1.3 g of triphenylphosphine; with hexane + 20% benzene, 1.6 g (85%) of olefin **13** was eluted: bp 84° (0.1 mm); ir ($CHCl_3$) 1640, 1580, 890 $cm^{-1}$; uv (EtOH) 269 nm (ε 4760); nmr ($CCl_4$) δ 1.0 (3 H, s), 1.7 (3 H, s), 2.4 (2 H, s broad), 4.6–5.0 (2 H, m), 5.4–6.0 (3 H, m); mass spectrum (70 eV) *m/e* (rel intensity) 188 (61), 145 (68), 91 (100).

*Anal.* Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 88.95; H, 10.95.

In a similar experiment the reaction mixture was worked up shortly after the addition of dihydrocarvone (**12**). Purification by column chromatography (silicic acid, benzene + 10% AcOEt) gave pure ketone **14**: ir ($CHCl_3$) 1700, 1640, 960, 890 $cm^{-1}$; nmr ($CCl_4$) δ 1.0 (3 H, s), 2.0 (6 H, m), 2.3 (2 H, m), 4.7 (2 H, s broad), 5.2–5.5 (2 H, m); mass spectrum (70 eV) *m/e* (rel intensity) 206 (26), 123 (26), 109 (100).

*Anal.* Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.36; H, 10.67.

**Hydrogenation of Triene 13.** A mixture of 0.4 g (2.2 mmol) of triene **13** in 60 ml of ethyl acetate was hydrogenated over 100 mg of Lindlar catalyst. After absorption of 1 equiv of hydrogen the reaction was interrupted and the mixture was filtered and evaporated. The remaining oil was distilled to give 0.4 g of diene **15**: bp 76° (0.1 mm); ir ($CHCl_3$) 1640, 1380, 890 $cm^{-1}$; nmr ($CCl_4$) δ 1.1 (3 H, s), 1.7 (3 H, s with fine splitting), 4.7 (2 H, s broad), 5.2–5.5 (1 H, m); mass spectrum (70 eV) *m/e* (rel intensity) 190 (57), 175 (45), 147 (100).

*Anal.* Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.12; H, 11.10.

**Annelation of Hydroxytetrahydrocarvone (16).** To a suspension of 7.4 g (10 mmol) of phosphonium salt **9** in 100 ml of dry ether was added, at −20°, 4.5 g (40 mmol) of potassium *tert*-butoxide. To the resulting brown mixture was added dropwise a solution of 1.7 g (10 mmol) of hydroxy ketone **16** in 6 ml of dry *tert*-butyl alcohol and 60 ml of dry ether. The mixture was kept for 1 hr at −20° and was then stirred for 10 hr at room temperature, poured into cold water, extracted with hexane, washed with water, dried ($Na_2SO_4$), and evaporated. The residue (4.6 g) was chromatographed on 50 g of silica gel. Elution with benzene gave 2.0 g of triphenylphosphine. Benzene + 10% AcOEt eluted 1.45 g (73%) of an epimeric mixture **17** and **18** in a ratio of 4:1. Pure samples were obtained by preparative glc.

**Epimer 17:** ir ($CHCl_3$) 3610, 1590, 1390, 1370 $cm^{-1}$; nmr ($CCl_4$) δ 0.9 (3 H, s), 1.1 (3 H, s), 1.2 (3 H, s), 2.2 (1 H, s, disappears on exchange with $D_2O$), 5.4–6.0 (3 H, m); uv (EtOH) 269 nm (ε 5360); mass spectrum (70 eV) *m/e* (rel intensity) 206 (15), 188 (100), 173 (45), 145 (82), 117 (94).

*Anal.* Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.72; H, 10.97.

**Epimer 18:** mass spectrum (70 eV) *m/e* (rel intensity) 206 (23), 188 (100), 173 (58), 145 (84), 117 (77).

In a similar experiment the reaction mixture was worked up shortly after the addition of hydroxytetrahydrocarvone (**16**). Purification by column chromatography (silica gel, benzene + 20% AcOEt) gave pure hydroxy ketone **19**: ir ($CHCl_3$) 3640, 1700, 970 $cm^{-1}$; nmr ($CCl_4$) δ 0.9 (3 H, s), 1.2 (6 H, s), 1.7 (3 H, d, $J$ = 6 Hz), 2.0 (1 H, s, disappears on exchange with $D_2O$), 5.3–5.5 (2 H, m); mass spectrum (70 eV) *m/e* (rel intensity) 224 (6), 206 (30), 49 (100).

*Anal.* Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.33; H, 10.67.

**Hydrogenation of Diene 17.** A mixture of 2.1 g (10 mmol) of diene **17**, 120 ml of ethyl acetate, and 0.5 g of Lindlar catalyst was hydrogenated. Hydrogen uptake ceased after 1 equiv had been absorbed. The mixture was filtered and evaporated and the remaining oil was distilled to afford 2.0 g of alcohol **20**: bp 92° (0.1 mm); ir ($CHCl_3$) 3550, 1650, 940 $cm^{-1}$; nmr ($CCl_4$) $\delta$ 1.1 (6 H, s), 1.2 (3 H, s), 1.4 (1 H, s, disappears on exchange with $D_2O$), 2.1–2.4 (2 H, m), 5.2–5.5 (1 H, m); mass spectrum (70 eV) *m/e* (rel intensity) 208 (4), 190 (69), 175 (60), 147 (100).

*Anal.* Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.55; H, 11.43.

**Preparation of Triene 13 Using Bromophosphonium Salt 10.**[9] To a solution of 1.5 g (10 mmol) of dihydrocarvone (**12**), 6.7 g (60 mmol) of potassium *tert*-butoxide, and 80 ml of *tert*-butyl alcohol was added, at 5–15°, a slurry of 4.8 g (10 mmol) of bromophosphonium salt **10**[9] and 60 ml of *tert*-butyl alcohol. After the addition was complete, the mixture was stirred for 10 hr at room temperature. The dark brown mixture was heated under reflux for 5 hr, poured into cold water, extracted with hexane, washed with water, dried ($Na_2SO_4$), and evaporated. The remaining oil was distilled to afford 1.2 g (64%) of triene **13**. According to glc this product was contaminated with 15% of ketone **14** and 10% of dihydrocarvone **12**.

**Preparation of Alcohol 17–18 Using Bromophosphonium Salt 10.** A solution of 1.7 g (10 mmol) of hydroxy ketone **16**, 4.5 g (40 mmol) of potassium *tert*-butoxide, and 50 ml of dry *tert*-butyl alcohol was placed into a flask. A suspension of 4.8 g (10 mmol) of bromophosphonium salt **10** in 60 ml of dry *tert*-butyl alcohol was added dropwise at 5–15°. The mixture was stirred for 10 hr at room temperature and then heated under reflux for 3 hr. The reaction mixture was poured into cold water, extracted with hexane, washed with water, dried ($Na_2SO_4$), and evaporated. The remaining oil was distilled to afford 1.8 g (86%) of alcohol **17**, bp 90–95° (0.1 mm). According to glc this product was contaminated with 10% of **16** and 5% of ketone **19**.

**Diethyl 1-Pentynyl-4-phosphonate (24).** To a stirred solution of 34.0 g (0.20 mol) of diethyl ethylphosphonate (**23**) in 400 ml of dry tetrahydrofuran at −40°, 140 ml (0.2 mol) of butyllithium in hexane (15%) was added. Stirring was continued for 15 min at the same temperature, then a solution of 24.0 g (0.20 mol) of freshly distilled propargyl bromide in 200 ml of tetrahydrofuran was added dropwise. After 1 hr at room temperature, the mixture was poured into 1 l. of water, extracted with hexane, washed with water, dried ($Na_2SO_4$), and evaporated. Distillation of the residue afforded 24.3 g (58%) of alkynyl phosphonate **24**: bp 87° (0.5 mm); ir ($CHCl_3$) 3350, 1260, 1030 $cm^{-1}$; nmr ($CCl_4$) $\delta$ 1.3 (6 H, t, $J$ = 7 Hz), 1.2 (3 H, d of d, $J_1$ = 7 Hz, $J_2$ = 18 Hz), 2.1 (1 H, t, $J$ = 2.5 Hz), 4.0 (4 H, d of q, $J_1$ = 7 Hz, $J_2$ = 7 Hz).

*Anal.* Calcd for $C_9H_{17}O_3P$: C, 52.96; H, 8.39. Found: C, 52.19; H, 8.34.

**Diethyl 1,3-Pentadiene-4-phosphonate (25).** A solution of 5.6 g (0.05 mol) of potassium *tert*-butoxide and 10.2 g (0.05 mol) of alkynyl phosphonate **24** in 100 ml of dry *tert*-butyl alcohol was heated at reflux for 2 hr. After removal of most of the solvent *in vacuo* water was added and the mixture extracted with hexane. The organic layer was washed with water, dried ($Na_2SO_4$), and evaporated. Distillation gave 8.5 g (82%) of **25**: bp 85° (0.5 mm); ir ($CHCl_3$) 1630, 1585, 1250, 965 $cm^{-1}$; nmr ($CCl_4$) $\delta$ 1.3 (6 H, t, $J$ = 7 Hz), 1.9 (3 H, d, $J$ = 15 Hz), 4.1 (4 H, d of q, $J_1$ = 7 Hz, $J_2$ = 7 Hz), 5.3–5.7 (2 H, m), 6.4–7.2 (2 H, m); uv (EtOH) 237 nm ($\epsilon$ 25,870); mass spectrum (70 eV) *m/e* (rel intensity) 204 (42), 148 (100), 147 (85), 66 (54).

*Anal.* Calcd for $C_9H_{17}O_3P$: C, 52.96; H, 8.39. Found: C, 52.31; H, 8.54.

**Acknowledgment.** We are indebted to Firmenich SA, Geneva, for generous financial support.

**Registry No.**—**9**, 18189-24-7; **10**, 53142-03-3; **12**, 7764-50-3; **13**, 53142-04-4; **14**, 53142-05-5; **15**, 53142-06-6; **16**, 7712-37-0; **17**, 53142-07-7; **18**, 53142-08-8; **19**, 53142-09-9; **20**, 53177-30-3; **23**, 78-38-6; **24**, 53142-10-2; **25**, 53142-11-3.

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