CH_2), 6.98–7.31 (m, 2.0, aliphatic CH_2), 8.02–8.63 (m, 6.0, aliphatic CH_2).

Anal. Calcd for $C_{15}H_{15}Cl$: C, 78.09; H, 6.55. Found: C, 78.33; H, 6.66.

Later fractions of the chromatograph, eluted with 75% petroleum ether (bp 60–70°) in benzene, gave 1.55 g (8.4% yield) of **19**, mp 46.5–48.5°. Pure **19** (mp 52–53° from ethanol) was obtained as white crystals: uv max (95% ethanol) 228 mμ (log ε 5.00), 252 (sh) (3.41), 262 (3.58), 270.5 (3.70), 281 (3.71), 290.5 (3.51), 302 (sh) (2.63), 317 (sh) (2.50), 323 (sh) (2.56); nmr (CCl_4) τ 2.12–2.80 (m, 6.0, aromatic H), 6.40–6.70 (t, 2.0, benzylic CH_2), 7.12–7.32 (t, 2.0, CH_2 Cl), 8.00–8.57 (m, 6.0, aliphatic CH_2).

Anal. Calcd for $C_{15}H_{16}Cl_2$: C, 67.42; H, 6.04. Found: C, 67.12; H, 5.91.

Tetramethyl 3-Chloro-1,2,4,5-benzene Tetracarboxylate. 1. From Chlorodurene.—Chlorodurene (0.20 g, 0.119 mol) was oxidzed as previously described for **3d**[3,11] The crude acid (white powder, mp 155–175°) was digested in benzene to give 0.50 g (72.8% yield) of acid melting at 248° dec. This acid (0.20 g) was esterified with excess diazomethane in ether to give, subsequent to recrystallization of the product from petroleum ether (bp 60–70°), 0.22 g (91.2% yield from the acid), mp 118–122°. The pure ester was obtained by preparative tlc (silica gel PF_{254}; eluent, 70% ether in petroleum ether) and recrystallization from petroleum ether (bp 60–70°): mp 122.6–123.1°; ir (Nujol-halocarbon oil) 1730, 1740, 1760 cm^{-1} (C=O); uv max (95% ethanol) 213 mμ (log ε 4.59), 243 (sh) (3.91), 291 (3.43), 300 (3.47); nmr ($CDCl_3$) τ 1.53 (s, 1, aromatic H), 6.05 (s, 6, OCH_3), 6.10 (s, 6, OCH_3).

Anal. Calcd for $C_{14}H_{13}ClO_8$: C, 48.78; H, 3.80; Cl, 10.29. Found: C, 48.74; H, 3.60; Cl, 10.39.

2. **From 18.**—The oxidation of **18** (0.25 g, 1.08 mmol) and esterification of the derived acid(s) were carried out essentially as described in 1 above. The crude ester (80 mg) was chromatographed on silica gel (30 g; eluent, petroleum ether, bp 60–70°), and the product was recrystallized from petroleum ether (bp 60–70°). The product (mp 122.6–123.4°) was identical (mixture melting point) with that described in 1 above.

Independent Synthesis of 2-(5-Chloropentyl)-3-chloronaphthalene (19). 1. 2-(5-Chloropentyl)indene (23).—The crude product, obtained by allowing 2-indanone (11.6 g, 0.80 mol) to react with the Grignard reagent [prepared from pentamethylenechloroiodide (25.0 g, 0.108 mol) and magnesium (2.7 g, 0.108 g-atom)] was chromatographed on alumina (100 g; eluent, petroleum ether, bp 60–70°), and the oil was distilled to give 1.2 g (4.6% yield) of **23** (67% pure by glpc). Pure **23** was obtained by preparative glpc (20% SE-30 on Chromosorb W, 80–100 mesh; 225°; helium flow, 60 ml/min): nmr (CCl_4) τ 2.63 (m, 5, aromatic H), 3.32 (broad s, 1, olefinic H), 6.42 (broad t, 2, CH_2Cl), 6.70 (broad s, 2, benzylic CH_2), 7.51 (broad t, 2, allylic CH_2), 8.41 (m, 6, aliphatic CH_2).

Anal. Calcd for $C_{14}H_{17}Cl$: C, 76.16; H, 7.78. Found: C, 76.32; H, 7.79.

2. **2-(5-Chloropentyl)-3-chloronaphthalene (19).**—The crude product obtained from **23** (0.34 mg, 0.155 mmol) and phenyl(trichloromethyl)mercury (2 equiv; see preparation of **3a**) was chromatographed on alumina (10 g; eluent, 20% benzene in petroleum ether, bp 60–70°). The product was recrystallized from petroleum ether (bp 60–70°) to give pure **19** (20 mg, 49%, mp 51–52.5°) which was identical (mixture melting point) with that obtained from **1a**.

Registry No.—*o*-(1-Cyclooctenyl)-benzonitrile, 23069-13-8; *o*-(1-cyclooctenyl)-benzylamine hydrochloride, 23115-92-6; **1b**, 23069-14-9; **3b**, 23069-15-0; **4b**, 23069-16-1; **5**, 23069-17-2; **6**, 23069-18-3; **8**, 23069-19-4; **9**, 23069-20-7; **12**, 23069-21-8; **14**, 23069-22-9; **15**, 23069-23-0; **16**, 23069-24-1; **18**, 23069-25-2; **19**, 23069-26-3; **23**, 23069-27-4; tetramethyl-3-chloro-1,2,4,5-benzene tetracarboxylate, 23069-28-5.

A Study on the Condensation of Mesityl Oxide with Acetoacetic Ester

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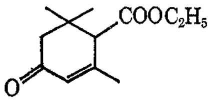
Received July 7, 1969

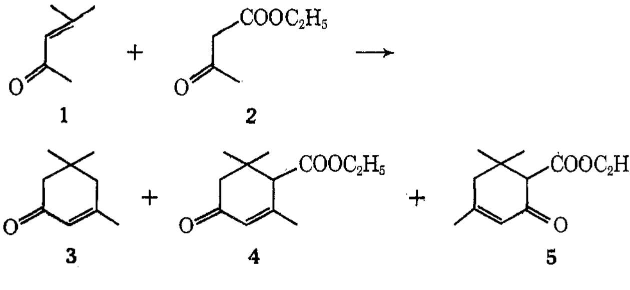
The zinc chloride catalyzed condensation of mesityl oxide with ethyl acetoacetate resulted in the formation of two structural isomers: 3,5,5-trimethyl-2-cyclohexen-1-one-4-carboxylic acid ethyl ester (**4**) and 3,5,5-trimethyl-2-cyclohexen-1-one-6-carboxylic acid ethyl ester (**5**). Isomer **5** was readily converted into isophorone by selective hydrolysis. The syntheses of two substituted β-ionones, 3-ethylenedioxy-β-ionone (**17**) and 3-ethoxy-3,4-dehydro-β-ionone (**20**), and a number of novel by-products are reported.

Merling and Welde[1] and Knoevenagel[2] reported the preparation of the cyclohexenone **4** from the condensation of acetoacetic ester with 2-isopropylidene acetoacetate. Rubinstein[3] obtained **4** in *ca.* 40% yield by condensing mesityl oxide and acetoacetic ester in the presence of boron trifluoride etherate. Since substituted intermediates which would find application for the preparation of the higher polyenes are not readily available, additional study of this interesting condensation was desirable.



4

The zinc chloride catalyzed condensation of mesityl oxide (**1**) with ethyl acetoacetate (**2**) afforded 19% isophorone (**3**) and 40% a fraction distilling at 75–78° (0.2 mm). This was found to consist of two isomers, **4** and **5**, in a ratio of 4:1.



The isomeric ratio was measured by vpc, while analytical samples of **4** and **5** were prepared by column chromatography. The relative ease with which isophorone was formed by hydrolysis and decarboxylation of **5** made it convenient to prepare **4** by selectively hydrolyzing the mixture before fractionation.

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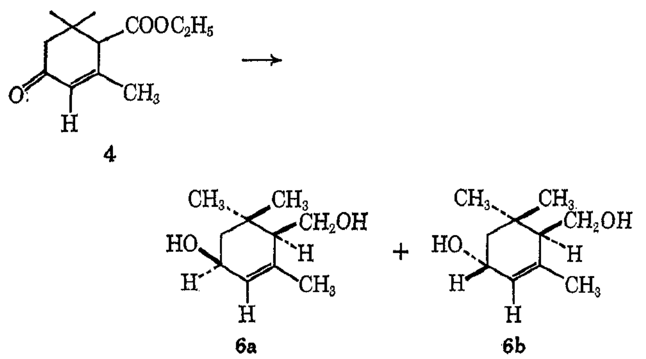
[1] G. Merling and R. Welde, *Ann.*, **366**, 141 (1909).

[2] E. Knoevenagel, *ibid.*, **297**, 185 (1897).

[3] H. Rubinstein, *J. Org. Chem.*, **27**, 3886 (1962).

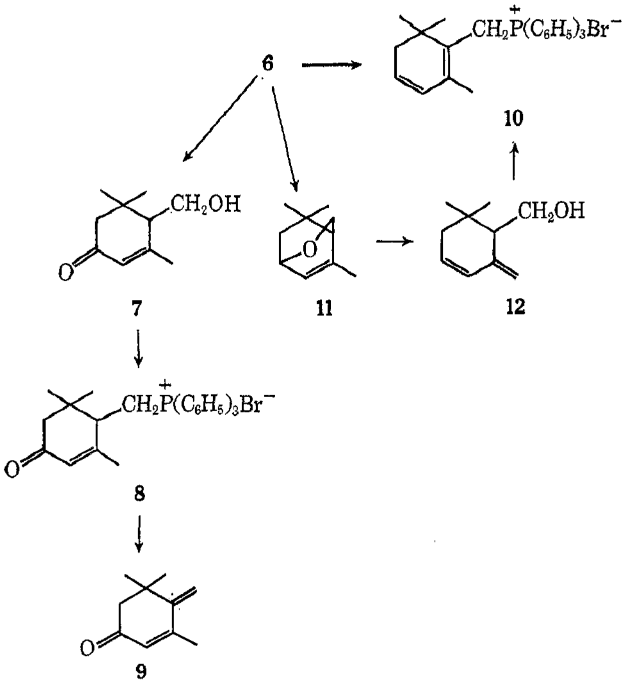
Reduction of **4** with lithium aluminum hydride afforded two isomeric cyclohexenediols, **6a** and **6b**.



According to the nmr spectra, both of the cyclohexenediols contain the $-CH{=}\overset{|}{C}CH_3$, $>CHCH_2O-$, and $>CHO-$ groups establishing them as structural isomers. The C_4 methine protons were narrow ($w_{1/2}$ = 10 Hz) for **6a** and broad ($w_{1/2}$ = 22 Hz) for **6b** and were, therefore, assigned the pseudoequatorial (e′) and pseudoaxial (a′) configuration, while the C_4 hydroxyls are a′ and e′, respectively.

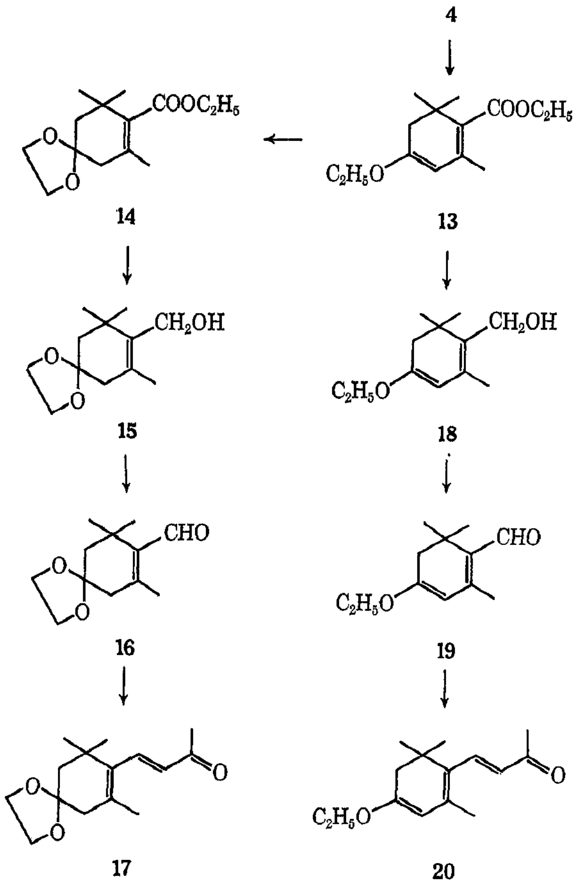
Results of our investigation to prepare substituted intermediates which would be suitable for polyene synthesis are shown in Charts I and II. An Oppenauer oxidation of **6a** led to the keto alcohol (**7**), which, on condensation with triphenylphosphonium bromide in methylene chloride, afforded the phosphonium salt **8**. The product **8** failed to form a phosphorane on treatment with sodium methoxide, but cleaved instead to yield triphenylphosphine and the dienone **9**.

Chart I



Condensation of **6a** with triphenylphosphonium bromide[4] in methylene chloride resulted in a dehydration affording the phosphonium salt **10**. When **6a** was stirred in methylene chloride containing a trace of hydrogen chloride, the bicyclic ether **11** was formed which rearranged to the dienol **12**. Condensation of compound **12** with triphenylphosphonium bromide resulted in a rearranged phosphonium salt (**10**). Treatment of **10** with sodium methoxide resulted in the corresponding phosphorane, which reacted with crocetindialdehyde to yield 3,4,3′,4′-bisdehydro-β-carotene. Preparation of this carotenoid will be discussed in a subsequent publication.

Chart II



The enol ether **13** was prepared in 70% yield by treating **4** with triethyl orthoformate and anhydrous ethyl alcohol in the presence of sulfuric acid catalyst. The reaction of **13** with ethylene glycol in benzene led to a 48% yield of the ketal **14**. An attempt at direct ketalization of **4** to **14** resulted in considerable resin formation. Reduction of **14** with lithium aluminum hydride resulted in the alcohol **15**. The aldehyde **16** was prepared by oxidation of **15** with manganese dioxide in methylene chloride. Condensation of **16** with acetone afforded the ionone **17**, mp 39°, after recrystallization from hexane.

The substituted ionone **20** was prepared from **13** by following the same sequence of reactions which were described for **17**. Reduction of **13** with lithium aluminum hydride led to the alcohol **18**, which, on oxidation with manganese dioxide, resulted in the aldehyde **19**. Condensation of **19** with acetone afforded the ionone **20**. The nmr, ir, and uv spectra and the analytical data were compatible with the structures assigned to the products shown by Charts I and II.

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[4] J. D. Surmatis and A. Ofner, *J. Org. Chem.*, **28**, 2735 (1963).

Experimental Section[5]

3,5,5-Trimethyl-2-cyclohexen-1-one-4-carboxylic Acid Ethyl Ester (4).—A mixture of mesityl oxide (196 g), ethyl acetoacetate (260 g), $ZnCl_2$ (40 g), heptane (200 ml), and benzene (200 ml) was refluxed for 72 hr. The H_2O which was formed during the reaction was azeotropically distilled and collected in a separator. The cooled reaction mixture was washed with H_2O (500 ml), with 5% $NaHCO_3$ (500 ml), and again with H_2O (200 ml). The oil layer was dried over $CaCl_2$, and the solvent was removed under vacuum. The remaining oil was distilled in a packed column with an efficiency of approximately 10 theoretical plates. After a forecut consisting of unreacted mesityl oxide and ethyl acetoacetate, there was obtained 52.5 g (19%) of isophorone, 2,4-dinitrophenylhydrazone derivative, mp 191°, and 168 g (40%) of a condensation product distilling at 75–78° (0.2 mm), n^{25}D 1.4771. The distillate contained two compounds, **4** and **5**, in a ratio of 4:1 as determined by vpc using a 0.5% Carbowax M–Chromosorb G column. An analytical sample of **4** was prepared by column chromatography on silica gel G using a solvent system consisting of hexane–ethyl ether in a ratio of 7:3: n^{25}D 1.4763; uv max (EtOH) 235 mμ ($E^{1\%}_{1\,\mathrm{cm}}$ 508); ir (film) 1735 (s), 1675 (s), 1645 cm^{-1} (m); nmr (CCl_4) δ 5.82 (m, 1, $-CH=$), 4.16 (quartet, 2, J = 7 Hz, $-OCH_2-$), 2.90 (s, 1, $=CHCOOC_2H_5$), 2.65, 1.93 (AB, 2, J = 16 Hz, $-CH_2-$), 1.90 (d, 3, J = 1.5 Hz, $=CHCH_3$), 1.28 (t, 3, J = 7 Hz, $-CH_2CH_3$), 1.05 (s, 6, $2CH_3$). *Anal.* Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.82; H, 8.69.

3,5,5-Trimethyl-2-cyclohexen-1-one-6-carboxylic Acid Ethyl Ester (5).—This isomer was eluted as the first fraction from the chromatogram of **4**: uv max (EtOH) 237 ($E^{1\%}_{1\,\mathrm{cm}}$ 584); ir (film) 1740 (s), 1675 (s), 1640 cm^{-1} (m); nmr (CCl_4) δ 5.79 (m, 1, $-CH=$), 4.13 (quartet, 2, J = 7 Hz, OCH_2-), 2.97 (s, 1, $=CHCOOC_2H_5$), 2.50, 2.04 (AB, 2, J = 17 Hz, $-CH_2-$), 1.96 (broad s, 3, $=CHCH_3$), 1.26 (t, 3, J = 7 Hz, $-CH_2CH_3$), 1.10 (s, 3, CH_3), 1.05 (s, 3, CH_3). *Anal.* Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.65; H, 8.62.

Hydrolysis of 3,5,5-Trimethyl-2-cyclohexen-1-one-6-carboxylic Acid Ethyl Ester (5) to Isophorone (3).—The isomer **5** (12.0 g), H_2O (500 ml), and $ZnCl_2$ (3.0 g) were stirred on a steam bath for 24 hr. The cooled reaction mixture was extracted with hexane. The combined extracts were washed with 5% $NaHCO_3$ and H_2O and the solvent was removed under vacuum. The resulting oil, 6.1 g (92.8%), was identified as isophorone by the 2,4-dinitrophenylhydrazone derivative, mp and mmp 191°. One peak was obtained by vpc which was identical with an authentic sample of isophorone.

Purification of 3,5,5-Trimethyl-2-cyclohexen-1-one-4-carboxylic Acid Ethyl Ester (4) by Selective Hydrolysis of the Isomer Mixture.—A distilled mixture of **4** and **5** (1650 g) was placed in a flask with H_2O (5.0 l.), 95% C_2H_5OH (500 ml), and $ZnCl_2$ (50 g) and stirred on a steam bath for 24 hr. The cooled reaction mixture was extracted with benzene, and the combined extracts were washed with H_2O (2 l.), with 5% $NaHCO_3$ (2 l.), and finally with H_2O (2 l.). The benzene was removed under vacuum and the residue was distilled through a Vigreux column. The main fraction, which consisted of **4** as determined by vpc, weighed 1300 g (78.7%) and distilled at 77–78° (0.2 mm), n^{25}D 1.4764.

4-Hydroxy-2,6,6-trimethyl-2-cyclohexene-1-methanol (6).—3,5,5-Trimethyl-2-cyclohexen-1-one-4-carboxylic acid ethyl ester (**4**, 25 g) was reduced by adding it to a suspension of $LiAlH_4$ (4.3 g) in ethyl ether (200 ml) at such a rate as to maintain a gentle refluxing. The stirring and refluxing were then continued for an additional 4 hr. H_2O (22 ml) was added to the cold reaction mixture (5°) drop by drop; then the inorganic precipitate was filtered off by suction. The filtrate was dried over Na_2SO_4, and the solvent was removed under vacuum. The crude diol **6**, 19.5 g (96.4%), was obtained as a viscous oil. *Anal.* Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.27; H, 10.45.

The Separation of Isomers 6a and 6b.—The isomer mixture **6** (19.0 g) was chromatographed on 300 g of silica gel G with 10% acetone and 90% hexane. The acetone content was gradually increased to 25% during the elution of the product. The first isomer (**6a**), which was obtained from the column crystallized from ethyl ether (2.0 g): mp 95–96°; nmr ($CDCl_3$) δ 0.92 (3, s, CH_3), 0.97 (3, s, CH_3), 1.63 (3, m, $J \sim 1$ Hz, CH_3), 3.38 (2, s, OH), 3.83 (2, d, J = 6.5 Hz, $-CH_2O-$), 4.48 (1, m, $w_{1/2}$ = 10 Hz, $=CHO-$), 5.43 (1, m, $-CH=$). *Anal.* Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.39; H, 10.60. The more strongly absorbed isomer (**6b**) was obtained as a viscous oil: nmr ($CDCl_3$) δ 0.85 (3, s, CH_3), 1.00 (3, s, CH_3), 1.72 (3, m, $J \sim 1$ Hz, CH_3), 2.45 (2, s, OH), 3.72 (2, d, J = 4 Hz, $-CH_2O-$), 4.13 (1, m, $w_{1/2}$ = 22 Hz, $-CHO-$). *Anal.* Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.71; H, 10.56.

3,5,5-Trimethyl-2-cyclohexen-1-one-4-methanol (7).—The cyclohexenediol (**6**, 19 g) was refluxed for 20 hr with aluminum isopropoxide (11.0 g) in acetone (150 ml). Most of the solvent was removed by distilling under reduced pressure. The residue was transferred to a separator with 5% H_2SO_4 (500 ml) and extracted with ethyl ether. The ether extract was washed with $NaHCO_3$ (5%), and dried over Na_2SO_4, and the solvent was removed under vacuum. The residue which crystallized from ethyl ether–hexane afforded 6.2 g (33.0%) of **7**: mp 63–65°; uv max (EtOH) 238 mμ ($E^{1\%}_{1\,\mathrm{cm}}$ 722); ir (KBr) 3350 (s), 1660 cm^{-1} (s). *Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.55; H, 9.50.

(4-Oxo-2,6,6-trimethyl-2-cyclohexen-1-yl)methyltriphenylphosphonium Bromide (8).—3,5,5-Trimethyl-2-cyclohexen-1-one-4-methanol (**7**, 16.8 g) and triphenylphosphonium bromide (36 g) in CH_2Cl_2 (200 ml) were stirred for 20 hr at room temperature. The solution was washed with H_2O and dried over Na_2SO_4, and the solvent was removed under vacuum. The crystalline residue which was obtained was recrystallized from methyl alcohol–ethyl acetate to afford 39.5 g (80%) of **8**: mp 192–194°; ir (KBr) 1660 (s), 1590 (m), 1440 (s), 750 s, 690 cm^{-1} (s). *Anal.* Calcd for $C_{28}H_{30}OPBr$: C, 68.16; H, 6.13. Found: C, 68.14; H, 6.17.

3,5,5-Trimethyl-4-methylene-2-cyclohexen-1-one (9).—Sodium methoxide (4 g) was added to a solution of **8** (39.5 g) in CH_3OH (100 ml) and the reaction was stirred for 1 hr at room temperature. The crystalline triphenylphosphine which was formed was filtered off and the filtrate was diluted with H_2O (200 ml) and extracted with hexane (200 ml). The solvent layer was dried over anhydrous Na_2SO_4 and fractionated to yield 10.0 g (82.5%) of **9**: bp 64–66° (0.75 mm); n^{25}D 1.5173; uv (EtOH) 272 mμ ($E^{1\%}_{1\,\mathrm{cm}}$ 1007); ir (film) 1840 (w), 1770 (w), 1680 cm^{-1} (s); nmr (CCl_4) δ 2.50 (m, 1, $-CH=$), 2.90 and 2.83 (s and d, respectively, 2, $=CH_2$), 2.25 (s, 2, $-CH_2-$), 2.07 (d, 3, J = 1 Hz, CH_3), 1.20 [s, 6, $=C(CH_3)_2$]. *Anal.* Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.15; H, 9.44.

(2,6,6-Trimethyl-1,3-cyclohexadien-1-yl)methyltriphenylphosphonium Bromide (10).—Compound **6a** (15 g) and triphenylphosphonium bromide (39 g) were stirred in CH_2Cl_2 (200 ml) for 24 hr. The solution was washed with H_2O and dried over Na_2SO_4, and the solvent was removed under vacuum. The resulting residue was crystallized from acetone–ethyl ether to yield 33 g (78.5%) of **10**, mp 124–125°. *Anal.* Calcd for $C_{28}H_{30}PBr$: C, 70.44; H, 6.33; Br, 16.74. Found: C, 70.14; H, 6.11; Br, 16.64.

5,8,8-Trimethyl-2-oxabicyclo[2.2.2]oct-5-ene (11) and 2-Methylene-6,6-dimethyl-3-cyclohexene-1-methanol (12).—A trace of hydrogen chloride was introduced into a methylene chloride solution (200 ml) of **6a** (40 g), and the reaction was stirred for 2 hr. The contents of the flask were neutralized with NH_4OH and dried over Na_2SO_4, and the solvent was removed under vacuum. Fractionation through a Vigreux column yielded a forecut, 3.0 g (8.4%), which, after purification by chromatography on aluminum oxide with ethyl ether, was assigned the structure **11**: n^{25}D 1.4663; ir (film) 1050 (s), 1025 (s), 970 (s), 820 cm^{-1} (s); nmr (CCl_4) δ 5.90 (m, 1, $-CH=$), 4.08 (m, 1, $=CHO-$) 3.94 and 2.94 (two d of d, 2, J_{gem} = 8 Hz, OCH_2), 1.87 (d, 3, CH_3), 1.83 (m, 1, CH), 165 and 1.05 (two d of d, 2, J_{gem} 12 Hz, CH_2), 1.11 (s, 3, CH_3), 0.84 (s, 3, CH_3). *Anal.* Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.80; H, 10.57.

The main fraction from the distillation, 15.0 g (41.9%), bp 58–61° (0.3 mm), n^{25}D 1.506, was assigned structure **12**. An analytical sample was purified by chromatography on silica gel G with hexane–ethyl ether (4:1): uv max (EtOH) 231 mμ ($E^{1\%}_{1\,\mathrm{cm}}$ 1114); ir (film) 3400 (s), 1640 (m), 1600 (m), 1060 (m), 1030 (s), 880 (m), 850 cm^{-1} (w); nmr (CCl_4) δ 6.03 (d, 1, J = 10 Hz, $=CH-$), 5.62 (m, 1, $-CH=$), 4.94 and 4.87 (singlets, 2, $=CH_2$), 3.55 and 3.25 (m, 2, $-CH_2OH$), 2.20–1.65 (m, 4, $-CH_2-$, $=CH-$, OH), 1.00 (s, 3, CH_3), 0.87 (s, 3, CH_3). *Anal.* Calcd for $C_{10}H_{16}O$: C, 78.70; H, 10.59. Found: C, 78.65; H, 10.55.

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(5) Melting points were determined in vacuum capillaries and are uncorrected. Nuclear magnetic resonance (nmr) spectra were obtained with a Varian A-60 spectrometer.

Preparation of 2-Methylene-6,6-dimethyl-3-cyclohexene-1-methanol (12) from 11.—An analytical sample of **11** which was purified by chromatography (4.0 g) was stirred for 4 hr in CH_2Cl_2 (50 ml) containing a catalytic quantity of hydrogen chloride. The reaction mixture was neutralized with NH_4OH and the solvent was removed under vacuum to yield 3.6 g (90.0%) of residue. The ir, uv, and nmr spectra of the product were identical with the spectra which were obtained for **12**.

Preparation of the Wittig Salt (10) from 2-Methylene-6,6-dimethyl-3-cyclohexene-1-methanol (12).—Compound **12** (3.0 g) and triphenylphosphonium bromide (8.0 g) were stirred in CH_2Cl_2 (40 ml) for 24 hr. The reaction was worked up by the same procedure described for the preparation of **10** from **6a**. The product consisted of 6.5 g (68.9%) of **10**, mp and mmp 124–125°.

2,6,6-Trimethyl-4-ethoxy-1,3-cyclohexadiene-1-carboxylic Acid Ethyl Ester (13).—A solution of 3,5,5-triethyl-2-cyclohexen-1-one-4-carboxylic acid ethyl ester (4,800 g), trimethyl orthoformate (720 g), absolute C_2H_5OH (1.5 l.), and concentrated H_2SO_4 (4 ml) was allowed to stand at room temperature overnight. The dark blue solution was poured into a separator containing hexane (2 l.) and saturated $NaHCO_3$ solution (2 l.). The hexane layer was separated, washed with H_2O, and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was distilled to yield 600 g (66.0%) of **13**: bp 84–86° (0.3 mm); $n^{25}\mathrm{D}$ 1.4885; uv max (EtOH) 397 mμ ($E^{1\%}_{1\,\mathrm{cm}}$ 315); ir (film) 1710 1630 (s), 1580 cm^{-1} (s). *Anal.* Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.30. Found: C, 70.30; H, 9.26.

7,9,9-Trimethyl-1,4-dioxaspiro[4.5]dec-7-ene-8-carboxylic Acid Ether Ester (14).—2,6,6-Trimethyl-4-ethoxy-1,3-cyclohexadiene-1-carboxylic acid ethyl ester (**13**, 680 g) and ethylene glycol (185 g) were heated for 2 hr in benzene (3 l.) in the presence of *p*-toluenesulfonic acid (3.0 g). The reaction was stopped when 1.5 l. of benzene was distilled off. The cooled reaction mixture was washed with $NaHCO_3$ solution (5%) and H_2O, and the benzene was removed under vacuum. The product, 320 g (44.1%), distilled at 92–94° (0.1 mm); $n^{25}\mathrm{D}$ 1.4788; ir (film) 1715 (s), 1090 cm^{-1} (s). *Anal.* Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.42; H, 8.92.

7,9,9-Trimethyl-1,4-dioxaspiro[4.5]dec-7-ene-8-methanol (15).—A solution of 7,9,9-trimethyl-1,4-dioxasporo[4.5]dec-7-ene-8-carboxylic acid ethyl ester (**14**, 300 g) in ethyl ether (1 l.) was added slowly to a stirred suspension of $LiAlH_4$ (50 g) in ethyl ether (1 l.). The temperature was maintained at 15° during the addition. The stirring then was continued for 4 hr at 20–25° under an atmosphere of N_2. The reaction mixture was decomposed by the addition of H_2O (250 ml) drop by drop at 5–10°. The inorganic salt was filtered off and the product was dried over Na_2SO_4. The ether was removed by distillation and the residue was crystallized from hexane–ethyl ether to yield 270 g (80.3%) of **15**, mp 35°. *Anal.* Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.74; H, 9.67.

7,9,9-Trimethyl-1,4-dioxaspiro[4.5]dec-7-ene-8-carboxaldehyde (16).—7,9,9-Trimethyl-1,4-dioxaspiro[4.5]dec-7-ene-8-methanol (**15**, 150 g) was oxidized with MnO_2[6] (3.0 kg) in CH_2Cl_2 (3 l.) by stirring for 3 days under an atmosphere of N_2. The spent MnO_2 was filtered off and the solvent was removed under vacuum. The product **16**, 120 g (80.8%), distilled at 80–82° (0.1 mm): $n^{25}\mathrm{D}$ 1.5060; uv max (EtOH) 246 mμ ($E^{1\%}_{1\,\mathrm{cm}}$ 524); ir (film) 1670 (s), 1615 (w), 1085 cm^{-1} (s); nmr (CCl_4) δ 10.1 (s, 1, CHO), 3.87 (s, 4, CH_2CH_2), 2.38 (m, 2, J = 1 Hz, CH_2), 2.10 (m, 3, J = 1 Hz, CH_3), 1.59 (m, 2, J = 1 Hz, CH_2), 1.22 [s, 6, $C(CH_3)_2$]. *Anal.* Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.46; H, 9.00.

3-Ethylenedioxy-β-ionone (17).—A mixture of 7,9,9-trimethyl-1,4-dioxaspiro[4.5]dec-7-ene-8-carboxaldehyde (120 g), acetone (500 ml), and 10% aqueous KOH (60 ml) was refluxed under an atmosphere of N_2 for 16 hr. Most of the solvent was distilled off, and the residue was added to hexane (500 ml) and washed neutral with H_2O. After removal of the solvent under vacuum, the product crystallized from low-boiling petroleum ether (30–60°) at −10° to afford 60 g (41.8%) of **17**: mp 38–39°; uv max (EtOH) 291 mμ ($E^{1\%}_{1\,\mathrm{cm}}$ 383); ir (KBr) 1670 (s), 1605 (s), 1085 cm^{-1} (s); nmr (CCl_4) δ 7.10 and 6.05 (AB, 2, J = 16.5 Hz, –CH═CH–), 3.88 (s, 4, CH_2CH_2), 2.24 (s, 2, CH_2), 2.20 (s, 3, CH_3CO), 1.76 (s, 3, CH_3), 1.63 (s, 2, CH_2), 1.12 [s, 6, $C(CH_3)_2$]. *Anal.* Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.16; H, 8.55.

2,6,6-Trimethyl-4-ethoxy-1,3-cyclohexadiene-1-methanol (18).—2,6,6-Trimethyl-4-ethoxy-1,3-cyclohexadiene-1-carboxylic acid ethyl ester (**13**, 250 g) was reduced with $LiAlH_4$ (50 g) by the same procedure used for the preparation of **15**. The product **18**, 165 g (80.2%), distilled at 60–62° (0.2 mm). *Anal.* Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.26. Found: C, 73.22; H, 10.35.

2,6,6-Trimethyl-4-ethoxy-1,3-cyclohexadiene-1-carboxaldehyde (19).—Product **18** (150 g) was oxidized with MnO_2 (3 kg) by the same procedure used to prepare **16**. The resulting aldehyde (**19**), 76 g (51.2%), distilled at 88° (0.3 mm); $n^{25}\mathrm{D}$ 1.5487; uv max (EtOH) 342 mμ ($E^{1\%}_{1\,\mathrm{cm}}$ 692); ir (film) 1660 (s), 1622 (s), 1550 cm^{-1} (s). *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.33. Found: C, 74.02; H, 9.30.

3-Ethoxy-3,4-dehydro-β-ionone (20).—2,6,6-Trimethyl-1,3-cyclohexadiene-1-carboxaldehyde (**19**, 40 g), acetone (400 ml), and a 10% aqueous solution of KOH (80 ml) was refluxed to prepare compound **20** by the same procedure described for **17**. The ionone **20** was obtained as crystals from CH_3OH: 23 g (47.4%); mp 43–45°; uv max (EtOH) 383 mμ ($E^{1\%}_{1\,\mathrm{cm}}$ 670); ir (KBr) 1655 (s), 1595 (s), 1540 cm^{-1} (s); nmr (CCl_4) δ 7.25 and 6.03 (AB, 2, J = 16.5 Hz, –CH═CH–), 4.92 (s, 1, –CH═), 3.83 (quartet, 2, OCH_2), 2.57 (s, 3, CH_3), 2.12 (s, 2, CH_2), 1.92 (s, 3, CH_3CO), 1.32 (t, 3, CH_3CH_2), 1.17 [s, 6, $C(CH_3)_2$]. *Anal.* Calcd for $C_{15}H_{22}O_2$: 76.89; H, 9.46. Found: C, 76.80; H, 9.35.

Registry No.—**4**, 23068-96-4; **5**, 23068-97-5; **6a**, 23068-98-6; **6b**, 23068-99-7; **7**, 23069-00-3; **8**, 23069-01-4; **9**, 20548-00-9; **10**, 23069-03-6; **11**, 23069-04-7; **12**, 23069-05-8; **13**, 23115-91-5; **14**, 23069-06-9; **15**, 23069-07-0; **16**, 23069-08-1; **17**, 23069-09-2; **18**, 23069-10-5; **19**, 23069-11-6; **20**, 23069-12-7.

Acknowledgment.—We wish to thank Dr. T. Williams for the nmr spectra, Dr. F. Forrester for the ir and uv spectra, and Dr. A. Steyermark for the microanalyses.

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(6) Available from General Metallics Oxides Corp., Jersey City, N. J. (manganese hydrate no. 37).