TABLE II

CHLORINE METATHESIS OF CHLOROTRIFLUOROETHYLENE WITH 1,2-DICHLOROHEXAFLUOROCYCLOBUTANE

Expt no.	Catalyst	Vol,[a] cc	Mole ratio, C_2ClF_3/ $C_4Cl_2F_6$	Temp, °C	Contact time, sec	Material balance, wt %	Product composition, mol %					
							CClF=CF$_2$	CClF—CClF / CF$_2$—CF$_2$	CF=CF / CF$_2$—CF$_2$	CCl$_2$FCClF$_2$	CClF$_2$CF=CFCF$_3$[b]	CCl=CCl[b] / CF$_2$—CF$_2$
1	NaF on F-1 alumina	15	1.4	500	8.2	81.9	35.3	52.0	3.0	9.3		
2	Same	15	1.2	500	9.1	95.3	37.8	53.5	2.0	6.2		
3	Carbon	300	0.80	300	66.7	78.8	2.0	42.5	10.0	22.2	5.1	18.2

[a] The reaction was carried out in a Pyrex tube or a stainless steel 1-in. tube. [b] The structure of these two compounds was assigned on the basis of their mass spectra.

The heats of chlorination are smaller for compounds with more chloro or perfluoroalkyl groups. One possibility of a less expensive "chlorine sink" than tetrafluoroethylene is acetylene.

By-Products.—The formation of by-products appears to be thermally induced. Although the amounts are small below 450°, there is a marked increase with temperature.

Previous studies of the thermal reactions of chlorotrifluoroethylene at 300–500° by Atkinson and Stedman[11] had shown that the first-formed 1,2-dichlorohexafluorocyclobutane appeared to open to form 1,4-dichlorohexafluorobutene-2. Miller[12] indicated that pyrolysis of chlorotrifluoroethylene at 560° seemed to give the products shown below. At 650° hexafluorocyclobutane was also observed.

$$CClF{=}CF_2 \xrightarrow{560^\circ} \underset{\substack{| \\ CF_2{-}CF_2 \\ 34\%}}{CClF{-}CClF} + \underset{30\%}{CF_2{=}CFCClFCClF_2} +$$

$$\underset{10\%}{CF_2{=}CFCClF_2} + \underset{10\%}{CF_2{=}CFCCl_2F}$$

By-products which have been identified in the experiment utilizing chlorotrifluoroethylene and 1,2-dichlorohexafluorocyclobutane were 1-chloroheptafluoro-2-butene, 3,4-dichlorohexafluoro-1-butene, and 1,2-dichlorotetrafluorocyclobutene. Those identified from the reaction of chlorotrifluoroethylene with 1,1,2,2-tetrachloro-1,2-difluoroethane were 2-chloroheptafluoro-2-butene, 2,3-dichlorohexafluoro-2-butene, and 1,2-dichlorohexafluorocyclobutane.

Experimental Section

Reaction of Chlorotrifluoroethylene with 1,2-Dichlorohexafluorocyclobutane.—Three experiments were carried out to demonstrate the direct reaction of these two materials by chlorine metathesis. In the first two the catalyst was 15 cc of NaF-coated Alcoa F-1 Alumina in a 16-mm Pyres tube. The third used Columbia CXA 6-8 mesh carbon in a 1-in. stainless steel tube. The conditions used and the results observed are presented in Table II.

Reaction of Chlorotrifluoroethylene with 1,1,2,2-Tetrachloro-1,2-difluoroethane.—The 1-in. stainless steel tube mentioned above was charged with Columbia CXA 6–8 mesh activated carbon. This had been used in the third experiment mentioned above, discharged, and allowed to stand for 3 weeks. The catalyst was recharged and heated to 300° in a nitrogen purge. 1,1,2,2-Tetrachloro-1,2-difluoroethane was fed over the catalyst for 5.5 hr to condition it. At first there was much acid in the condensate, but this decreased rapidly after 2 hr. A mixture of 47 g of chlorotrifluoroethylene and 77.5 g of 1,1,2,2-tetrachloro-1,2-difluoroethane was passed over the catalyst over a 2-hr period. The contact time was 60 sec at a temperature of 300°. Products were collected in Dry Ice cooled traps and analyzed by gas chromatography and mass spectroscopy.

The products included 47.7 g (94.4%) of 1,2-dichloro-1,2-difluoroethylene, 37.4 g of 1,1,2-trichloro-1,2,2-trifluoroethane, 4.5 g of recovered 1,1,2,2-tetrachloro-1,2-difluoroethane, a trace of chlorotrifluoroethylene, and 5.3 g of 1,2-dichlorohexafluorocyclobutane.

Registry No.—Chlorotrifluoroethylene, 79-38-9; 1,2-dichlorohexafluorocyclobutane, 356-18-3; 1,1,2,2-tetrachloro-1,2-difluoroethane, 76-12-0.

(11) B. Atkinson and M. Stedman, *J. Chem. Soc.*, 512 (1962).
(12) W. T. Miller, U. S. Patent 2,733,277 (Jan 31, 1956).

Facile Synthesis of Tricyclo[5.3.1.0^{3,8}]undecane and Spiro[5.5]undecane Systems from a Common Intermediate

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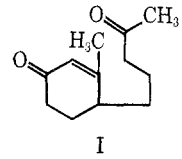
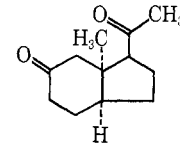
Barton and his coworkers[1] and Johnson's group[2] reported that the cyclization of the unsaturated diketone of type I led stereoselectively to the *cis*-hydrindanone II.



I

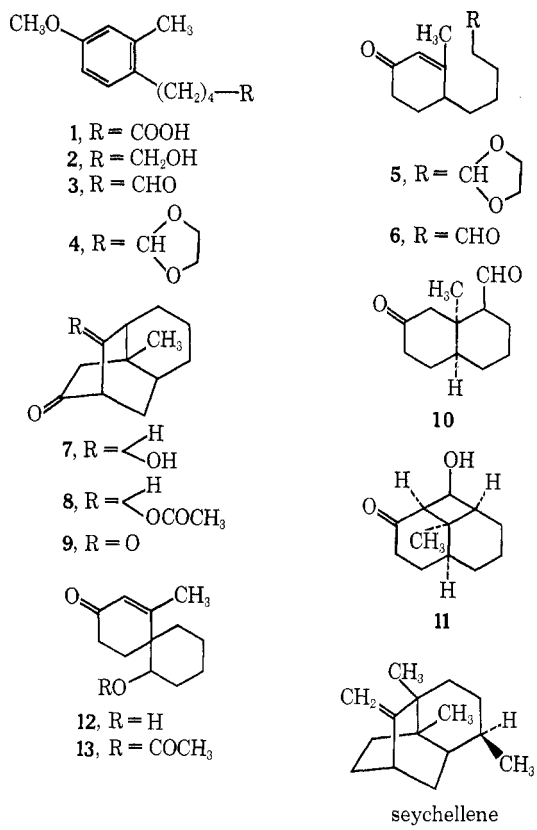


II

In an attempt to investigate the stereochemical outcome of cyclization of the compound carrying the side chain with one more methylene unit in I, we have examined cyclization of 3-methyl-4-(4′-formylbutyl)-2-cyclohexenone (**6**) under a variety of conditions. The cyclohexenone aldehyde **6** employed in this study was prepared as follows. The Wolff–Kishner reduction of γ-(2-methyl-4-methoxybenzoyl)butyric acid[3] afforded δ-(2-methyl-4-methoxyphenyl)valeric acid (**1**). Lithium aluminum hydride reduction of the methyl ester of the acid **1** gave an alcohol **2**, which, on Pfitzner–Moffatt oxidation yielded an aldehyde **3**. The corresponding acetal **4** was submitted to the Birch reduction and the resulting enol ether was hydrolyzed with

(1) D. H. R. Barton, A. S. Campos-Neves, and A. I. Scott, *J. Chem. Soc.*, 2698 (1957).
(2) W. S. Johnson, S. Shulman, K. L. Williamson, and R. Pappo, *J. Org. Chem.*, **27**, 2015 (1962).
(3) D. Chakravarti and N. K. Roy, *J. Indian Chem. Soc.*, **42**, 607 (1965).

oxalic acid to afford the β,γ-unsaturated ketone acetal, which was converted to the α,β-unsaturated ketone acetal **5**. The structure of the acetal **5** was secured by spectral data. Deacetalization of **5** in hot aqueous acetic acid afforded the desired cyclohexenone aldehyde **6**.



The intramolecular Michael condensation of **6** was examined using various amines and alkoxides. Cyclization was effected with pyrrolidine in methanol at room temperature and a crystalline product, $C_{12}H_{18}O_2$, was obtained in 70% yield. While the ultraviolet spectrum showed no absorption, the infrared spectrum ($CHCl_3$) of the cyclized product exhibited bands at 3640, 3400, and 1720 cm^{-1}, and the nuclear magnetic resonance spectrum revealed a singlet due to a tertiary methyl group at δ 1.02, a broad singlet of a hydroxyl at δ 2.5 which disappeared on addition of deuterium oxide, and a broad doublet (J = 4.5 Hz) of a hydrogen on carbon bearing the hydroxyl at δ 4.00. These spectral data suggest that the product is a saturated keto alcohol. The structure of the cyclized product was, therefore deduced to be **7**. Further, the cyclization product **7** formed the monoacetate **8** with acetic anhydride and pyridine, and was oxidized with chromium trioxide–pyridine to the diketone **9**, which showed two carbonyl bands at 1740 and 1710 cm^{-1} in the infrared spectrum. The infrared spectral data of the diketone **9** exclude the possibility of **11** for the structure of the cyclized product. The cyclization of **6** to form **7** could also be carried out in *tert*-butyl alcohol containing potassium *tert*-butoxide, but in a yield less than in the pyrrolidine–methanol solution.

Since the cyclized product **7** corresponds to the tricyclic carbon skeleton of a unique sesquiterpene, seychellene,[4,5] this mode of cyclization would be potentially useful for the synthesis of the sesquiterpene.

The formation of the tricyclic compound **7** from the cyclohexenone aldehyde **6** implies that the *cis*-decalone **10** was initially formed, which underwent further intramolecular aldol condensation. Although the reaction mixture was analyzed periodically by thin layer chromatography and vapor phase chromatography during the cyclization reaction in pyrrolidine–methanol, intermediates or other products could not be observed. Presumably the *cis*-decalone **10** was directly formed from **6** without intervention of the corresponding *trans*-decalone.

On the other hand the acid-catalyzed cyclization of the cyclohexenone aldehyde **6** proceeded in a different manner: on treatment of **5** in hydrochloric acid in aqueous tetrahydrofuran under reflux a crystalline compound $C_{12}H_{18}O_2$ was obtained, the structure of which was proved to be **12** containing a spiro[5.5]undecane skeleton on the basis of the spectral data. The compound **12** retains the original α,β-unsaturated ketone group [ν_{max} 1660, 1615 cm^{-1}; λ_{max} (CH_3OH) 241 nm (ϵ 12,000)] and a secondary hydroxyl group [ν_{max} 3660, 3470 cm^{-1}; δ_{CDCl_3} 3.9 (CHOH) as a multiplet]. On acetylation with acetic anhydride–pyridine the monoacetate **13** [δ 5.1 ($CHOCOCH_3$) as a multiplet] was obtained.

Experimental Section

General.—Melting points were uncorrected. The ultraviolet spectra were measured in methanol with a Perkin-Elmer Model 202 spectrophotometer. The infrared spectra were recorded with a JASCO Model IRS spectrophotometer. Nuclear magnetic resonance spectra were determined on a JNMC-60H (60 MHz) spectrometer: chemical shifts are expressed in parts per million downfield from tetramethylsilane as internal standard (δ). The mass spectra were obtained on a Hitachi RMU-6D mass spectrometer operating with an ionization energy of 70 eV. Vapor phase chromatographic analyses (vpc) were carried out on a Hitachi K-52 instrument using a flow rate of 20 ml/min on 2 m × 3 mm columns packed with 5% SE-30 on Chromosorb W at 230°. Thin layer chromatography (tlc) was performed on silica gel GF_{254} (E. Merck, A.G.). For column chromatography Mallinckrodt silicic acid (100 mesh, Mallinckrodt) was used. The organic solutions were dried over anhydrous sodium sulfate, and evaporated under reduced pressure.

δ-(2-Methyl-4-methoxyphenyl)valeric Acid (1).—A mixture of 17.3 g (73.3 mmol) of γ-(2-methyl-4-methoxybenzoyl)butyric acid,[3] mp 133–135°, 8 ml of $NH_2NH_2 \cdot H_2O$, 14 g of 85% KOH, and 100 ml of diethylene glycol was refluxed under nitrogen for 2 hr, and then was allowed to distil until the temperature of the solution reached 210°. The solution was kept at 210° for a further 2 hr. After cooling, the solution was diluted with 20 ml of water and then 15 ml of dimethyl sulfate was added. The mixture was heated under reflux for 1 hr, and after cooling poured slowly into a mixture of excess HCl and ice. The precipitate obtained was collected by filtration, washed with water, and dried. Recrystallization from benzene afforded 13.2 g (82%) of **1**, mp 109–111°.

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.08; H, 8.10.

5-(2′-Methyl-4′-methoxyphenyl)pentan-1-ol (2).—Treatment of the valeric acid **1** with excess diazomethane in ether afforded the methyl ester. To a suspension of 1.0 g (26 mmol) of $LiAlH_4$ in 50 ml of ether was added dropwise a solution of 7.6 g (32 mmol) of crude methyl ester of **1** in 20 ml of ether with stirring

(4) N. Tsubaki, K. Nishimura, and Y. Hirose, *Bull. Chem. Soc. Jap.*, **40**, 597 (1967); G. Wolffe, and G. Ourisson, *Tetrahedron Lett.*, 3849 (1968).

(5) For the synthesis of seychellene, see E. Piers, R. W. Britton, and W. deWaal, *Chem. Commun.*, 1069 (1969); K. J. Schmalzl and R. N. Mirrington, *Tetrahedron Lett.*, 3219 (1970).

at −20° in a Dry Ice–acetone bath. After the mixture was stirred at 0° for 1 hr, 5 ml of ethyl acetate in 10 ml of ether was added. A saturated aqueous solution of sodium potassium tartarate was slowly added to the mixture until the gray granular precipitate was formed. The ethereal solution was separated by decantation and the precipitate was washed with two 20-ml portions of ether. The combined ethereal solution was washed with a saturated NaCl solution and dried. Evaporation of solvent afforded a crude product, which was distilled to afford 6.2 g (67%) of **2**: bp 155–156° (2 mm); ir ($CHCl_3$) 3680 (OH), 3550 cm^{-1} (OH); mass spectrum *m/e* 208 (parent ion). The analytical sample was fractionally distilled through a Vigreux column.

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.70; H, 9.51.

5-(2′-Methyl-4′-methoxyphenyl)pentan-1-al (3).—A solution of 2 g of 100% phosphoric acid in 2.5 ml of DMSO was added dropwise under ice-bath cooling to a mixture of 10.0 g (49.5 mmol) of the alcohol **2**, and 30 g of dicyclohexylcarbodiimide in 40 ml of benzene and 45 ml of DMSO with stirring. After the addition of the phosphoric acid solution the mixture was kept at room temperature with stirring for 5 hr. The mixture was diluted with 100 ml of ether and a solution of 14 g of oxalic acid in 40 ml of methanol was added. The resulting mixture was stirred for 2 hr and the precipitated dicyclohexylurea was filtered. The filtrate was washed with water twice, a saturated $NaHCO_3$ solution three times, and a saturated NaCl solution, and dried. Evaporation of solvent afforded 15.7 g of an oily product containing dicyclohexylurea. The crude product was chromatographed on 200 g of silicic acid with $CHCl_3$; each fraction eluted was examined by tlc. Fractions containing the aldehyde **3** were combined and evaporated to afford 8.5 g (86%) of a colorless liquid **3**, which showed one peak in vpc analysis: ir ($CHCl_3$) 2840 (CHO), 2720 (CHO), 1725 cm^{-1} (CHO). The product **3** was directly employed without further purification for the next step. The 2,4-dinitrophenylhydrazone was obtained as orange needles, which was recrystallized from ethanol, mp 108–110°.

Anal. Calcd for $C_{19}H_{22}O_5N_4$: C, 59.06; H, 5.74; N, 14.50. Found: C, 59.08; H, 5.69; N, 14.79.

Preparation of the Acetal (4) of the Aldehyde (3).—A mixture of 4.0 g (19 mmol) of **3**, 6 ml (107 mmol) of ethylene glycol, and 100 mg of *p*-toluenesulfonic acid in 50 ml of toluene was kept under reflux for 4 hr with stirring in a system containing a water separator. After cooling solid $NaHCO_3$ was added to the mixture for neutralization. The mixture was washed with water and a saturated NaCl solution, and dried. Evaporation of solvent afforded a colorless liquid, which was distilled to give 3.8 g (78%) of the acetal **4**, exhibiting one peak in vpc: bp 158–160° (2 mm); nmr (CCl_4) δ 6.89 and 6.49 (AB type q, 2, J = 9.0 Hz, aromatic H), 6.55 (s, 1, aromatic H), 4.70 (t, 1, J = 4.5 Hz, acetal methine), 3.76 (m, 4, $-OCH_2CH_2O-$), 3.69 (s, 3, CH_3O), 2.24 (s, 3, aromatic CH_3); mass spectrum *m/e* 250 (parent ion).

Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.03; H, 8.99.

3-Methyl-4-(4′-formylbutyl)-2-cyclohexenone (6).—To a solution of 3.0 g (12 mmol) of **4** in 150 ml of *tert*-butyl alcohol, 150 ml of THF, and 300 ml of liquid ammonia was added 15 g of lithium wire with stirring over a period of 30 min. After the addition was complete, the dark blue mixture was stirred at the refluxing temperature (*ca.* −33°) for 10 hr, and then allowed to stand overnight at room temperature. Methanol was slowly added first to decompose excess lithium, and water was added. The resulting mixture was concentrated to give a white residue, to which 100 ml of benzene and 50 ml of water were added. The benzene layer was separated and the aqueous layer was further extracted with three 50-ml portions of benzene. The combined benzene solution was concentrated, giving a residue, which was dissolved in 20 ml of a saturated aqueous solution of oxalic acid and 100 ml of methanol. The resulting solution was stirred at room temperature for 1 hr and concentrated, affording a residue, which was extracted with four 50-ml portions of benzene. The benzene solution was washed with water twice and a saturated NaCl solution, and dried. On removal of solvent there was obtained 2.7 g of crude β,γ-unsaturated ketone: ir ($CHCl_3$) 1712 cm^{-1}.

A solution of 2.6 g of the β,γ-unsaturated ketone in 95 ml of methanol containing 105 mg of sodium methoxide was stirred at room temperature for 2 hr, neutalized with oxalic acid, and concentrated, giving a yellow residue. The benzene solution of the residue was washed with water and a saturated NaCl solution, and dried. Evaporation of solvent afforded 2.1 g of crude ketone **5**, which was chromatographed on 100 g of silicic acid with $CHCl_3$; fractions containing **5**, detected by tlc and vpc analyses were combined, giving 1.5 g (*ca.* 52% from **4**) of colorless liquid **5**: ir ($CHCl_3$) 1660 (conjugated C=O), 1630 cm^{-1} (conjugated C=C); nmr ($CDCl_3$) δ 5.38 (q, 1, J = 0.5 Hz, $CH{=}CCH_3$), 4.87 (t, 1, J = 4.5 Hz, acetal methine), 3.93 (m, 4, $-OCH_2-CH_2O-$), 1.98 (d, 3, J = 0.5 Hz, $CH{=}CCH_3$); mass spectrum *m/e* 238 (parent ion).

A solution of 1.45 g of **5** obtained above in 30 ml of acetic acid–water (2:1 v/v) was heated at 90° for 4 hr, and diluted with 50 ml of water and 100 ml of benzene. To the mixture was added solid $NaHCO_3$, making the aqueous layer basic. The organic layer was separated and the aqueous phase was extracted with three 20-ml portions of benzene. The combined benzene solution was washed with water, dried, and evaporated, affording 1.0 g (*ca.* 43% from **4**) of slightly yellow liquid **6**: ir ($CHCl_3$) 2840 (CHO), 2720 (CHO), 1660 (conjugated C=O), 1630 cm^{-1} (conjugated C=C). The α,β-unsaturated ketone aldehyde **6** obtained above, the purity of which was examined by vpc, was used directly in the next step.

2-Hydroxy-8-methyltricyclo[5.3.1.0^{3,8}]undecan-10-one (7).—A. Cyclization in Pyrrolidine–Methanol.—A solution of 60 mg (0.31 mmol) of **6** in 4 ml of methanol containing 15 mg (0.22 mmol) of pyrrolidine was stirred at room temperature for 24 hr and concentrated, affording a yellow oil. The residue was dissolved in 0.5 ml of a saturated aqueous oxalic acid solution and 5 ml of $CHCl_3$. The organic layer was washed with water and a saturated NaCl solution, dried, and evaporated to give 54 mg of a crystalline solid. Analysis by tlc showed formation of a single compound. Column chromatogaphy on 2 g of silicic acid with $CHCl_3$–CH_3OH (96:4 v/v) afforded 43 mg (*ca.* 70%) of crystals. Recrystallization from benzene–petroleum ether (bp 30–60°) gave pure **7**: mp 161–162°; ir ($CHCl_3$) 3640 (OH), 3400 (broad, OH), 1720 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.00 (br d, 1, J = 4.5 4.5 Hz, CHOH), 2.5 (br s, 1, CHOH, disappeared on addition of D_2O), 1.02 (s, 3, C–CH_3); mass spectrum *m/e* 194 (parent ion).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.08; H, 9.36.

B. Cyclization in *tert*-Butyl Alcohol–Potassium *tert*-Butoxide.—A solution of 142 mg (0.73 mmol) of **6** in 9.6 ml of *tert*-butyl alcohol containing 110 mg (1.0 mmol) of potassium *tert*-butoxide was stirred at 30° for 18 hr under nitrogen. The brown solid deposited in the mixture was filtered. The filtrate was neutralized by aqueous oxalic acid, concentrated, and extracted with three 10-ml portions of $CHCl_3$. The combined organic phase was washed with water and a saturated NaCl solution, dried, and evaporated, giving 75 mg of a crystalline solid, which showed a main spot in tlc. Column chromatography on 3 g of silicic acid as described in A was carried out to give 50 mg (35%) of colorless crystals **7**.

Acetylation of the Tricyclic Compound 7.—A mixture of 24 mg (0.124 mmol) of **7** in 0.3 ml of acetic anhydride and 0.4 ml of pyridine was kept at room temperature for 24 hr and diluted with 10 ml of benzene. The resulting mixture was successively washed with dilute HCl solution, a saturated $NaHCO_3$ solution, water, and a saturated NaCl solution, and dried. Evaporation of solvent afforded a solid, which was purified by preparative tlc with chloroform–ethyl acetate (1:1 v/v). Crystalline solid eluted from silica gel with ethyl acetate was recrystallized from hexane, giving 21 mg (72%) of the acetate **8**: mp 115–117°; ir ($CHCl_3$) 1735 (ester C=O), 1720 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.05 (dd, 1, J = 4.5, 1.5 Hz, $CHOCOCH_3$), 2.55 (m, 1, CHC=O), 2.00 (s, 3, CH_3COO), 1.02 (s, 3, CCH_3); mass spectrum *m/e* 236 (parent ion).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.11; H, 8.55.

Oxidation of the Tricyclic Compound 7.—To a solution of 14 mg (0.057 mmol) of **7** in 0.3 ml of pyridine was added 88 mg of chromium trioxide in 1.5 ml of pyridine at 0°. The mixture was kept at room temperature for 17 hr, concentrated, and diluted with 2 ml of ethyl acetate and 2 ml of water. The resulting precipitate was filtered and washed with four 2-ml portions of ethyl acetate. The combined ethyl acetate solution was washed with a saturated NaCl solution and dried. Evaporation of solvent afforded 11 mg of a colorless oil, which showed one spot in tlc. Column chromatography on 1 g of silicic acid with $CHCl_3$ gave 9 mg (64%) of amorphous powder **9**: ir ($CHCl_3$) 1745 (C=O), 1710 cm^{-1} (C=O); mass spectrum *m/e* 192 (parent ion).

1-Methyl-7-hydroxyspiro[5.5]undec-1-en-3-one (12).[6]—A solution of 55 mg (0.25 mmol) of **5** in 0.9 ml of 6 *N* HCl and 1.8 ml of THF was refluxed for 2 hr, and after cooling extracted with three 5-ml portions of benzene. The combined benzene solution was washed with water until the aqueous layer became neutral and with a saturated NaCl solution and dried. Evaporation of solvent afforded a crystalline residue, which showed a main spot in tlc. Preparative tlc using ethyl acetate afforded 26 mg (58%) of colorless needles, which was recrystallized from hexane–benzene, affording pure **12**: mp 103–104°; uv max (CH_3OH) 241 nm (ϵ 12,000); ir ($CHCl_3$) 3400 (OH), 1660 (conjugated C=O), 1615 cm^{-1} (conjugated C=C); nmr ($CDCl_3$) δ 5.91 (q, 1, J = 1.0 Hz, C**H**=CCH_3), 3.9 (m, 1, C**H**OH), 2.02 (d, 3, J = 1.0 Hz, CH=CCH_3); mass spectrum m/e 194 (parent ion).

(6) Since the product **12** was obtained from both **5** and **6** under the same condition, the result employing **5** is described.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.93; H, 9.24.

Acetylation of the Spiro Compound 12.—A mixture of 36 mg (0.18 mmol) of **12** in 0.25 ml of acetic anhydride and 0.5 ml of pyridine was stirred at room temperature for 24 hr, diluted with 10 ml of benzene. By the same work-up as described in the acetylation of **7**, an oily product was obtained, which showed a single spot in tlc. Preparative tlc using ethyl acetate afforded 25 mg of purified **13** as a colorless semisolid: ir ($CHCl_3$) 1730 (ester C=O), 1663 (conjugated C=O), 1615 cm^{-1} (conjugated C=C); nmr ($CDCl_3$) δ 5.90 (q, 1, J = 1.0 Hz, C**H**=CCH_3), 5.1 (m, 1, C**H**$OCOCH_3$), 1.98 (s, 3, CH_3COO), 1.91 (d, 3, J = 1.0 Hz, CH=CCH_3); mass spectrum m/e 234 (parent ion).

Registry No.—**1**, 31603-60-8; **2**, 31603-61-9; **3**, 31603-62-0; **3** 2,4-DNP, 31603-63-1; **4**, 31603-64-2; **5**, 31603-65-3; **6**, 31603-66-4; **7**, 31603-67-5; **8**, 31603-68-6; **9**, 31603-69-7; **12**, 31603-70-0; **13**, 31603-71-1.