in THF (35 mL) was added 1 N HCl (5.5 mL) under ice-cooling. The mixture was stirred at room temperature for 24 h and basified with 1 N $NaHCO_3$ (6 mL). The organic material was extracted with CH_2Cl_2 and dried (Na_2SO_4). After evaporation of the solvent, the residue was dissolved in MeOH (5 mL). To this solution was added 1 N HCl (1.5 mL) to adjust the pH to 4 and then $NaBH_3CN$ (0.100 g, 1.6 mmol). The mixture was stirred at room temperature for 6 h and poured into 2 N NaOH (20 mL). The organic material was extracted with ether, and the organic solution was dried (Na_2SO_4). The solvent was evaporated, and the residue was purified by Kugelrohr distillation (100 °C (20 mmHg)) to give a mixture of 1 and 8 (0.232 g, 63%, 1:8 = 70:30 by GLC).

b. Catalytic Reductive Cyclization with 10% Pd–C. A mixture of 7 (0.1660 g, 0.65 mmol), 1 N HCl (0.2 mL), and 10% Pd-C (0.056 g) in MeOH (10 mL) was stirred under an atmosphere of H_2 for 4 days. The catalyst was removed by filtration through Celite, and the filtrate was poured into 1 N NaOH (20 mL). The organic material was extracted with CH_2Cl_2, and the organic solution was dried (Na_2SO_4). The solvent was evaporated, and the residue was purified by Kugelrohr distillation (85 °C (15 mmHg)) to give 1 (0.076 g, 60%). The isomer 8 was not detected by GLC or NMR analysis. 1: MS *m/e* (rel intensity) 195 (M^+, 2), 180 (3), 138 (100); ^1H NMR ($CDCl_3$) δ 0.75–3.00 (br m, 22H), 1.13 (d, 3 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 67.2 (d), 62.8 (d), 60.2 (d), 39.8 (t), 36.0 (t), 31.1 (t), 30.5 (t), 29.8 (t), 29.4 (t), 25.1 (t), 23.0 (t), 22.9 (q), 13.9 (q). The ^{13}C NMR spectrum of 1 was identical with the reported one.[4e]

A Stereoselective Synthesis of (±)-*cis*-α-Irone

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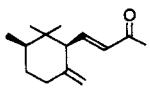
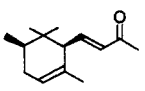
The main constituents of natural iris oil, *cis*-γ-irone (1), *cis*-α-irone (2), and *trans*-α-irone (3),[1,2] have received much attention from synthetic chemists for a long time. Most



1



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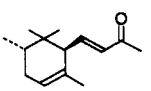
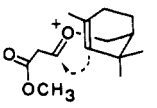


3

of the known[3] syntheses, however, produce mixtures of isomers that are difficult to separate on a preparative scale. So far, only one stereoselective approach has been described for 3,[4] but none for 1 and 2. We now report a stereoselective synthesis of (±)-*cis*-α-irone (2) from readily available[5] (2,2,4-trimethyl-3-cyclohexen-1-yl)methanol (4) in which the side chain is introduced by a conceptually novel method (Scheme I).

Addition of alcohol 4 to methyl propiolate in the presence of *N*-methylmorpholine[6] afforded the (*E*)-β-alkoxyacrylate 5 (88% yield). Upon exposure of 5 to catalytic amounts of methanesulfonic acid in dichloromethane at −10 °C, smooth cyclization to the 3-oxabicyclo[3.3.1]nonene derivative 6 occurred (yield 94%). For cleavage of the tetrahydropyran moiety, the bicyclic ester 6 was first hydrolyzed with aqueous base to the crystalline acid 7 (yield 78%), which was then treated with 2 equiv of LDA in THF at −70 °C, followed by warmup to 0 °C and quenching to give acid 8 in 88% yield after crystallization.[7] Making use of the hydroxymethyl group of 4, the side chain had thus been introduced in four steps with complete stereocontrol and simultaneous shift of the ring double bond. The synthesis was completed by first reducing the hydroxymethyl group of 8 via the corresponding mesylate 9, which was then treated with zinc and sodium iodide in refluxing DME[8] to give the crystalline acid 10 (yield 71%). Finally, reaction of 10 with methyllithium in diethyl ether afforded the title compound 2 in 89% yield. The (±)-*cis*-α-irone (2) thus obtained proved to be very pure; no other isomers could be detected by capillary GC or 400-MHz ^1H NMR analysis.

The key step of the above synthesis is the β-alkoxyacrylate–olefin cyclization reaction 5 → 6, which ensures the cis relationship of the substituents. This transformation most likely proceeds through the oxonium ion **a**.



a

The endo configuration[9] at C-4 in the cyclization product 6 points to a chairlike transition state with the carbomethoxymethyl group in a quasi-equatorial position. The corresponding transition state with this substituent in an axial position would suffer from a severe 1,3-diaxial interaction.

Except Johnson's pioneering work[10] on acetal–olefin cyclizations, which occur in an exocyclic mode with respect to the initiator and thus give carbocyclic products, oxonium ion initiated cyclizations have not received much attention. Recently, however, a number of papers[11] describe endocyclic acetal–olefin cyclizations leading to oxacyclic products. To the best of our knowledge, enol ethers have not been used previously as starter units in cationic olefin cyclizations.

In conclusion, *cis*-α-irone (2) has been stereoselectively synthesized for the first time via a novel β-alkoxyacrylate–olefin cyclization 5 → 6. Mechanistic details as

(1) (a) Rautenstrauch, V.; Ohloff, G. *Helv. Chim. Acta* **1971**, *54*, 1776; *Ibid.* **1972**, *55*, 2686. (b) Ohloff, G.; Otto, E.; Rautenstrauch, V.; Snatzke, G. *Helv. Chim. Acta* **1973**, *56*, 1874. (c) Rautenstrauch, V.; Willhalm, B.; Thommen, W.; Ohloff, G. *Helv. Chim. Acta* **1984**, *67*, 325.

(2) Krick, W.; Marner, F.-J.; Jaenicke, L. *Helv. Chim. Acta* **1984**, *67*, 318.

(3) (a) Takazawa, O.; Kogami, K.; Hayashi, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 389. (b) Kitahara, T.; Tanida, K.; Mori, K. *Agric. Biol. Chem.* **1983**, *47*, 581. (c) Comte, M.-T. Ph.D. Thesis, Strasbourg, 1983. (d) Miyashita, M.; Makino, N.; Singh, M.; Yoshikoshi, A. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1303. (e) Garnero, J.; Joulain, D. *Bull. Soc. Chim. Fr.* **1979**, *II*, 15. For synthetic activities in this field prior to 1980, see ref 4–9 in ref 4.

(4) Torii, S.; Uneyama, K.; Matsunami, S. *J. Org. Chem.* **1980**, *45*, 16.

(5) Jitkow, O. N.; Bogert, M. T. *J. Am. Chem. Soc.* **1941**, *63*, 1979. For the preparation of (*S*)-(−)-4, see: Wolleb, H.; Pfander, H. P. *Helv. Chim. Acta* **1986**, *69*, 646. Formally, with (*S*)-(−)-4 our synthesis would lead to (−)-*cis*-α-irone.[2]

(6) Winterfeldt, E.; Preuss, H. *Chem. Ber.* **1966**, *99*, 450.

(7) For an analogous transformation, see: Seebach, D.; Pohmakotr, M. *Helv. Chim. Acta* **1979**, *62*, 843.

(8) (a) Fujimoto, Y.; Tatsuno, T. *Tetrahedron Lett.* **1976**, *17*, 3325. (b) Kočovský, P.; Černý, V. *Collect. Czech. Chem. Commun.* **1979**, *44*, 246.

(9) Deduced by NOE difference spectroscopy ($CDCl_3$, 400 MHz); irradiation of the signal at 1.22 ppm (CH_3 at C-9) showed a 17% enhancement of the signal at 4.36 ppm (H at C-4).

(10) Johnson, W. S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 9.

(11) (a) Nishiyama, H.; Itoh, K. *J. Org. Chem.* **1982**, *47*, 2496. (b) Nishiyama, H.; Narimatsu, S.; Sakuta, K.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1982**, *459*. (c) Cockerill, G. S.; Kocienski, P. *J. Chem. Soc., Chem. Commun.* **1983**, 705. (d) Kay, I. T.; Williams, E. G. *Tetrahedron Lett.* **1983**, *24*, 5915. (e) Bunnelle, W. H.; Seamon, D. W.; Mohler, D. L.; Ball, T. F.; Thompson, D. W. *Tetrahedron Lett.* **1984**, *25*, 2653. (f) Melany, M. L.; Lock, G. A.; Thompson, D. W. *J. Org. Chem.* **1985**, *50*, 3925. (g) Cockerill, G. Kocienski, P.; Treadgold, R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2093. (h) Overman, L. E.; Castañeda, A.; Blumenkopf, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 1303.

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well as application of this reaction to the synthesis of various oxacyclic products will be reported elsewhere.

Experimental Section

Melting points were measured in open capillary tubes and are uncorrected. UV spectra were measured on a Beckman 25 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 681 spectrophotometer.

^1H and ^{13}C NMR spectra were determined on a Bruker AM 400 spectrometer. Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad.

Mass spectra (MS) were obtained on a Varian MAT CH-5 mass spectrometer.

Gas chromatography (GC) was performed on a Carlo Erba GC 6000 Vega Series instrument equipped with a SE-30 glass capillary column.

Elemental analyses were performed by the analytical division of F. Hoffmann-La Roche & Co. Ltd., Basle.

Commercial-grade reagents and solvents were used without further purification except as indicated below. Diethyl ether was distilled from $LiAlH_4$. Dichloromethane was distilled from P_2O_5. THF was distilled from sodium/benzophenone ketyl. Diisopropylamine was distilled from CaH_2. Butyllithium and methyllithium were titrated by the method of Kofron and Baclawski.[12]

Reactions sensitive to the atmosphere were conducted in oven-dried (130 °C) glassware under an atmosphere of dry nitrogen. Sensitive liquids and solutions were transferred via syringes and were introduced into the reaction flask through rubber septa. Column chromatography was performed at normal pressure with Merck silica gel 60 (230–400 mesh).

Methyl (2*E*)-3-[(2,2,4-Trimethyl-3-cyclohexen-1-yl)methoxy]-2-propenoate (5). To a solution of methyl propiolate (3.70 g, 44 mmol) in 40 mL of dry ether were added successively *N*-methylmorpholine (4.45 g, 44 mmol) and an ethereal solution (10 mL) of (2,2,4-trimethyl-3-cyclohexenyl)methanol (**4**) (6.17 g, 40 mmol).[5] The resulting mixture was stirred at room temperature under N_2 for 26 h, then poured onto 100 mL of 0.35 M aqueous acetic acid, and extracted with ether (2 × 200 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. Chromatography of the residual yellow oil on silica gel (75 g) with hexane/ethyl acetate (20:1) as eluent and distillation [Kugelrohr, 150 °C (0.4 mmHg)] afforded 8.40 g (88%) of *trans*-enol ether **5** as a colorless liquid. Later fractions of the chromatography showed (NMR) trace amounts of the *Z* isomer: IR (film) 1720 (sh), 1715, 1645, 1625, 1465, 1435, 1330, 1285, 1210, 1138, 1050, 970, 950 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 231 nm (4.22); ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (s, 3 H), 1.04 (s, 3 H), 1.38–1.50 (m, 1 H), 1.63 (br s, 3 H), 1.66–2.00 (m, 4 H), 3.63 (t, J = 9.5 Hz, 1 H), 3.70 (s, 3 H), 3.98 (dd, J = 4.5, 9.5 Hz, 1 H), 5.03 (m, 1 H), 5.22 (d, J = 12.6 Hz, 1 H), 7.62 (d, J = 12.6 Hz, 1 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 22.5 (t), 23.4 (q), 23.8 (q), 29.3 (t), 29.8 (q), 33.6 (s), 42.9 (d), 50.9 (q), 72.4 (t), 96.0 (d), 131.3 (s), 132.3 (d), 162.7 (d), 168.0 (s); MS (70 eV) m/z 238 (2, M^+), 206 (5), 137 (15), 121 (100), 96 (39), 95 (33), 93 (61), 81 (65). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.57; H, 9.53.

Methyl (6,9,9-Trimethyl-3-oxabicyclo[3.3.1]non-6-en-4-*endo*-yl)acetate (6). To a solution of enol ether **5** (2.39 g, 10 mmol) in 25 mL of dry CH_2Cl_2 at −20 °C was added methanesulfonic acid (0.4 mL, ca. 6 mmol, Fluka) dropwise over 1 min. The solution was warmed up to −5 °C under N_2, and stirring was continued at the same temperature until TLC indicated complete disappearance of the starting material (ca. 2 h). The reaction mixture was then poured onto 100 mL of a cold 0.25 M $KHCO_3$ solution and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. Distillation of the crude product [Kugelrohr, 130 °C (0.4 mmHg)] gave 2.25 g (94%) of a colorless oil (95% pure by capillary GC). An analytical sample was prepared by chromatography on silica gel with hexane/ethyl acetate (10:1) as eluent: IR (film) 1742, 1435, 1165, 1100, 1015, 820 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (s, 3 H), 1.22 (s, 3 H), 1.24–1.29 (m, 1 H), 1.56 (br s, 1 H), 1.72 (q, J = 2 Hz, 3 H), 2.10 (br d, J = 18.5 Hz, 1 H), 2.28–2.38 (m, 1 H), 2.33 (dd, J = 4.5, 15 Hz, 1 H), 2.44 (dd, J = 9, 15 Hz, 1 H), 3.59 (dd, J = 2, 11.5 Hz, 1 H), 3.69 (s, 3 H), 4.04 (dt, J = 11.5, 1.5 Hz, 1 H), 4.36 (ddd, J = 2, 4.5, 9 Hz, 1 H, OC*H*$CH_2CO_2CH_3$), 5.62 (m, 1 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 24.8 (q), 25.6 (q), 27.6 (q), 31.5 (t), 32.5 (s), 36.9 (d), 39.8 (t), 49.4 (d), 51.4 (q), 70.3 (d), 71.1 (t), 124.5 (d), 130.8 (s), 172.0 (s); MS (70 eV) m/z 238 (15, M^+), 206 (9), 165 (4), 134 (21), 121 (100), 105 (23), 93 (74). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.65; H, 9.43.

(6,9,9-Trimethyl-3-oxabicyclo[3.3.1]non-6-en-4-*endo*-yl)acetic Acid (7). To a solution of ester **6** (2.38 g, 10 mmol) in 6 mL of CH_3OH was added 25 mL of a 2.5 M solution of NaOH (62.5 mmol) in water. The resulting mixture was stirred at room temperature for 23 h and then acidified with 4 N HCl (16 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL) after saturation with NaCl. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. Crystallization from ethyl acetate/hexane afforded 1.75 g (78%) of acid **7** as white needles: mp 151–152 °C; IR ($CHCl_3$) 3500–2500 (br), 1745 (sh), 1713, 1170, 1095 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.96 (s, 3 H), 1.23 (s, 3 H), 1.25–1.30 (m, 1 H), 1.62 (br s, 1 H), 1.73 (q, J = 2 Hz, 3 H), 2.05 (br d, J = 18 Hz, 1 H), 2.30 (dd, J = 8.5, 15.5 Hz, 1 H), 2.30–2.40 (m, 1 H), 2.36 (dd, J = 5, 15.5 Hz, 1 H), 3.52 (dd, J = 2, 11.5 Hz, 1 H), 4.05 (dt, J = 11.5, 1.5 Hz, 1 H), 4.36 (ddd, J = 2, 5, 8.5 Hz, 1 H), 5.59 (m, 1 H); ^{13}C NMR (25 MHz, CD_3OD) δ 25.0 (q), 25.8 (q), 27.9 (q), 32.3 (t), 33.2 (s), 38.1 (d), 40.4 (t), 50.4 (d), 71.4 (d), 71.8 (t), 125.3 (d), 132.0 (s), 174.5 (s); MS (70 eV) m/z 224 (6, M^+), 206 (15), 164 (5), 134 (13), 121 (100), 105 (27), 93 (58). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.49; H, 8.88.

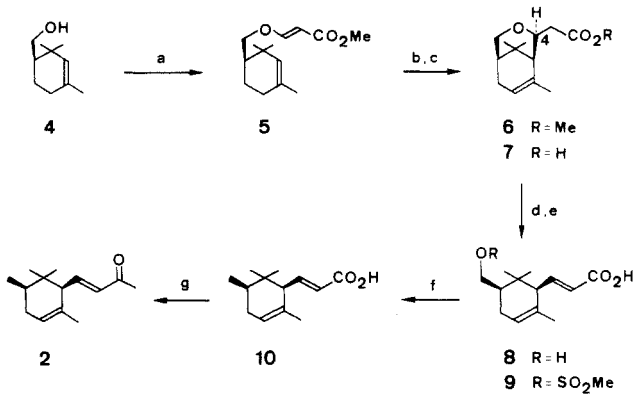
***cis*(1′,5′)-(2*E*)-3-[2′,6′,6′-Trimethyl-5′-(hydroxymethyl)-2′-cyclohexen-1′-yl]-2-propenoic Acid (8).** A solution of diisopropylamine (3 mL, 21 mmol) in 50 mL of dry THF was cooled to 0 °C under N_2 while *n*-butyllithium (12 mL of a 1.25 M solution in hexane, 15 mmol) was added over 5 min. The mixture was stirred at 0 °C for 12 min and then cooled to −70 °C. A solution of **7** (1.73 g, 7.71 mmol) in 15 mL of dry THF was added with a syringe over 4 min. The resulting solution was vigorously stirred at −70 °C for 1 h; the colloidal mixture was then warmed up to −5 °C during 90 min and kept another 30 min at −5 °C. After addition of HCl (20 mL of a 2 N aqueous solution), the mixture was extracted with ether (2 × 200 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. Crystallization from ethyl acetate/hexane gave 1.52 g (88%) of pure acid **8** as white crystals: mp 140–141 °C; IR (Nujol) 3500–2400 (br), 3300, 1680, 1670 (sh), 1630, 1460, 1375, 1310, 1280 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.79 (s, 3 H), 0.97 (s, 3 H), 1.46–1.53 (m, 1 H), 1.54 (br s, 3 H), 1.82–1.94 (m, 1 H), 2.20–2.30 (m, 1 H), 2.59 (br d, J = 11 Hz, 1 H), 3.35 (dd, J = 8.5, 10.5 Hz, 1 H), 3.79 (dd, J = 4.5, 10.5 Hz, 1 H), 5.57 (m, 1 H), 5.86 (d, J = 15.5 Hz, 1 H), 6.71 (dd, J = 11, 15.5 Hz, 1 H); ^{13}C NMR (25 MHz, CD_3OD) δ 17.9 (q), 23.0 (q), 27.4 (q), 27.5 (t), 35.6 (s), 46.7 (d), 56.5 (d), 63.4 (t), 123.1 (d), 125.7 (d), 132.8 (s), 150.8 (d), 169.1 (s); MS (70 eV) m/z 206 (3, M^+), 138 (35), 93 (100). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.51; H, 8.90.

***cis*(1′,5′)-(2*E*)-3-[2′,6′,6′-Trimethyl-5′-[[(methylsulfonyl)oxy]methyl]-2′-cyclohexen-1′-yl]-2-propenoic Acid (9).** To a suspension of **8** (310 mg, 1.38 mmol) in 12 mL of dry CH_2Cl_2 was added pyridine (3 mL, 37 mmol). The resulting solution was cooled to 0 °C, and methanesulfonyl chloride (0.5 mL, ca. 6 mmol) was added dropwise. This mixture was stirred at 0 °C under N_2 for 3 h, and then 3 mL of aqueous pyridine (1:1) was added. The solution was stirred at room temperature for 90 min, then acidified with dilute HCl, and extracted with CH_2Cl_2 (2 × 100 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated in vacuo. Crystallization of the residue from CH_2Cl_2/hexane afforded 392 mg (94%) of mesylate **9** as white crystals: mp 125 °C; IR ($CHCl_3$) 3500–2500 (br), 1697, 1648, 1358, 1336, 1172, 970, 945 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (s, 3 H), 1.00 (s, 3 H), 1.56 (br s, 3 H), 1.79–1.99 (m, 2 H), 2.20–2.30

(12) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

(13) Our sample has been compared (capillary GC) with Irone alpha (Givaudan), which contains ca. 43% *cis*-α-, 51% *trans*-α-, and 4% β-irone, and also with a mixture of *cis,trans*-γ-irone, provided by the late Professor F. Leyendecker (Strasbourg).

Scheme I[a]



[a] Reagents and conditions: (a) methyl propiolate, *N*-methylmorpholine, Et_2O, 25 °C; (b) CH_3SO_3H, CH_2Cl_2, −5 °C; (c) NaOH, H_2O, CH_3OH, 25 °C; (d) 2 equiv of LDA, THF, −70 °C → 0 °C, then H_3O^+; (e) CH_3SO_2Cl, pyridine, CH_2Cl_2, 0 °C; (f) zinc, NaI, DME, reflux; (g) CH_3Li, Et_2O, reflux.

(m, 1 H), 2.64 (br d, J = 11 Hz, 1 H), 3.02 (s, 3 H, CH_3SO_3), 4.06 (dd, J = 9, 10 Hz, 1 H), 4.42 (dd, J = 4.5, 10 Hz, 1 H), 5.56 (m, 1 H), 5.92 (d, J = 15.5 Hz, 1 H), 6.86 (dd, J = 11, 15.5 Hz, 1 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 17.1 (q), 22.7 (q), 26.3 (t), 26.7 (q), 34.9 (s), 37.2 (q), 42.9 (d), 55.3 (d), 71.0 (t), 121.6 (d), 124.6 (d), 131.9 (s), 151.2 (d), 170.9 (s); MS (70 eV) m/z 206 (6), 138 (25), 93 (100), 79 (17), 41 (18). Anal. Calcd for $C_{14}H_{22}O_5S$: C, 55.61; H, 7.33; S, 10.60. Found: C, 55.58; H, 7.29; S, 10.66.

***cis*(1′,5′)-(2*E*)-3-(2′,5′,6′,6′-Tetramethyl-2′-cyclohexen-1′-yl)-2-propenoic Acid (10).** A mixture of mesylate **9** (303 mg, 1 mmol), sodium iodide (600 mg, 4 mmol), zinc (520 mg, 8 mmol, powder), and 6 mL of dimethoxyethane was heated in an oil bath at 90 °C for 4 h. After cooling, the reaction mixture was filtered through Celite and the flask rinsed with ether and water. The combined filtrates were acidified with dilute hydrochloric acid and extracted with ether (2 × 150 mL). The organic extracts were dried ($MgSO_4$), filtered, and concentrated in vacuo. Filtration through a pad of silica gel (5 g) with pentane/ether (1:1) as eluent afforded 158 mg (76%) crystalline **10**. An analytical sample was prepared by recrystallization from pentane at −30 °C: mp 115–116 °C; IR ($CHCl_3$) 3500–2500 (br), 1695, 1645 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.71 (s, 3 H), 0.86 (d, J = 7 Hz, 3 H), 0.87 (s, 3 H), 1.42–1.52 (m, 1 H), 1.53 (m, 3 H), 1.68–1.81 (m, 1 H), 1.89–1.99 (m, 1 H), 2.59 (br d, J = 11 Hz, 1 H), 5.51 (m, 1 H), 5.89 (d, J = 15.5 Hz, 1 H), 6.95 (dd, J = 11, 15.5 Hz, 1 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 15.1 (q), 15.4 (q), 22.7 (q), 26.7 (q), 32.0 (t), 35.9 (s), 38.1 (d), 56.0 (d), 123.0 (d), 123.9 (d), 131.8 (s), 152.9 (d), 171.6 (s); MS (70 eV) m/z 208 (6, M^+), 138 (41), 123 (8), 93 (100). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.92; H, 9.66.

***cis*(1′,5′)-(3*E*)-4-(2′,5′,6′,6′-Tetramethyl-2′-cyclohexen-1′-yl)but-3-en-2-one (*cis*-α-Irone, 2).** A solution of acid **10** (168 mg, 0.81 mmol) in 10 mL of dry ether under N_2 was cooled to −55 °C, and methyllithium (1.3 mL of a 1.6 M solution in ether, ca. 2 mmol) was added with vigorous stirring over 1 min. The homogeneous solution was stirred 5 min at −55 °C, warmed up to 0 °C during 20 min, and then refluxed for 90 min. The heterogeneous reaction mixture was cooled and then transferred with a dry syringe to a vigorously stirred solution of 0.1 N HCl (25 mL). [The flask was rinsed with ether (2 × 3 mL) under N_2 with a dry syringe.] After 5 min, the mixture was extracted with ether (3 × 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residual oil was chromatographed on silica gel (5 g) with pentane/ether (11:1) as eluent. The appropriate fractions were combined and distilled [Kugelrohr, 130 °C (1 mmHg)] to give 148 mg (89%) of (±)-*cis*-α-irone (**2**) as a colorless liquid. No other irone isomers could be detected by capillary GC and ^1H NMR (400 MHz).[13] ^1H NMR (400 MHz, $CDCl_3$) δ 0.71 (s, 3 H), 0.86 (s, 3 H), 0.87 (d, J = 7 Hz, 3 H), 1.43–1.51 (m, 1 H), 1.53 (m, 3 H), 1.69–1.81 (m, 1 H), 1.90–2.00 (m, 1 H), 2.28 (s, 3 H, CH_3CO), 2.55 (br d, J = 11 Hz, 1 H), 5.52 (m, 1 H), 6.12 (d, J = 16 Hz, 1 H), 6.65 (dd, J = 11, 16 Hz, 1 H), MS (70 eV) m/z 206 (6, M^+), 191 (2), 136 (41), 121 (100), 109 (10), 93 (73), 91 (17), 77 (14), 43 (39).

Electronic Structure of 2,4-Methano-2,4-didehydroadamantane: A [3.1.1]Propellane. Photoelectron and Semiempirical Studies

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Since the first syntheses of small propellanes[1] this intriguing class of compounds has been intensively investigated, both experimentally[2-8] and theoretically.[2,3,9,10] Recently, a photoelectron spectroscopic study (PE) of the smallest homologue of the propellane family, [1.1.1]propellane (**1**), was carried out.[11] The most remarkable feature of its PE spectrum was the appearance of an extremely narrow ionization band corresponding to the highest occupied molecular orbital of **1**, indicating that electron ejection from the HOMO leads only to a minute change in the geometry of the molecular frame. Lack of a geometry change accompanying the transition $1 \rightarrow 1^+$ might be, as pointed out in ref 11, a consequence of the nonbonding or slightly antibonding character of the HOMO of **1**, but it could also be due to the rather tight cage structure of **1**, which makes geometry distortions very difficult. The results of recent ab initio[4] and PRDDO[12]

(1) Wiberg, K. B.; Burgmaier, G. J. *Tetrahedron Lett.* **1969**, 317. Wiberg, K. B.; Hiatt, J. E.; Burgmaier, G. J. *Ibid.* **1968**, 5855. Gassman, P. G.; Topp, A.; Keller, J. W. *Ibid.* **1969**, 1093.
(2) Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379.
(3) Reviews: Ginsburg, D. *Propellanes*; Verlag Chemie: Weinheim, 1975 (and its sequels I and II; Department of Chemistry, Technion: Haifa, 1981 and 1985, respectively).
(4) Wiberg, K. B.; Dailey, W. P.; Walker, F. H.; Waddell, S. T.; Crocker, L. S.; Newton, M. *J. Am. Chem. Soc.* **1985**, *107*, 7247.
(5) Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 7257.
(6) Chakrabarti, P.; Seiler, P.; Dunitz, J. D.; Schlüter, A.-D.; Szeimies, G. *J. Am. Chem. Soc.* **1981**, *103*, 7378.
(7) Mlinarić-Majerski, K.; Majerski, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7389. Mlinarić-Majerski, K.; Majerski, Z. *Ibid.* **1980**, *102*, 1418.
(8) [1.1.1]Propellane: Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239. Semmler, K.; Szeimies, G.; Belzner, J. *Ibid.* **1985**, *107*, 6410. Wiberg, K. B.; Waddell, S. T.; Laidig, K. *Tetrahedron Lett.* **1986**, *27*, 1553. [2.1.1]Propellane: Wiberg, K. B.; Walker, F. K.; Pratt, W. E.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 3638. [2.2.1]Propellane: Walker, F. H.; Wiberg, K. B.; Michl, J. *Ibid.* **1982**, *104*, 2056. [3.1.1]Propellane: Gassman, P. G.; Proehl, G. S. *Ibid.* **1980**, *102*, 6862. Vinković, V.; Majerski, Z. *Ibid.* **1982**, *104*, 4027. Majerski, Z.; Mlinarić-Majerski, K. *J. Org. Chem.* **1986**, *51*, 3219. Majerski, Z.; Mlinarić-Majerski, K.; Meić, Z. *Tetrahedron. Lett.* **1980**, *21*, 4117. Baumgart, K.-D.; Harnisch, H.; Szeimies-Seebach, U.; Szeimies, G. *Chem. Ber.* **1985**, *118*, 2883. Szeimies-Seebach, U.; Szeimies, G.; van Meersche, M.; Germain, G.; Declercq, J.-P. *Nouv. J. Chim.* **1979**, *3*, 357. Reference 6. Reference 7. [2.2.2]-Propellane: Eaton, P. E.; Temme, G. H., III. *J. Am. Chem. Soc.* **1973**, *95*, 7508. [3.2.1]Propellane: Gassman, P. G.; Armour, E. A. *Tetrahedron Lett.* **1971**, 1431. Wiberg, K. B.; Burgmaier, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 7396. Wiberg, K. B.; Burgmaier, G. J.; Shen. K.; La Placa, S. J.; Hamilton, W. C.; Newton, M. D. *Ibid.* **1972**, *94*, 7402. Wiberg, K. B.; Connon, H. A.; Pratt, W. E. *Ibid.* **1979**, *101*, 6970. Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *Ibid.* **1977**, *99*, 2297. Aue, D. H.; Reynolds, R. N. *J. Org. Chem.* **1974**, *39*, 2315. Reference 1. [4.1.1]Propellane: Hamon, D. P. G.; Trenerry, V. C. *J. Am. Chem. Soc.* **1981**, *103*, 4962. Szeimies-Seebach, U.; Szeimies, G. *Ibid.* **1978**, *100*, 3966. Declercq, J.-P.; Germain, G.; van Meersche, M. *Acta Crystallogr., Sect. B.* **1978**, *34*, 3472.
(9) For reviews, see: (a) Newton, M. D. *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol 4, p 223. (b) Epiotis, N. D. *Unified Valence Bond Theory and Electronic Structure. Applications*; Springer Verlag: New York, 1983; pp 372–390.
(10) (a) Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227. (b) Jackson, J. E.; Allen, L. C. *Ibid.* **1984**, *106*, 591. (c) Stohrer, W.-D.; Hoffmann, R. *Ibid.* **1972**, *94*, 779. (d) Newton, M. D.; Schulman, J. M. *Ibid.* **1972**, *94*, 773. (e) Zilberg, S. P.; Ioffe, A. I.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 358.
(11) Honegger, E.; Huber, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *J. Am. Chem. Soc.* **1985**, *107*, 7172.

0022-3263/87/1952-2098$01.50/0 © 1987 American Chemical Society