6-Methylenetricyclo[3.3.0.0^{3,7}]octan-2-one (6). A solution of **32** (361 mg, 2.65 mmol) in CH_2Cl_2 (4 mL) was added to a suspension of pyridinium chlorochromate (943 mg, 4.37 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred for 3 h at room temperature. The CH_2Cl_2 solution was separated, and the inorganic residue was rinsed with CH_2Cl_2. The combined CH_2Cl_2 solutions were concentrated, and the residue was chromatographed on neutral alumina. Fractions eluted with pentane gave a solid which was sublimed at 30 °C (5 mm) to afford **6**: 125 mg (35% yield); mp 35.5–36 °C (in a sealed tube); UV (isooctane) λ_{max} 286 nm (ϵ 24.1); IR (KBr) 3075, 1770, 860 cm^{-1}; NMR (CCl_4) δ 1.65 (s, 4 H), 2.22 (br s, 2 H), 2.72 (br s, 2 H), 4.62 (s, 2 H).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.56; H, 7.52.

Tricyclo[3.3.0.0^{3,7}]octane-2,6-dione (7). A mixture of **6** (84 mg, 0.626 mmol), osmium tetraoxide (100 mg, 0.393 mmol), THF (2 mL), and water (2 mL) was stirred for 30 min at room temperature, and sodium metaperiodate (268 mg, 1.25 mmol) was added by portions over 40 min. After the mixture was stirred at room temperature for 14 h, the deposited inorganic solid was filtered, and this was rinsed with CH_2Cl_2. The CH_2Cl_2 extracts were combined with the original filtrate, and the mixture was made basic with 2 N aqueous NaOH (4 mL) and extracted with CH_2Cl_2. The extracts were washed with water and dried ($MgSO_4$). After removal of the solvent, the residue was chromatographed on neutral alumina. Early pentane–ether eluates recovered **6** (40 mg), and subsequent pentane–ether eluates afforded **7** (7 mg, 8% yield) which was recrystallized from hexane: mp 94–97 °C (in a sealed tube); UV (hexane) λ_{max} 281 nm (ϵ 28.7), 294 (sh) (ϵ 25.7); IR (KBr) 1765 cm^{-1}; NMR ($CDCl_3$) δ 1.85 (s, 4 H), 2.55 (s, 4 H).

Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 74.75; H, 5.15.

Registry No. 6, 82431-26-3; **7**, 82431-27-4; **12**, 67913-05-7; **13**, 82431-28-5; **14**, 82431-29-6; **15**, 56679-25-5; **16**, 82431-30-9; **17**, 82431-31-0; **18**, 82431-32-1; **19**, 82431-33-2; **20**, 82431-34-3; **21**, 82431-35-4; **22**, 82431-36-5; **23**, 82431-37-6; **24**, 82431-38-7; **25**, 82431-39-8; **26**, 82431-40-1; **27**, 82431-41-2; **28**, 82431-42-3; **29**, 82431-43-4; **30**, 82431-44-5; **31**, 82431-45-6; **31** *N*-oxide, 82431-46-7; **32**, 82431-47-8; cyclopentadiene–maleic anhydride adduct, 129-64-6.

Geometrically Biased Homoconjugated Ketones. Synthetic Avenues to 1-Acyl-2,4-cyclohexadienes

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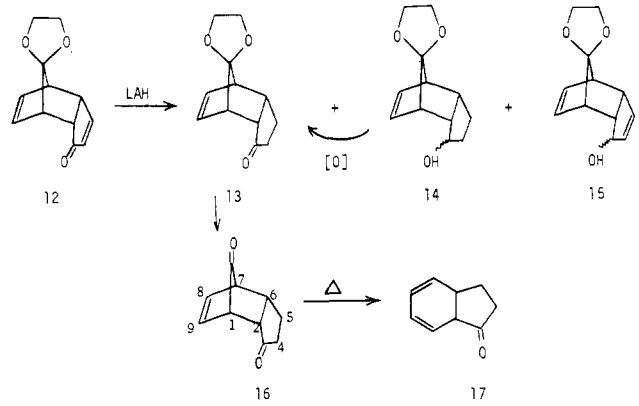
Synthetic approaches to a series of open (**1**), fused (**2**), and spiroannelated (**3**) 2,4-cyclohexadien-1-yl ketones, which differ in the geometrical juxtaposition of the homoconjugated chromophores, have been worked out. A series of prototropic rearrangements was found to occur, establishing an equilibrium between **28**–**30**.

We have recently initiated an investigation of the photochemical and photophysical properties of (homoconjugated) $\beta,\gamma,\delta,\epsilon$-unsaturated ketones as a function of the spacial juxtaposition of the respective chromophores. For reasons given elsewhere[1,2] we chose 1-acyl-2,4-cyclohexadiene as the basic system for study. We present now an account of the preparative methods and procedures we have worked out in this framework.

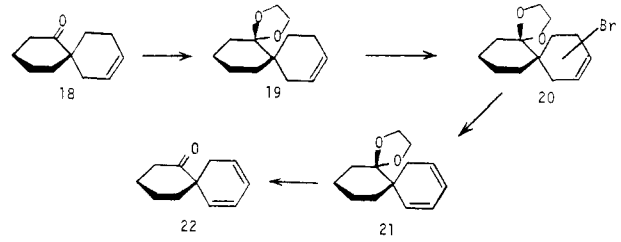
The attainment of open members of the series, adequately substituted to avoid aromatization, was relatively simple, and, e.g., **1** (Chart I) was secured by following largely literature procedures.[3] It is readily seen that in **1** and its analogues, the acyl group can freely rotate to assume various, albeit conformationally biased, spacial positions of the carbonyl vs. the π system. This bias becomes configurational and therefore much more severe in fused systems of type **2** or in spiro ketones of type **3**.

Following past experience,[4] we thought of developing a unified synthetic approach to all the needed compounds of types **2** and **3**, with the first step being a Diels–Alder cycloaddition to a cyclopentadienone ketal (**4**).[4-6] Thus, the reaction of **4** with, e.g., cyclopenten-3-one (**5**) was supposed to yield the precursor **7** for **2** (n = 1) whereas with 2-methylenecyclohexanone (**6**) the intermediate **8** was expected, leading to **3** (n = 3).

Scheme I



Scheme II

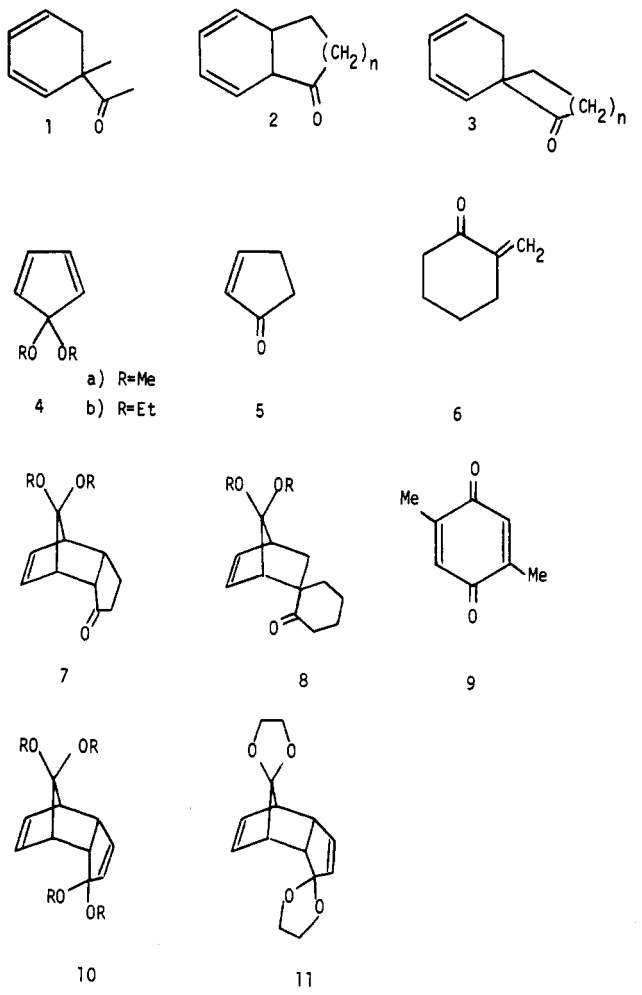


Unfortunately none of these cycloadditions could be realized. This, and further unsuccessful experiments with various dienophiles (e.g., **9**), led us to the conclusion that *4 cannot cycloadd to nonplanar or substituted dienophiles* and dimerizes instead. It appears that the steric hindrance (exercised by tetrahedral substituents) to the diene–

(1) Abramson, S.; Fuchs, B. *Tetrahedron Lett.* **1980**, *21*, 1165.
(2) (a) Zizuashivili, J.; Fuchs, B., submitted for publication. (b) Zizuashvili, J.; Abramson, S.; Shmueli, U.; Fuchs, B. *J. Chem. Soc., Chem. Commun.*, in press.
(3) Schiess, P.; Fünfschilling, P. *Tetrahedron Lett.* **1972**, 5195.
(4) (a) Fuchs, B.; Scharf, G. *Isr. J. Chem.* **1977**, 16, 335. (b) Fuchs, B.; Scharf, G. *J. Org. Chem.* **1979**, *44*, 604.
(5) Eaton, P. E.; Hudson, R. A. *J. Am. Chem. Soc.* **1965**, *87*, 4629.
(6) Allred, E. L.; Anderson, C. *J. Org. Chem.* **1967**, *32*, 1874.

0022-3263/82/1947-3474$01.25/0

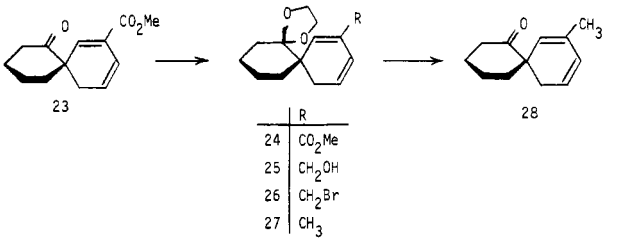
Chart I



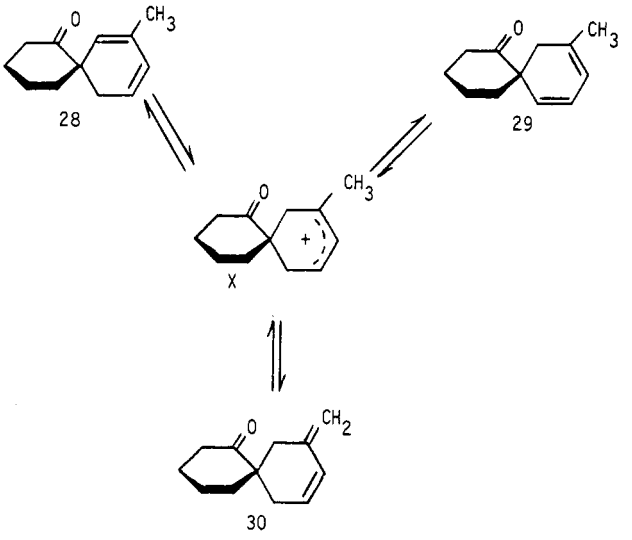
dienophile approach renders the process too activation energy demanding to compete with dimerization to **10**. Mercifully, the latter could be used itself as a suitable precursor for a type-**2** compound, namely, **17**. While we have described in preliminary form the use of the diethyl ketal dimer **10b** for this purpose,[1] it was subsequently recognized that the ethylene ketal dimer **11** is more readily formed and more convenient to prepare,[5,7] making the latter the starting material of choice. Monodeketalization of **11** readily yielded **12** which was then used in the preparation of the desired 2,3,8,9-tetrahydroinden-1-one (**17**), according to Scheme I. It should be mentioned that, due to the lability of **17**, the most sensitive step in the above reaction sequence (Scheme I) is the last, thermal decarbonylation of **16**. Therefore, this had to be carefully optimized and was hence performed in the gas phase (in vacuo) in a heated (300 °C) glass spiral.

Turning now to the spiro ketones **3** and since **4** was of no use in this case (vide supra), we chose to start with the Diels–Alder cycloaddition product (**18**) of 2-methylenecyclohexanone (**6**) with butadiene.[10] Indeed (Scheme II), ketalization of **18** followed by allylic bromination and dehydrobromination provided, after removal of the protective group, the desired spiro[5.5]undeca-1,3-dien-7-one

Scheme III



Scheme IV



(**22**). The latter was fully characterized both spectroscopically and chemically (via its 4-phenyltriazolinedione adducts). For purposes outlined elsewhere,[2] we sought also derivatives of **22** bearing a substituent label, viz., a methyl group of the diene chromophore. Unfortunately the obvious choice of piperylene to replace butadiene in the above-mentioned cycloaddition with **6** led to poor yields of difficultly resolvable mixtures of all four possible methyl-substituted derivatives of **18**, and subsequent reactions further complicated the analytic and separative work. We preferred to obviate this inconvenience by using a relatively readily available starting material, namely, Danishefsky's 2-(carbomethoxy)spiro[5.5]undeca-1,3-dien-7-one (**23**).[11] The latter was converted in five steps (Scheme III; 40% overall yield) into the desired 2-methyl derivative (**28**).

An interesting and pleasant surprise awaited us on probing the acid-catalyzed behavior of **28**. No skeletal rearrangement was registered[11] but instead a solvent-, time-, and acid-strength-dependent double bond rearrangement was observed, leading to an equilibrum between the dienes **28–30** (Scheme IV). We deal here with a prototropic shift series involving a common carbenium ion intermediate (X), which, in fact, puts at our disposal an additional, labeled spiro[5.5]undeca-1,3-dien-7-one (**29**) for photochemical study. This, as well as the chiral resolution and chiroptical investigation of these dienones, is now under active study.[2]

Experimental Section

Melting points are uncorrected. IR spectra were measured on a Perkin-Elmer 297 spectrophotometer and UV spectra on a Cary

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(9) Abramson, S.; Zizuashvili, J.; Fuchs, B. *Tetrahedron Lett.* **1980**, *21*, 2351.
(10) Mousseron, M.; Jacquier, R.; Christol, H. *Bull. Soc. Chim. Fr.* **1957**, 346.
(11) Danishefsky, S.; Eggler, J.; Koppel, G. *Tetrahedron Lett.* **1969**, 4333. We are indebted to Professor S. Danishefsky for putting the unpublished detailed procedure at our disposal.
(12) Cargill, R. L.; Jackson, T. E.; Peet, N. P.; Pond, D. M. *Acc. Chem. Res.* **1974**, *7*, 106.

219 spectrophotometer. NMR spectra were measured on a JEOL JNM-C-60 HL and/or a Brucker WH-90 spectrometer. Mass spectra were taken on a Du Pont 21-491B mass spectrometer. Gas chromatography was performed on a Packard 427 instrument with a capillary column (SE-30, 25 m).

***endo*-Tricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,10-dione (16, Scheme I).** The dicyclopentadienone diethylene ketal dimer **11**[5,8] was transformed by following known procedures[7-9] into the monoketal **12** which in turn was reduced with $LiAlH_4$ as follows: a solution of **12** (3.2 g) in tetrahydrofuran (10 mL) was added to a stirred and cooled (−78 °C) suspension of $LiAlH_4$ (0.29 g) in ether (100 mL). The reaction was continuously monitored by TLC. after 6 h, the cooling bath was removed, and after another 30 min all the starting material was gone. The excess of $LiAlH_4$ was quickly destroyed by means of an ether/ethyl acetate solution, and the mixture was acidified (H_2SO_4, 10%) to pH 4. The organic layer was separated from the aqueous one, the latter was extracted twice with ether, and the unified organic phase was dried on $MgSO_4$. The solvent was evaporated and the oily residue (3.1 g) chromatographed on basic alumina (grade 3).

Three products were thus isolated: the desired diketone monoketal **13** (1.6 g, 50%) followed by the alcohols **14** (0.5 g, 16%) and **15** (0.32 g, 10%).

13: IR (neat) ν_{max} 1730 cm^{-1} (C=O); mass spectrum, m/z 206 (M^+); ^1H NMR ($CDCl_3$, 60 MHz) δ 1.2–2.3 (m, 4, $H_{4,5}$), 3.0 (m, 4, $H_{1,2,6,7}$) 3.9 (m, 4, H_{ket}), 6.3 (m, 2, $H_{8,9}$).

14: IR (neat) ν_{max} 3450 cm^{-1} (OH); mass spectrum, m/z 208 (M^+); ^1H NMR ($CDCl_3$, 60 MHz) δ 1.0–2.3 (m, 5, $H_{4,5,OH}$), 2.8 (m, 4, $H_{1,2,6,7}$), 3.85 (m, 4, H_{ket}), 4.38 (m, 1, H_3) 6.6 (m, 2, $H_{8,9}$). Oxidation of **14** by Jones reagent provided in 77% yield an additional amount of the ketone **13**.[13]

15: IR (neat) ν_{max} 3460 cm^{-1} (OH); mass spectrum, m/z 206 (M^+); ^1H NMR ($CDCl_3$, 60 MHz) δ 2.12 (s, H_{OH}), 2.7 (m, 2, $H_{1,7}$), 2.9–3.6 (m, 2, $H_{2,6}$), 3.75 (m, 4, H_{ket}), 4.75 (m, 1, H_3), 5.7–6.2 (m, 4, $H_{4,5,8,9}$).[13]

Deketalization of the monoketal **13** was performed by following the deketalization procedure of **12** as reported by Vogel et al.[8] The crude product was purified by chromatography on basic alumina and crystallized from ether/petrol ether to give an 81% yield of diketone **16**: mp 120 °C dec; IR ($CDCl_3$) ν_{max} 1737, 1782 cm^{-1} (C=O); mass spectrum, m/z 162 (M^+); ^1H NMR ($CDCl_3$, 90 MHz) δ 1.5–2.5 (m, 4, $H_{4,5}$), 3.03 (m, 2, $H_{2,6}$), 3.26 (m, 2, $H_{1,7}$), 6.5 (m, 2, $H_{8,9}$).

2,3,8,9-Tetrahydroinden-1-one (17). The diketone **16** was subjected to thermal decarbonylation in a pyrolysis assembly consisting of a heated (300–320 °C) spiral made of 2 m of glass tubing (5-mm i.d.) connected at one end to a small test tube and at the other end to a high-vacuum system via a liquid nitrogen cooled receiver. All connections were grease-free glass flanges with Viton ring seals and spring clamps. The vacuum was 10^{-4}–10^{-5} torr.

The test tube containing the diketone **16** (0.62g) was heated by using a heat gun until sublimation of **16** into the spiral started and continued at a rate to maintain the vacuum at 10^{-3}–10^{-4} torr. After all the starting material was gone, the product accumulated in the liquid nitrogen trap was collected and found to consist of 0.478 g (97% yield) virtually pure product (**17**): colorless oil; IR (neat) ν_{max} 1737 cm^{-1} (C=O); mass spectrum, m/z 134 (M^+); UV (MeCN) λ_{max} 263 nm (ϵ 3.6 × 10^3), 271 (3.3 × 10^3); ^1H NMR ($CDCl_3$, 60 MHz) δ 1.6–2.5 (m, 4, $H_{2,3}$), 3.1 (m, 2, $H_{3a,7a}$), 5.85 (m, 4 H).

Chemical characterization of **17** was also obtained by allowing it to react with *N*-phenylmaleimide in refluxing benzene. Only one (presumably exo) adduct was isolated: mp 248 °C dec; IR (KBr) ν_{max} 1735, 1700 cm^{-1} (C=O); mass spectrum, m/z 307 (M^+).

Spiro[5.5]undeca-1,3-dien-7-one (22; Cf. Scheme II). Ketalization of 18. A benzene solution of the ketone **18** (0.5 g), ethylene glycol (280 mg), and *p*-toluenesulfonic acid (10 mg) was refluxed with a Dean–Stark head for 1 h. The cooled reaction mixture was washed with aqueous $NaHCO_3$ (3%) and saturated NaCl solutions and dried on $MgSO_4$, and the solvent was evaporated. The ethylene ketal **19** was obtained: 0.56 g (90%); ^1H NMR (CCl_4, 60 MHz) δ 1.3–2.1 (m, 14, H_{sat}), 4.8 (m, 4, H_{ket}), 5.4 (m, 2, H_{vin}); mass spectrum, m/z 208 (M^+).

Bromination of 19. A CCl_4 (10 mL) solution of the above ketal **19** (0.56 g), *N*-bromosuccinimide (0.6 g), and benzoyl peroxide (10 mg) was heated to reflux for 30 min. After cooling, the solution was filtered and the solvent removed to give 700 mg (90%) of a bromide mixture (**20**) having one major isomer (94% by GLC): mass spectrum, m/z 286, 288 (M^+); ^1H NMR (CCl_4, 60 MHz) δ 1.2–2.2 (m, 12, H_{sat}), 3.85 (m, 4, H_{ket}), 4.4 (m, 1, H_{Br}), 5.6 (m, 2, H_{vin}).

Dehydrobromination of 20. A benzene solution of the bromide mixture **20** (700 mg) and triethylamine (4 mL) was refluxed for 10 h. After the mixture cooled, is was washed with aqueous HCl (3%) and aqueous NaCl (saturated) and dried over $MgSO_4$, and the solvent was removed to give 0.31 g (62%) of the diene **21**: bp 100 °C (0.05 torr); mass spectrum, m/z 206 (M^+); ^1H NMR (CCl_4) δ 1.3–2.4 (m, 10, H_{sat}), 3.75 (4, H_{ket}), 5.55 (m, 4, H_{vin}).

Deketalization of 21. The above ketal **21** (0.3 g) was applied onto a column of silica gel (10 g) and eluted with a mixture of petroleum ether–methylene chloride (3:1). Only the ketone **22** was obtained: 200 mg (85%); colorless oil; mass spectrum, m/z 162 (M^+); IR (neat) ν_{max} 1710 cm^{-1} (CO); UV (MeCN) λ_{max} 263 nm (ϵ 3800), 305 (300); ^1H NMR (CCl_4) δ 1.5–2.8 (m, 10, H_{sat}), 5.6–5.9 (m, 4, H_{vin}).

The 4-phenyl-1,2,4-triazoline-3,5-dione adduct of **22** was prepared as usual:[14] mp 155 °C; mass spectrum, m/z 337 (M^+); ^1H NMR ($CHCl_3$) δ 1.6–2.0 (m, 8, H_{sat}), 2.1 (m, 2 H_{sat}), 5.0 (m, 2, $_{Al}$), 6.5 (m, 2, H_{vin}), 7.4 (m, 5, H_{ar}).

2-Methylspiro[5.5]undeca-1,3-dien-7-one (28, Scheme III). 2-(Carbomethoxy)spiro[5.5]undeca-1,3-dien-7-one (23). A scaled up procedure of Danishefsky et al.[11] was used as follows. To a Me_2SO^-/Me_2SO solution, obtained by adding NaH (56%, 20 g) to Me_2SO (2 L) in an inert atmosphere at 75 °C, were added 2-formylcyclohexanone (190 g) and methyl β-vinylacrylate (97 g) dropwise and with stirring. The reaction mixture was further stirred at 75–80 °C for 3 days and then worked up by pouring it into ice–water (2 L) followed by extraction with ether. The unified organic layers were washed with cold water and dried, and the solvent was removed. The product (**23**) crystallized from the crude residue and was recrystallized from petroleum ether: 63 g (33%); mp 62 °C; IR (KBr) ν_{max} 1720 (CO) cm^{-1}; mass spectrum, m/z 220 (M^+); UV (cyclohexane) λ_{max} 279 nm (ϵ 2600); ^1H NMR (CCl_4) δ 1.5–3.0 (m, 10, H_{sat}), 3.65 (s, 3, H_{Me}), 5.7 (m, 1, H_{vin}), 6.15 (m, 1, H_{vin}), 6.8 (s, 1, H_{vin}).

Ketalization of 23. A benzene solution of the keto ester **23** (22 g), ethylene glycol (7.5 g), and *p*-toluenesulfonic acid (0.3 g) was refluxed by using a Dean–Stark water-separating head. After about 2 mL of water was collected (ca. 2 h), the solution was washed with 3% aqueous $NaHCO_3$ and water and dried over $MgSO_4$. Removal of the solvent gave the ethylene ketal **24** (23 g, 87%) in better than 95% purity (GLC); mass spectrum, m/z 264 (M^+).

2-(Hydroxymethyl)spiro[5.5]undeca-1,3-dien-7-one Ethylene Ketal (25). An ethereal solution of the ethylene ketal **24** (20 g) was added dropwise to a suspension of $LiAlH_4$ (3.8 g) in absolute ether (300 mL) at 0 °C with stirring. After an additional 2 h at room temperature, saturated aqueous NH_4Cl was carefully added followed by 15% aqueous H_2SO_4 to pH 7. The ethereal layer was separated, washed with saturated aqueous NaCl, and dried. The solvent was removed, and the hydroxy ketal **25** was isolated in 90% yield (16 g) in better than 95% purity (GLC): mass spectrum, m/z 236 (M^+); IR (neat) ν_{max} 3420 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–1.8 (m, 8, H_{sat}), 2.1–2.4 (m, 2, H_{al}), 3.9 (m, 4, H_{ket}), 4.0 (s, 2, $H_{\alpha-OH}$), 5.6–5.8 (m, 3, H_{vin}).

2-(Bromomethyl)spiro[5.5]undeca-1,3-dien-7-one Ethylene Ketal (26). A solution of the hydroxy ketal **25** (4.8 g) and pyridine (2.25 g) in acetonitrile (10 mL) was added dropwise at 0 °C to a stirred mixture made of PPh_3 (10.6 g), Br_2 (6.4 g), and pyridine (1.15 g) in acetonitrile (30 mL). After another 15 min the mixture was filtered, the filtrate was flashed off, and the residue was chromatographed on silica gel. Fast elution (petroleum ether/

(13) The configuration of the hydroxyl group was not determined, although chemical rationale would indicate a syn (endo) configuration. Cf.: Dilling, W. L.; Plepys, R. A. *J. Org. Chem.* **1970**, *35*, 2971.

(14) Ashkenazi, P.; Scharf, G.; Fuchs, B.; Ginsburg, D. *Tetrahedron* **1977**, *33*, 1345.

Table I. Percent Yield with Time

	time, h					
compd	0.25	1	14	20	37	60
28	90	73	43	39	34	31
29	0	7	27	32	40	46
30	7	19	30	28	25	23

CH_2Cl_2, 4:1) gave the bromide **26**: 3 g (50%); mass spectrum, m/z 298, 300 (M^+); IR (neat) ν_{max} 790 cm^{-1} (C–Br); ^1H NMR (CCl_4) δ 1.2–1.7 (m, 8, H_{sat}), 2.1–2.4 (m, 2, H_{al}), 3.85 (m, 6, $H_{\alpha\text{-}O}$ and $H_{\alpha\text{-}Br}$), 5.6–5.85 (m, 3, H_{vin}).

2-Methylspiro[5.5]undeca-1,3-dien-7-one Ethylene Ketal (27). A solution of the bromide **26** (3 g) in dry tetrahydrofuran (20 mL) was added at 0 °C to a stirred suspension of $LiAlH_4$ (0.38 g) in THF (50 mL). After another hour at room temperature, the excess LiAlH was destroyed by careful addition of saturated aqueous NH_4Cl followed by 15% aqueous H_2SO_4 until pH 7. The reaction mixture was dried on $MgSO_4$ and filtered, the solvent was removed, and the residue was chromatographed on silica gel. Elution with petroleum ether/CH_2Cl_2 (5:1) gave the ketal **27**: 2 g (90% yield); mass spectrum, m/z 220 (M^+); ^1H NMR (CCl_4) δ 1.2–1.7 (m, 8, H_{sat}), 1.75 (s, 3, H_{Me}), 2.3 (m, 2, H_{al}), 3.9 (m, 4, H_{ket}), 5.4 (s, 1, H_{vin}), 5.7 (m, 2, H_{vin}).

Deketalization of 27. A suspension of silica gel (5 g) and 1% aqueous H_2SO_4 (2 mL) in CH_2Cl_2 (15 mL) was stirred for 10 min, after which a solution of the ketal **27** (1.1 g) in CH_2Cl_2 (2 mL) was added. The reaction was complete after 12 h (GLC monitoring). The mixture was filtered and the solvent removed to give a crude product, which was purified by column chromatography (SiO_2; CH_2Cl_2/petroleum ether, 3:7), whereby small amounts of the starting material and of **30** (vide infra) were eluted first, followed by the pure keto diene **28**: (81%; mass spectrum, m/z 176 (M^+); IR (neat) ν_{max} 1710 cm^{-1} (CO); UV (cyclohexane) λ_{max} 264 nm (ϵ 3300), 312 (300); ^1H NMR ($CDCl_3$) δ 1.75 (d, 3, H_{Me}) 1.5–1.9 (m, 8, H_{sat}), 2.2–2.8 (m, 2, H_{al}) 5.5 (m, 1, H_{vin}) 5.7 (m, 2, H_{vin}).

The *N*-phenylmaleimide adduct of **28** was prepared: mp 145–148 °C; mass spectrum, m/z 349 (M^+).

Acid-Catalyzed Isomerization of 28. A typical isomerization procedure of **28** is as follows. The ketone **28** (100 mg) in CCl_4 (1.5 mL) was treated with 0.1 mL of trifluoroacetic acid (TFA), and the reaction was monitored by GLC to give the results shown in Table I.

The composition of the product mixture is strongly dependent on the reaction conditions. This is exemplified on the following preparative procedures.

2-Methylenespiro[5.5]undec-3-en-7-one (30). The ketone **28** (300 mg) was added with stirring to suspension of silica gel (6 g) which had been treated with 30% H_2/SO_4 (2 mL) in CH_2Cl_2 (15 mL). After another 12 h of being stirred at room temperature, the mixture was filtered and the solvent removed. The crude residue (250 mg) had a composition (GLC) of 50:10:40 **28/29/30**. It was dissolved in benzene (10 mL), *N*-phenylmaleimide (NPM, 200 mg) was added, and the reaction mixture was refluxed for 48 h (to remove the cyclohexadiene derivatives as NPM adducts). The solvent was evaporated and the residue (400 mg) chromatographed on silica gel. Elution with petroleum ether gave 60 mg (20%) of the methylene derivative **30**: mass spectrum, m/z 176 (M^+); IR (neat) ν_{max} 3080 (=CH_2), 1705 cm^{-1} (CO); UV (cyclohexane) λ_{max} 233 nm (ϵ 7700); ^1H NMR ($CDCl_3$) δ 1.5–2.0 (m, 6, H_{sat}), 2.0–2.7 (m, 6, H_{al}), 4.87 (m, 2, H_{met}), 5.7 (dt, 1, H_{vin}), 6.1 (dt, 1, H_{vin}).

4-Methylspiro[5.5]undeca-1,3-dien-7-one (29). A solution of the ketone **28** (1.05 g) and TFA (1 g) in carbon tetrachloride (20 mL) was stirred for 48 h at room temperature. After addition of K_2CO_3 (4 g) with stirring and subsequent filtering, the solvent was removed to give a crude product (900 mg) having a composition (GLC) of 28:52:20 **28/29/30**. Chromatography on silica gel gave, on elution with CH_2Cl_2/petroleum ether (1:5) the product **29**: 300 mg (30%); mass spectrum, m/z 176 (M^+); IR (neat) ν_{max} 1708 cm^{-1} (CO); UV (cyclohexane) λ_{max} 268 nm (ϵ 3660), 310 (400); ^1H NMR ($CDCl_3$) δ 1.5–2.0 (m, 8, H_{sat}), 2.0–2.8 (m, 4, H_{al}) 5.27 (dt, 1, H_{vin}), 5.56 (d, 1, H_{vin}), 5.94 (dd, 1, H_{vin}).

Further elution provided the 2-methylene isomer **30**, followed by the starting ketone **28**. Both were usually reequilibrated as above to improve the yield of **29**.

Catalytic Hydrogenation of the Ketone 28. The ketone **28** (176 mg) in cyclohexane (10 mL) was hydrogenated in the presence of 10% Pd/C (20 mg) until no more absorption occurred. After the mixture was filtered and the solvent removed, the residue contained, as expected, two stereoisomeric 8-methylspiro[5.5]-undecan-1-ones in a 7:3 ratio (GLC): mass spectrum, m/z 180 (M^+); IR ν_{max} 1705 cm^{-1} (CO); UV (cyclohexane) λ_{max} 299 nm (ϵ 20); ^1H NMR (CCl_4) δ 0.82, 0.85 (d, 3, H_{Me}), 1.3–2.3 (mm, 17, H_{sat}).

The same products were obtained from the hydrogenation of a mixture of the cycloaddition products of 2-methylenecyclohexanone (**6**) with piperylene along with two other isomers, proving the poor regioselectivity of the cycloaddition.

Registry No. 4a, 2931-31-9; **4b**, 2931-32-0; **11**, 4576-45-8; **12**, 4576-44-7; **13**, 82390-15-6; **14**, 82390-16-7; **15**, 75197-04-5; **16**, 75107-71-0; **17**, 68752-08-9; **17**–*N*-phenylmaleimide adduct, 82390-29-2; **18**, 7353-75-5; **19**, 82390-17-8; **20**, 82390-30-5; **21**, 82390-18-9; **22**, 82390-19-0; **23**, 82390-20-3; **24**, 82390-21-4; **25**, 82390-22-5; **26**, 82390-23-6; **27**, 82390-24-7; **28**, 82390-25-8; **28**–*N*-phenylmaleimide adduct, 82390-26-9; **29**, 82390-27-0; **30**, 82390-28-1.