Table II. MINDO/3 Geometries and Relative Energies for 3–5 Isomers[a]

species	$r(C_1C_3)$	$r(C_1C_2)$	$\angle C_1C_2C_3$	ΔH_f	rel E
3, $n = 3$	1.681[b]	1.424[b]	72.3[b]	230.3	0.0
3, $n = 4$	1.864	1.401	83.4	212.8	0.0
3, $n = 5$ exo	2.155	1.390	89.6	193.6	0.0
3, $n = 5$ endo	2.107	1.391	101.6	195.7	2.1
4, $n = 3$	2.401[b]	1.395[b]	118.7[b]	182.6	47.7[c]
4, $n = 4$	2.487	1.394	126.2	175.2	37.6
4, $n = 5$	2.555	1.393	132.9	169.2	24.4
5, C_s endo,exo	2.248	1.413	105.4	194.5	0.0
5, C_s endo,endo	2.266	1.411	106.8	195.2	0.7
5, C_s exo,exo	2.236	1.411	104.8	194.5	0.0
5, C_{2v} endo,endo	1.636	1.452	68.6	210.1	15.6
5, C_{2v} exo,exo	1.625	1.455	67.9	209.9	15.4

[a] Distance in angstroms, angles in degrees, energies in kilocalories/mole. "Exo" and "endo" refer to ring conformations. [b] Compare these values with the ab initio geometries in Table I. [c] The ab initio energy difference is 42.1 kcal/mol using the MP2/6-31G*//6-31G* energy for **3**, $n = 3$ (−232.85202) and the MP2/6-31G*//3-21G value for **4**, $n = 3$ (−232.91916). As expected,[8] higher values are obtained when electron correlation corrections are not included (i.e., at 3-21G//3-21G, $\Delta = 64.6$; 6-31G*, $\Delta = 60.1$ kcal/mol).

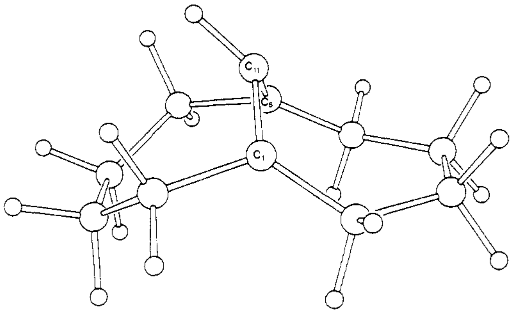

Figure 2. MINDO/3 geometry of the bicyclo[4.4.1]undecyl cation (**5**, R = H, C_s, endo, exo). The hydrogen at C_{11} is bent 37° out of the $C_1C_{11}C_6$ plane.

4 (n = 3–6), as well as by the model calculations on $C_3H_5^+$,[6] the larger systems are more flexible and allow a greater degree of opening and a closer approach to the allyl-type structure. However, in all these "partially opened" species (**4**) the disrotatory twisting of the terminal allyl groups produces a strong bending of the hydrogen bound to the central carbon out of the plane defined by the three neighboring carbons.[6]

The MINDO/3 calculations have inherent limitations for systems of this type (cyclopropane strain energies are too low,[9] and the degree of ring opening in **4** (n = 3) has proceeded to a lesser extent than indicated by the ab initio results), but the expected trend of relative energies between the corresponding **3** and **4** isomers is given nicely (Table II; note the good agreement between the energy difference between **3** and **4** (n = 3) and that at the highest ab initio level). This trend corresponds to the observed relative solvolysis rates in the exo and endo series.[2]

The ^{13}C NMR spectrum of **5** (R = CH_3) shows the two six-membered rings to be unsymmetrical.[7] That this is due to the bending of the C_{11}-methyl group out of the $C_1C_6C_{11}$ plane is confirmed by MINDO/3 calculations, which show (Table II, Figure 2) the C_s conformations of **5** (R = H) to be about 15 kcal/mol lower than the cyclopropyl cation (C_{2v}) forms (with the C_{11}-hydrogen in the $C_1C_6C_{11}$ plane).

Acknowledgment. Dedicated to Prof. Dr. Ulrich Schöllkopf on the occasion of his 60th birthday. We thank the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the CONVEX Corporation for support, the last through assistance in purchase of a CONVEX C1 computer on which the calculations were carried out.

Registry No. **3** (n = 3), 36348-18-2; **3** (n = 4), 38892-84-1; **3** (n = 5), 113857-81-1; **5** (R = CH_3), 63734-87-2; **5** (R = H), 113892-34-5.

Synthetic Application of Photoinduced Single Electron Transfer Reactions: A Convenient Synthetic Approach for the 2,2-Dimethyl-2*H*-chromene System[1]

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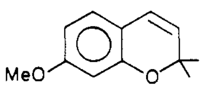
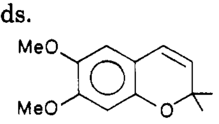
Ever since the visualization of precocene I and II (**1a** and **1b**) as antijuvenile hormone active compounds, isolated from *Ageratum houstonianum*,[2] several analogues of precocenes have been synthesized.[3] The 2,2-dimethyl-2*H*-benzopyran system has been noticed as parent molecule for all of these compounds.



1a



1b

Since these compounds represent the first insect endocrine antagonist to be discovered and appear to hold promise in the future development of insect control agents, a convenient synthetic approach is required. The synthetic procedures known so far are rather cumbersome and often end up in poor yields.[4]

We have reported[5] the photocyclization of substituted cinnamic acids to corresponding coumarins initiated by single electron transfer processes (Scheme I). In view of the mounting importance of the 2,2-dimethyl-2*H*-chromenes on the action of juvenile hormone antagonists, we herein extend the above observation for the synthesis of the 2,2-dimethyl-2*H*-chromene system.

Photolysis (>280 nm) of 3-aryl-1,1-dimethylprop-2-en-1-ol (**2a–f**), obtained by Grignard reaction of corresponding cinnamic acid esters, in the presence of 1,4-dicyanonaphthalene (DCN) generates an arene radical cation, which upon intramolecular nucleophilic attack by hydroxyl group on aromatic radical cation gave cyclized product (**3a–f**) as a single product in the identical manner as reported earlier.[5] The dissolved air present in the solvent system was enough to bring about the oxidation step. This reaction was also found to be slow in nitrogen atmosphere.[5,7] It must be noted here that most of the light was absorbed by **2a–f** under these experimental conditions. The chromenes **3a–f** were isolated by column chromatography and were characterized by IR, by ^1H NMR, and

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(1) RRL Communication No. 2072.

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0022-3263/88/1953-2364$01.50/0

Scheme I

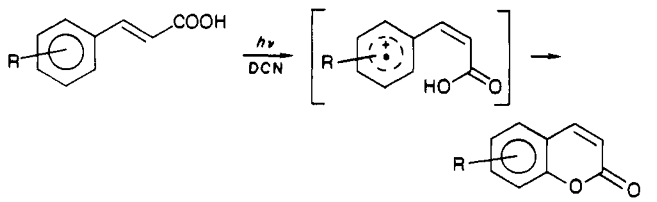
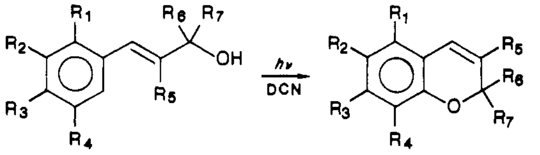


Table I. Photocyclization of 3-Aryl-1,1-dimethylprop-2-en-1-ol



2a-f 3a-f

entry	substituents	time of irradn, h	yield,[a] %	quantum yield[b]
a	$R_1 = R_2 = OMe, R_3 = R_4 = R_5 = H, R_6 = R_7 = Me$	2	62	2.96×10^{-2}
b	$R_1 = R_4 = OMe; R_2 = R_3 = R_5 = H, R_6 = R_7 = Me$	2	65	3.20×10^{-2}
c	$R_2 = R_3 = OMe, R_1 = R_4 = R_5 = H, R_6 = R_7 = Me$	3	60	2.10×10^{-2}
d	$R_2–R_3 = –OCH_2O–, R_1 = R_4 = H, R_5 = R_6 = R_7 = Me$	3	55	2.61×10^{-2}
e	$R_3 = OMe, R_1 = R_2 = R_4 = R_5 = H, R_6 = R_7 = H$	2.5	50	2.74×10^{-2}
f	$R_3 = OMe, R_1 = R_2 = R_4 = R_5 = H, R_6 = R_7 = Me$	2.5	60	2.5×10^{-2}

[a] Isolated yields. [b] Quantum yields were determined by using uranyl oxalate actinometry,[9] and chromenes were estimated by HPLC. [Column C_{18}; $MeOH/H_2O$ (25:75) monitoring at UV λ = 290 nm.]

by comparing with authentic samples made independently by a method similar to that reported earlier.[6] Longer irradiation resulted in the ring cleavage of chromenes.[8] The quantum efficiency of the reaction was estimated to be in the range of $\approx$0.03 (Table I).

Experimental Section

Melting points were determined in open capillaries with a Mettler FP51 melting point apparatus and are uncorrected. IR data were obtained on a Pye-Unicam SP3-200 spectrophotometer and ^{1}H NMR data on a Varian FT-80A spectrophotometer using tetramethylsilane as internal standard. HPLC analyses were carried out by utilizing a Shimadzu LC-6A system along with an SPD-6A UV variable-wavelength detector and C-R3A electronic integrator.

The alcohols **2a–f** were prepared by the Grignard reaction of methyl esters of cinnamic acids. A typical example for **2b** is described as follows.

A 100-mL three-necked flask equipped with a condenser, dropping funnel, magnetic stirring bar, and nitrogen inlet was charged with 1.95 g (0.08 g-atom) of magnesium turnings. The apparatus was flame-dried under a vigorous flow of nitrogen. After cooling to 30 °C, a few crystals of iodine and a solution of 4.75 mL (10.83 g, 76.3 mmol) of methyl iodide in dry ether were added over a period of 15 min. After the formation of the Grignard reagent, 8.05 g (36.3 mmol) of 2,5-dimethoxycinnamic acid methyl ester dissolved in dry ether was added and the reaction mixture was stirred for 30–40 min at 25 °C. The reaction mixture was quenched by adding 5% ammonium chloride solution (60 mL). The organic layer was removed, and the aqueous layer was extracted with ether (3 × 60 mL). The combined organic layer was washed with water followed by saturated sodium chloride solution and was dried over anhydrous sodium sulfate. After solvent removal under vacuum, the crude product was purified by column chromatography (silica gel, Merck 230–400 mesh) to give 6.40 g (79.5%) of **2b**: IR (neat, cm^{-1}) 3560–3200, 2960, 2840, 1590, 1480, 1220, 1040; ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 6 H), 2.36 (s, 1 H), 3.76 (s, 6 H), 6.32 (d, 1 H, J = 16.3 Hz), 6.74–6.99 (m, 4 H).

The ^{1}H NMR spectral characteristics for **2d** and **2e** are as follows. **2d**: δ 1.42 (s, 6 H), 1.87 (s, 3 H), 1.95 (s, 1 H), 5.93 (s, 2 H), 6.56 (s, 1 H), 6.74 (m, 3 H). **2e**: δ 1.58 (s, 1 H), 3.80 (s, 3 H), 4.29 (d, 2 H, J = 5.3 Hz), 6.30 (m, 1 H), 6.58 (d, 1 H, J = 16 Hz), 6.79–7.37 (m, 4 H).

The spectral pattern for the other alcohols (**2a**, **2c**, and **2f**) remains the same as that for **2b**.

General Irradiation Procedure. All the irradiations were carried out in an immersion-well type photoreactor using a 125-W mercury vapor lamp, surrounded by a Pyrex water jacket. The quantum yield was determined by using a Rayonet reactor equipped with Rayonet RUL 3000-Å lamps. A representative irradiation and workup procedure is given below.

2b (0.55 g, 2.47 mmol) and 0.08 g (0.45 mmol) of DCN were dissolved in 500 mL of an acetonitrile/water (80:20) mixture, and the reaction mixture irradiated for 2 h without removal of air from the solvent system. After the irradiation was stopped, solvent was removed under vacuum and the crude product was chromatographed over basic alumina with hexane/ethyl acetate (8.5:1.5) as eluent, which gave 0.35 g (65%) of **3b**: IR (neat, cm^{-1}) 2980, 2840, 1620, 1580, 1470, 1360, 1260, 930; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 6 H), 3.75 (s, 3 H), 3.78 (s, 3 H), 5.80 (d, 1 H, J = 12.6 Hz), 6.32 (d, 1 H, J = 12.6 Hz), 6.78–6.83 (m, 2 H).

The ^{1}H NMR spectral data for **3d** and **3e** are as follows. **3d**: δ 1.26 (s, 3 H), 1.33 (s, 3 H), 1.87 (s, 3 H), 5.91 (s, 2 H), 6.70 (m, 3 H). **3e**: δ 3.70 (s, 3 H), 4.31 (d, 2 H, J = 6.3 Hz), 5.70 (m, 1 H), 6.38 (d, 1 H, J = 11.7 Hz), 6.71–7.11 (m, 3 H).

The 2*H*-chromenes **3a**, **3c**, and **3f** show the same spectral pattern as **3b**.

Acknowledgment. We are thankful to Dr. A. V. Rama Rao for encouragement. A.K. is grateful to CSIR, New Delhi, for the award of Senior Research Fellowship.

Registry No. **2a**, 113949-25-0; **2b**, 113949-26-1; **2c**, 113949-27-2; **2d**, 113949-28-3; **2e**, 17581-85-0; **2f**, 57918-91-9; **3a**, 67015-34-3; **3b**, 113949-29-4; **3c**, 644-06-4; **3d**, 113949-30-7; **3e**, 18385-89-2; **3f**, 17598-02-6; 2,3-dimethoxycinnamic acid methyl ester, 15854-60-1; 2,5-dimethoxycinnamic acid methyl ester, 28689-10-3; 3,4-dimethoxycinnamic acid methyl ester, 5396-64-5; 2,3-methylenedioxy-α-methylcinnamic acid methyl ester, 7605-45-0; 4-methoxycinnamic acid methyl ester, 832-01-9.

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Synthesis of Spiro Heterocyclic Nitroxides Derived from 4-Piperidone

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Stable nitroxide free radicals[1] that carry substituents capable of further chemical reactions are of considerable interest as spin labels[2] and as possible contrast-enhancing

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(1) For a review, see: Keana, J. F. W. In *Spin Labeling in Pharmacology*; Holtzmann, J. L., Ed.; Academic: New York, 1984; Chapter 1.