Although the α-methoxy esters proved to be reasonably stable, they decomposed slowly during storage to complex mixtures. Column chromatography of the crude product mixture was unsuccessful on a few occasions and afforded little or no characterizable material. This leads us to believe that the isolated yields may be artificially low, owing to decomposition of the sensitive products on the silica gel.

These results demonstrate that the ortho ester Claisen rearrangement tolerates the presence of a heteroatomic substituent (OCH_3) directly on the allyl vinyl ether framework. While heteroatomic groups are present in the work of Johnson[4] (Cl) and Rauscher[6,7] (SePh, OCH_3), they are present in positions remote to the rearranging framework.

Experimental Section

Infrared spectra were determined on a Perkin-Elmer 137 sodium chloride spectrophotometer. ^1H NMR spectra were determined in $CDCl_3$, using a Varian EM 360L NMR spectrometer and were reported in parts per million relative to tetramethylsilane. Mass spectrometry was performed on a Finnigan 3200 GC/MS system. Vapor-phase chromatograms were obtained on a Varian Aerograph Series 1200 fitted with a $^1/_8$ in. × 12 ft 5% SE-30 on Gas Chrom Z column and a flame-ionization detector. Thin-layer chromatography was performed on precoated TLC sheets, using silica gel as supplied by E. Merck (no. 5575) and a solvent mixture of 7:2:1 of hexane–dichloromethane–acetone. Catalog 7734 silica gel 60 (particle size 0.063–0.2000 mm), available from Merck, was used as a support in column chromatography.

General Procedures for Ortho Ester Claisen Rearrangement. Method A. This procedure is a modification of Johnson's.[3] The allylic alcohol (5 mmol) and propionic acid (2 drops) were dissolved in trimethyl methoxyorthoacetate[9] (10 mmol). The solution was heated to 100–125 °C (depending on the boiling point of the alcohol) in a short-path distillation apparatus for 18 h, and methanol was collected in the receiving flask as it was formed. After cooling, the reaction mixture was diluted with ether and washed with saturated $NaHCO_3$, water, and brine. After the solution was dried ($MgSO_4$) and concentrated under reduced pressure, VPC analysis indicated the presence of the desired ester, trimethyl methoxyorthoacetate, the allylic alcohol, and 5–10 minor unidentified components. The esters were purified by column chromatography on silica gel, using a step gradient (0%, 1%, 2%, 5%, 10%, 20%, total volume = 600 mL) of ether/hexane mixtures as eluants. The remaining ortho ester is eluted in the early fractions (1–10, 0–1% Et_2O/hexane), the product is eluted in the middle fractions (20–40, 5–10% Et_2O/hexane), and the residual allylic alcohol generally eluted in the later fractions (>40, 20% Et_2O/hexane).

Method B. The allylic alcohol (5 mmol) and propionic acid (2 drops) were dissolved in trimethyl methoxyorthoacetate (10 mmol) and the solution was sealed in a 25-mL pressure reaction bottle (Cal-Glass, no. LG3921). After being heated at 125 °C for 18 h, the reaction mixture was worked up and purified as described in method A.

Methyl 2-Methoxy-4-pentenoate (2a). Methyl 2-methoxy-4-pentenoate was prepared from allyl alcohol in yields of 28% (method A) and 25% (method B). The desired product was eluted in fractions 43–50 (10 mL each, 10% ether/hexane): IR (film) ν_{max} 2900, 1730, 1640, 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.50 (t, 2 H, J = 6.0 Hz), 3.38 (s, 3 H), 3.73 (s, 3 H), 3.85 (t, 1 H, J = 6.0 Hz), 5.00–5.20 (m, 2 H), 5.50–6.17 (m, 1 H); TLC R_f 0.51; VPC (100 °C) t_R 2.45 min; mass spectrum, m/e 144, 112 ($M^+ - CH_3OH$), 103, 85 (100).

Methyl 2-Methoxy-3-methyl-4-pentenoate (2b). Methyl 2-methoxy-3-methyl-4-pentenoate was prepared from crotyl alcohol in yields of 25% (method A) and 20% (method B). The desired product was eluted in fractions 28–36 (12 mL each, 5% ether/hexane): IR (film) ν_{max} 2900, 1730, 1630, 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06/1.08 (d/d, 3 H, J = 7.0 Hz, 1:1 mixture of diastereomers), 2.57 (m, 1 H), 3.37 (s, 3 H), 3.67 (d, 1 H, J = 7.0 Hz), 3.73 (s, 3 H), 4.83–5.23 (m, 2 H), 5.40–6.00 (m, 1 H); TLC R_f 0.56; VPC (100 °C) t_R 3.78 min; mass spectrum, m/e 158, 126 ($M^+ - CH_3OH$), 104, 103, 99 (100).

Methyl 2-Methoxy-3-phenyl-4-pentenoate (2c). Methyl 2-methoxy-3-phenyl-4-pentenoate was prepared from cinnamyl alcohol in a yield of 55% (method A). The desired product was eluted in fractions 26–45 (12 mL each, 10% ether/hexane): IR (film) ν_{max} 2900, 1730, 1630, 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.30/3.50 (s/s, 3 H, 1:1 mixture of diastereomers), 3.60/3.65 (s/s, 3 H, 1:1 mixture of diastereomers), 3.67–4.17 (m, 2 H), 4.83–5.33 (m, 2 H), 5.77–6.50 (m, 1 H), 7.27 (s, 5 H); TLC R_f 0.40; VPC (170 °C) t_R 3.00 min; mass spectrum, m/e (no M^+ observed), 188 ($M^+ - CH_3OH$), 161, 117 (100).

Methyl 2-Methoxy-4-methyl-4-pentenoate (2d). Methyl 2-methoxy-4-methyl-4-pentenoate was prepared from methallyl alcohol in a yield of 23% (method B). The desired product was eluted in fractions 41–46 (10 mL each, 10% ether/hexane): IR (film) ν_{max} 2900, 1725, 1630, 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77 (s, 3 H), 2.43 (d, 2 H, J = 7.0 Hz), 3.37 (s, 3 H), 3.73 (s, 3 H), 3.93 (t, 1 H, J = 7.0 Hz), 4.80 (m, 2 H); TLC R_f 0.69; VPC (100 °C) t_R 4.25 min; mass spectrum, m/e 158, 126 ($M^+ - CH_3OH$), 103, 99 (100).

Acknowledgment. Financial support for this work was kindly provided by the Research Corporation (Grant C-1009 to G.W.D.), California Foundation for Biochemical Research (Grant to HMC Chemistry Department), the National Science Foundation Undergraduate Research Program (Grant to HMC Chemistry Department), the Harvey Mudd College Faculty Research Fund (Grant to G.W.D. for Summer 1979), and the Harvey Mudd College Chemistry Department.

Registry No. 1a, 107-18-6; **1b**, 6117-91-5; **1c**, 104-54-1; **1d**, 513-42-8; **2a**, 54020-52-9; **2b** (isomer 1), 76376-93-7; **2b** (isomer 2), 76376-94-8; **2c** (isomer 1), 76376-95-9; **2c** (isomer 2), 76376-96-0; **2d**, 76376-97-1; trimethyl methoxyorthoacetate, 34359-77-8.

Novel Synthetic Route to Angularly Functionalized Hydrofluorene Derivatives by a Regio- and Stereospecific Metalation–Carbonation Reaction

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Received July 10, 1980

A selective metalation–carbonation reaction has been used for the introduction of C-1 and C-9 carboxyl groups into hydrofluorene[1,2] and gibbane[3] systems (corresponding to the C-4 and C-6 positions in gibberellane), leading to a few useful gibberellin synthons. As shown by House,[1] the lithiation–carbonation of the tetrahydrofluorene **1a** produces mostly the benzylic carboxylic acid **2a** along with only a minor amount of its angular regioisomer **3a** (Scheme I) The acid **1b**,[1,2] on the other hand, results in an ~1:1 mixture of **2b** and **3b** under similar reaction conditions as depicted in Scheme I.

We report here a remarkable influence by a neighboring *gem*-carboxymethyl group in the tetrahydrofluorene sub-

(1) House, H. O.; Bare, T. M.; Hanners, W. E. *J. Org. Chem.* **1969**, *34*, 2209.

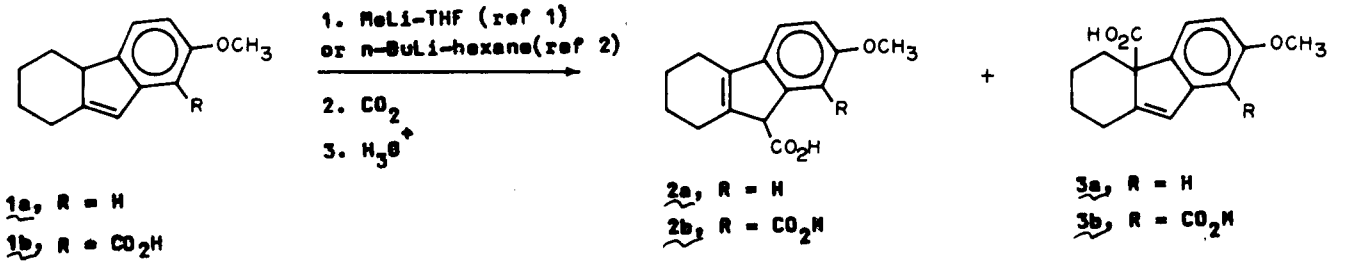
(2) House, H. O.; Strickland, R. C.; Zaiko, E. J. *J. Org. Chem.* **1976**, *41*, 2401.

(3) Loewenthal, H. J. E.; Schatzmiller, S. *J. Chem. Soc., Perkin Trans. 1*, **1976**, 944. Baker. A. J.; Goudie, A. C. *J. Chem. Soc., Chem. Commun.* **1972**, 951.

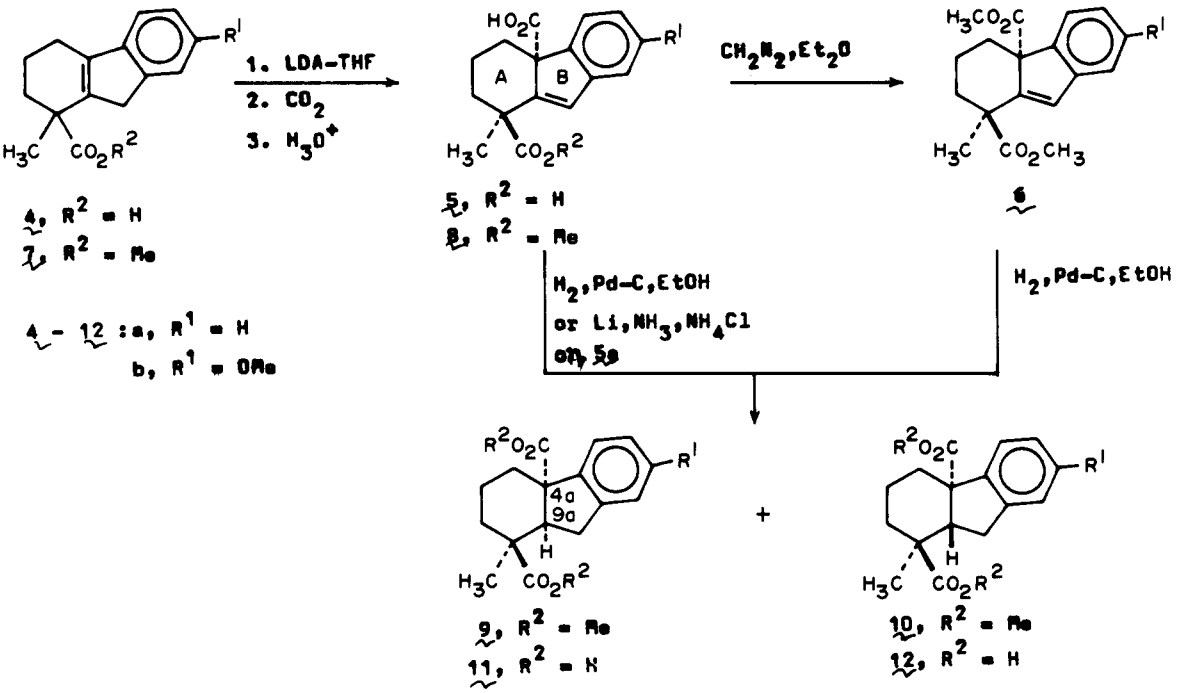
(4) Ghatak, U. R.; Dasgupta, R.; Chakravarty, J. *Tetrahedron* **1974**, *30*, 187.

0022-3263/81/1946-1486$01.25/0

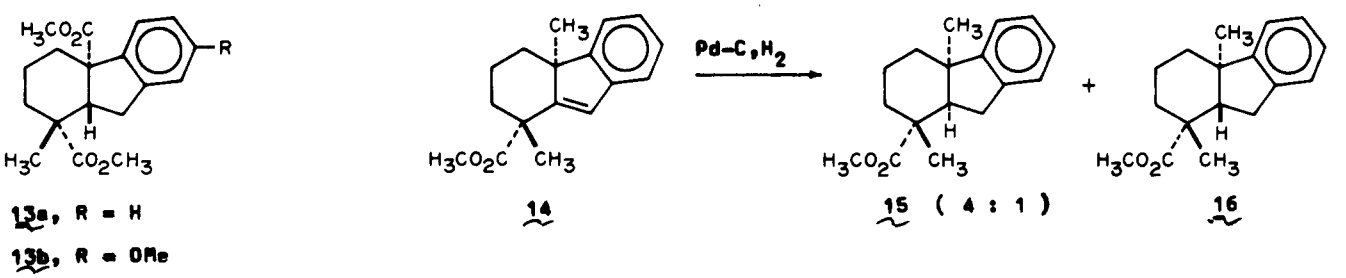
Scheme I



Scheme II



Scheme III

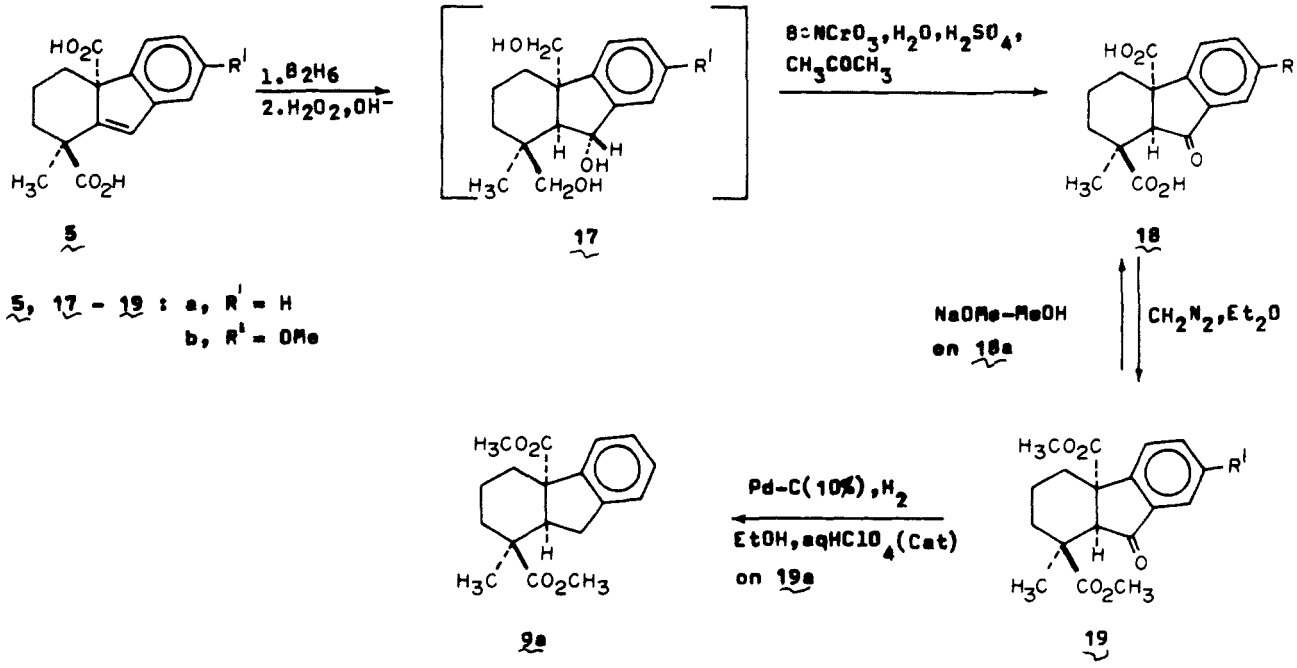


strates **4a**[4] and **4b**[5] on the regio- and stereospecificities in the carboxylation reaction, resulting in a new stereospecific synthesis of a few angularly carboxylated hydrofluorene derivatives (Scheme II). Conversion of the acid **4a** into its lithium dianion by treatment with an excess of lithium diisopropylamide (LDA) in THF followed by reaction with gaseous CO_2 afforded the dicarboxylic acid **5a** in 83% yield as the only isolable product. Esterification of **5a** with diazomethane yielded the corresponding crystalline dimethyl ester **6a**. Similarly, carboxylation of the acid **4b** and the ester **7a** gave the angular carboxylic acids **5b** and **8a** in 73% and 52% yields, respectively, which on esterification with diazomethane gave the respective dimethyl esters **6b** and **6a**. The assignment of the relative trans stereochemistry to the C-1 and C-4a carbomethoxy groups in **6a** and **6b** was based on the following transformation (Scheme II). Catalytic hydrogenation of the styrenoid bond in **6a** and **6b** in the presence of palladium on carbon (10%) in ethanol produced in each case a mixture of two crystalline diastereomeric esters (**9a** and **10a**; **9b** and **10b**) in a ratio of ~4:1 (GC and ^1H NMR) which were different from the corresponding epimeric trans A/B-ring diesters **13a**[6] and **13b**[6] (Scheme III) and had cis C-1 and C-4a carbomethoxy groups. Under the same conditions, catalytic hydrogenation of the acid **5a** gave the respective diastereomeric acid mixture **11a** and **12a** in the same ratio of ~4:1. Lithium–ammonia reduction of the acid **5a** with ammonium chloride as the proton donor gave a mixture of the two epimeric acids **11a** and **12a** in a ratio of 73:27 (GC and ^1H NMR of the methyl esters). An analogy of

(5) Ghosh, S.; Dasgupta, R.; Chakravarty, J.; Ghatak, U. R.; *J. Chem. Soc., Perkin Trans. 1* **1980**, 804.

(6) Ghatak, U. R.; Sanyal, B.; Ghosh, S. *J. Am. Chem. Soc.* **1976**, *98*, 3721.

Scheme IV

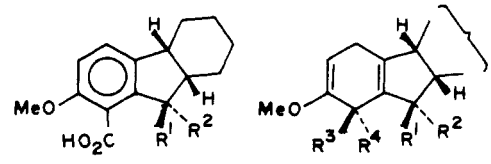


the stereochemical results reported by Tahara[7] in the palladium-catalyzed reduction of **14** leading to the respective cis and trans A/B-ring junction products **15** and **16** in an identical ratio allowed us initially to assign the ring junction stereochemistry to the major and minor reduction products.

An additional support for the assigned stereochemistry of the major product **9a** from reduction of **5a** was obtained from the sequence of reactions shown in Scheme IV. The hydroboration[8] of **5a** with an excess of diborane in THF followed by oxidation with alkaline hydrogen peroxide afforded the triol **17a** which was directly oxidized with an excess of Jones reagent to the crystalline keto acid **18a**.

The stereochemical homogenity of **18a** was firmly established by GC and ^{1}H NMR spectral analyses of corresponding liquid dimethyl ester **19a** (diazomethane). In a similar sequence, the methoxy analogue **5b** was transformed to the respective keto acid **18b** and dimethyl ester **19b**. The keto diester **19a** was recovered unchanged (GC and ^{1}H NMR) after treatment with an excess of refluxing sodium methoxide in methanol followed by esterification of the resulting acid with diazomethane. Since under equilibrating conditions the C-9a center in **19a** did not epimerize, it must be represented by the stable cis A/B-ring stereochemistry.[9,10] Finally, catalytic hydrogenolysis[11] of **19a** yielded the diester **9a**, identical with the major reduction product of **6a**. Thus, the establishment of the stereochemistry of **9a** leads automatically to the complete stereochemical assignment to the minor epimer **10a** from the reduction of **6a**, as well as to the triol **17a** and keto acid **18a**. By analogy, the stereochemistries of the corresponding methoxy analogues have been assigned.

The interesting feature of the lithiation–carbonation reaction in **4a**, **4b**, and **7a** is the regiospecificity of angular carboxylation from the side opposite that of the C-1 carboxyl (or ester) function. Similar stereochemical control by a neighboring C-9 carboxyl group in the epimeric diacids **20** and **21** has been observed by House[2] in the re-



20, R^1 = H; R^2 = CO$_2$H
21, R^1 = CO$_2$H; R^2 = H

22, R^1 = H; R^2 = R^4 = CO$_2$H; R^3 = Me
23, R^1 = R^3 = COOH; R^2 = H; R^4 = Me

ductive methylation [Li, NH_3(l), THF, CH_3I], leading in each case to the diacid product [**20** to **22** and **21** to **23**] by introduction of the C-1 methyl group from the side opposite the C-9 carboxyl group.

The metalation–carbonation reaction thus provides a simple stereospecific generation of angular functionalities in hydrofluorene systems[6] which are also of interest as intermediates for the preparation of angularly substituted octahydrophenanthrenes[10] through ring-B expansion.

Experimental Section

The compounds described are all racemates. The melting points are uncorrected. Petroleum ether and petroleum refer to the fractions boiling in the range 40–60 and 60–80 °C, respectively. UV spectra were determined in 95% ethanolic solutions on a Beckman DU spectrometer, and IR spectra were determined on a Beckman Acculab-4 spectrometer. ^{1}H NMR spectra were recorded with a Varian T-60A spectrometer (Me_4Si as internal standard). Gas chromatography was performed by using a Hewlett-Packard Model 7127A employing a 20 in. × $^1/_8$ in. 10% UCW-982 column (A) and a 6 ft × $^1/_8$ in. 3% SE-52 column (B) at 190 °C with N_2 as the carrier gas. Elemental analyses were performed by Mr. B. Bhattacharya, Department of Chemistry, Jadavpur University, Calcutta.

(±)-1α-Methyl-1,2,3,4-tetrahydrofluorene-1β,4aα-dicarboxylic Acid (5a). To a magnetically stirred solution of lithium diisopropylamide (LDA) in THF, prepared from diiso-

(7) Tahara, A.; Hoshino, O.; Ohsawa, T. *Chem. Pharm. Bull*, **1969**, *17*, 68.
(8) Cf.: House, H. O.; Hanners, W. E.; Racah, E. J. *J. Org. Chem.* **1972**, *37*, 985.
(9) Ghatak, U. R.; Chakravarty, J.; Banerjee, A. K. *Tetrahedron* **1968**, *24*, 1577.
(10) Parham, W. E.; Czuba, L. J. *J. Org. Chem.* **1969**, *34*, 1899.
(11) The hydrogenolysis product does not indicate the involvement of an olefinic intermediate such as **6a**; cf. ref. 9.

propylamine (16.2 mL, 0.12 mol) in 70 mL of THF and an 8.0% Et_2O solution of *n*-BuLi (110 mL, 0.12 mol), cooled to −40 °C (acetone–liquid N_2) was added under N_2 a solution of the acid **4a** (4.5 g, 15 mmol) in 70 mL of THF over a period of 10 min. The resulting pale yellow solution was stirred at −40 °C for an additional 30 min. Dry CO_2 gas was bubbled through the reaction mixture, the yellow color gradually disappeared, and the white lithium salt of the dicarboxylic acid precipitated. The mixture was poured into ice–HCl (12 N). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried (Na_2SO_4), the solvent was evaporated, and the crude solid product was crystallized from THF–petroleum ether to afford the acid **5a**: 4.41 g (83%); mp 217–220 °C dec; IR (Nujol) 1705 cm^{-1}; UV 221 nm (log ε 4.3), 264 (4.1). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.53; H, 5.96.

The acid **5a** (200 mg) was esterified with an excess of ice-cold ethereal diazomethane solution to afford a pale yellow solid. It was purified by being filtered through a short column of neutral alumina to produce the dimethyl ester **6a** (198 mg; 90%), which was crystallized from Et_2O: mp 144 °C; IR ($CHCl_3$) 1720 cm^{-1}; UV 220 nm (log ε 4.3), 262 (4.1); NMR (CCl_4) 1.56 (s, 3 H, CCH_3), 1.66–3.61 (complex m, 6 H, methylenes), 3.46 (s, 3 H, CO_2CH_3), 3.50 (s, 3 H, CO_2CH_3), 6.70 (s, 1 H, C=CHAr), , 7.23 (m, 4 H, Ar H) ppm. Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.69; H, 6.54.

(±)-1α-Methyl-7-methoxy-1,2,3,4-tetrahydrofluorene-1β,4aα-dicarboxylic Acid (5b). Under the conditions described for **4a**, the methoxy analogue **4b** (3.0 g, 12 mmol) in 50 mL of THF was lithiated with LDA, prepared from diisopropylamine (12.24 mL, 96 mmol) in 50 mL of THF and an 8% Et_2O solution of *n*-BuLi (75 mL, 96 mmol), and reacted with CO_2 gas. After the usual workup, the crude product was crystallized from THF–petroleum ether to afford the acid **5b**: 2.60 g (73%); mp 226–228 °C dec; IR (Nujol) 1705 cm^{-1}; UV 234 nm (log ε 4.5), 267 (3.8), 298 (3.5). Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.26; H, 6.03.

The acid **5b** (200 mg) was esterified with an excess of cold ethereal diazomethane solution to afford a pale yellow solid. This was dissolved in ether and filtered through a short column of neutral alumina to give **6b** as colorless cyrstals: 200 mg (90%); mp 119–120 °C. The analytical sample was recrystallized from Et_2O: mp 122 °C; IR ($CHCl_3$) 1720 cm^{-1}; UV 232 nm (log ε 4.4), 266 (3.7), 298 (3.3); NMR (CCl_4) 1.53 (s, 3 H, CCH_3), 1.66–3.61 (m, 6 H), 3.43 (s, 3 H, CO_2CH_3), 3.56 (s, 3 H, CO_2CH_3), 3.76 (s, 3 H, OCH_3), 6.63 (s, 1 H, C=CHAr partly overlapped with Ar H), 6.63–7.20 (3 H, d and q, J = 8, 2 Hz, Ar H) ppm. Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 68.92; H, 6.58.

(±)-1α-Methyl-1β-(carboxymethyl)-1,2,3,4-tetrahydrofluorene-4aα-carboxylic Acid (8a). To a magnetically stirred solution of LDA, prepared from diisopropylamine (1.6 mL, 11 mmol) in 5 mL of THF and a 4% Et_2O solution of *n*-BuLi (17 mL, 11 mmol) cooled to −12 °C, was added under N_2 a solution of the ester **7a** (500 mg, 2.06 mmol) in 5 mL of THF in 2–3 min. The temperature of the pale yellow reaction mixture was slowly raised to −5 to 0 °C, and the stirring was continued for 1 h. Dry CO_2 was bubbled through the reaction mixture, and the resulting product was worked up as described for **5a** to afford the crude half-ester acid **8a**: 301 mg (52%); mp 140–156 °C. Two recrystallizations from THF–petroleum ether afforded the pure sample, mp 182 °C dec. A small portion of **8a** was esterified wiith Et_2O–CH_2N_2 to afford the diester **6a**, mp and mmp (with the sample described above) 143–144 °C.

Catalytic Hydrogenation of 6a. (±)-Dimethyl 1α-Methyl-1,2,3,4,4a,9aα-hexahydrofluorene-1β,4aα-dicarboxylate (9a) and (±)-Dimethyl 1α-Methyl-1,2,3,4,4a,9aβ-hexahydrofluorene-1β,4aα-dicarboxylate (10a). A solution of the ester (**6a** 1.0 g, 3.33 mmol) in ethanol (48 mL) was hydrogenated in the presence of Pd/C (10%, 350 mg) as catalyst for 3 h. The catalyst was filtered off, and the solvent was removed to afford a solid mixture of **9a** and **10a**: 1.0 g (100%); mp 65–70 °C. GC analyses of this mixture showed the presence of **9a** and **10a** in a ratio of ~4:1. It was repeatedly crystallized from petroleum ether to afford **9a**: 402 mg; mp 89 °C; UV 258 nm (log ε 2.7), 272 (2.9); NMR ($CDCl_3$) 1.23 (3 H, s, CH_3) 1.46–3.50 (9 H, m, methylene and methine), 3.63 (3 H, s, CO_2CH_3), 3.67 (3 H, s, CO_2CH_3) ppm; GC 4.4 (column A), 39.8 min (column B). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.39; H, 7.21. From the mother liquor the epimeric ester **10a** (90 mg, mp 109 °C) was isolated: NMR ($CDCl_3$) 1.31 (3 H, s, CH_3), 3.45 (3 H, s , CO_2CH_3), 3.66 (3 H, s , CO_2CH_3) ppm; GC 32.4 (B), 3.6 min (A). Anal. Calcd for $C_{18}H_{22}O_4$ C, 71.50; H, 7.33. Found: C, 71.47; H, 7.44.

The rest of the material (~500 mg) was carefully chromatographed through neutral alumina (30 g) to afford **9a** (160 mg) and **10a** (59 mg) in benzene elutes. The total isolated yields of **9a** and **10a** are 56% and 15%, respectively.

Catalytic Hydrogenation of the Unsaturated Acid 5a. The acid **5a** (1.0 g) dissolved in ethanol (40 mL) was hydrogenated in the presence of Pd/C (10%, 300 mg) for 6 h. The catalyst was filtered off, and the solvent was removed to afford a solid: 1.0 g (100%); mp 175–190 °C. A small portion of this mixture was esterified with CH_2N_2–Et_2O which on GC analyses showed the presence of **9a** and **10a** in a ratio of ~4:1. Repeated crystallization of the acid mixture from methanol afforded **11a** (43 mg, mp 255–258 °C dec), the dimethyl ester of which was identical with **9a** by mixture melting poing and GC. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 69.86; H, 6.46. The remaining epimeric acid **12a** could not be separated from the mixture by fractional crystallization or by TLC.

Lithium–Ammonia Reduction of 5a. To a stirred solution of the acid **5a** (500 mg, 1.83 mmol) in 10 mL of THF and 250 mL of anhydrous liquid NH_3 directly distilled from the cylinder was added lithium wire (100 mg, 0.014 mol) in several lots during 10 min. The blue color was discharged by the cautious addition of solid NH_4Cl. The NH_3 was then allowed to evaporate completely at room temperature, 50 mL of moist ether was added, and the reaction mixture was acidified with excess 6 N HCl. The product was extracted with ethyl acetate, washed with water, and dried (Na_2SO_4). Removal of the solvent afforded a mixture of **11a** and **12a** as a white solid: 430 mg (86%); mp 190–193 °C. A portion of this was converted to the methyl ester (CH_2N_2–Et_2O) which on GC and NMR analyses showed the presence of the epimeric esters **9a** and **10a** in a ratio of ~77:23, similar to that observed in the catalytic hydrogenation product.

Catalytic Hydrogenation of Unsaturated Ester 6b. (±)-Methyl 1α-Methyl-7-methoxy-1,2,3,4,4a,9aα-hexahydrofluorene-1β,4aα-dicarboxylate (9b) and (±)-Methyl 1α-Methyl-7-methoxy-1,2,3,4,4a,9aβ-hexahydrofluorene-1β,4aα-dicarboxylate (10b). The ester **6b** (500 mg, 1.513 mmol) was hydrogenated in ethanol (25 mL) in the presence of Pd/C (10%, 150 mg) to produce a mixture of **9b** and **10b** in a ratio of ~4:1 by GC analyses. Repeated crystallization of the epimeric ester mixture from petroleum ether afforded **9b**: 120 mg (25%); mp 84 °C; NMR ($CDCl_3$) 1.22 (s, 3 H, CCH_3), 3.62 (s, 3 H, CO_2CH_3), 3.65 (s, 3 H, CO_2CH_3), 3.72 (s, 3 H, Ar OCH_3) ppm; GC 17.6 min (A). Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.65; H, 7.28. Found: C, 68.37; H, 7.60. From the mother liquor the epimeric ester **10b** was obtained: 50 mg (10%); mp 136 °C; NMR ($CDCl_3$) 1.31 (s, 3 H, CH_3), 3.45 (s, 3 H, CO_2CH_3), 3.65 (s, 3 H, CO_2CH_3), 3.71 (s, 3 H, Ar OCH_3); GC 12.9 min (A). Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.65; H, 7.28. Found: C, 68.51; H, 7.48.

Hydroboration of the Acid 5a Followed by Oxidation. (±)-1α-Methyl-9-oxo-1,2,3,4,4a,9aα-hexahydrofluorene-1β,4aα-dicarboxylic Acid (18a). Diborane [generated by adding a solution of $NaBH_4$ (2 g, 52.9 mmol) in diglyme (52 mL) to BF_3·Et_2O (14 mL) in diglyme (15 mL)] was passed through an ice-cold solution of the acid **5a** (1 g, 3.68 mmol) in THF (15 mL) for 2 h. The reaction flask was allowed to sit overnight (20 h in total). Excess diborane was decomposed by cautious addition of water (2 mL) to the ice-cold reaction mixture. Aqueous sodium hydroxide (3 N, 12 mL) was added in one lot followed by dropwise addition of H_2O_2 (30%, 12 mL). The mixture was magnetically stirred for 1 h at 35–40 °C. The precipitated solid was filtered out. The solid residue was repeatedly washed with ethyl acetate. The organic layer was separated, and the aqueous phase was repeatedly extracted with ethyl acetate. The combined organic extracts were washed with water and dried (Na_2SO_4). Removal of solvent under reduced pressure afforded the crude triol **17a** as a while semisolid mass: 895 mg (93%); IR ($CHCl_3$) 3450 cm^{-1}; UV 265 nm (log ε 3.03), 271 (2.98); NMR ($CDCl_3$) 0.90 (s, 3 H, CCH_3), 2.31 (d, 1 H, methine), 3.35–3.58 (m, 4 H, CH_2OH), 3.93

(br s, 1 H, OH, exchangeable), 4.9 (d, 1 H, CHOH) ppm. This without further purification was directly oxidized to **18a** by using the following method.

To a magnetically stirred and ice-cold solution of **17a** (682 mg, 2.60 mmol) in acetone (15 mL) was added, dropwise, Jones reagent (2 mL, 5.34 mmol). The mixture was stirred for 15 min in the cold and for 45 min at room temperature. It was cooled in ice. A second aliquot of Jones reagent (2 mL, 5.34 mmol) was added dropwise to the stirred solution. The reaction mixture was stirred cold for 15 min and at room temperature for 2 h. At the end of this period the mixture became completely dark green and was diluted with cold water. The organic material was extracted with ethyl acetate. The extract was washed with water (once) and repeatedly with saturated aqueous $NaHCO_3$ and water and dried (Na_2SO_4). Removal of the solvent gave a brown liquid (92 mg) which was not characterized further. The basic aqueous washing on acidification with cold 6 N HCl gave a white precipitate which was extracted with ethyl acetate to afford the crude acidic product, 160 mg (21%). Crystallization from THF–petroleum ether afforded the pure acid **18a**: 120 mg (16%); mp 209 °C; UV 245 nm (log ϵ 4.1), 294 (3.3). Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.41; H, 5.78.

The keto acid **18a** (110 mg, 0.39 mmol) was esterified with CH_2N_2–Et_2O to afford a pale yellow liquid. This, on filtration through a short column of neutral alumina, afforded **19a** as a colorless liquid: 112 mg (91%); IR (film) 1725, 1605, 1595 cm^{-1}; UV 248 nm (log ϵ 4.20), 286 (3.3); NMR (CCl_4) 1.58 (s, 3 H, CCH_3), 3.65 (s, 6 H, 2 CO_2CH_3), 3.70 (1 H, s, COCH), 7.13–7.70 (4 H, m, ArH) ppm; GC 7.2 min (A).

Equilibriation of 19a with NaOMe–MeOH. The keto diester **19a** (80 mg, 0.25 mmol) was treated with 2% NaOMe in MeOH (2 mL,87 mmol) under reflux for 2 h under N_2. The reaction mixture was cooled and diluted with water. Ether extraction revealed the absence of any unhydrolyzed material. The basic aqueous part on acidification allowed the separation of a solid which was extracted with ether to afford **18a**: 70 mg (97%); mp and mmp (with the sample described above) 209 °C. A part of this acid was esterified with Et_2O–CH_2N_2 to afford the starting ester **19a** as revealed by NMR and GC comparisons.

Hydrogenolysis of the Keto Diester 19a to 9a. The keto diester **19a** (24 mg, 0.076 mmol) in dry ethanol (4 mL) was stirred under an atmosphere of hydrogen in presence of Pd/C (10%, 20 mg) and 1 drop of $HClO_4$ (70%) for 24 h. The catalyst was filtered off and washed with ethanol. Powdered $NaHCO_3$ was added portionwise to the combined filtrate and washings until the evolution of CO_2 ceased. The undissolved substance was filtered off, and the filtrate was evaporated to dryness. The residue was digested with ether and filtered through a short column of neutral alumina to afford a solid, mp 81–84 °C. Crystallization from petroleum ether afforded the pure ester **9a**, mp and mmp 89 °C. GC analysis also confirmed the identity.

Hydroboration of the Acid 5b Followed by Oxidation. (±)-1α-Methyl-7-methoxy-9-oxo-1,2,3,4,4a,9a-hexahydrofluorene-1β,4aα-dicarboxylic Acid (18b). The acid **5b** (1 g, 3.49 mmol) in THF (15 mL) was reacted with diborane [generated from $NaBH_4$ (2 g, 52.9 mmol) in diglyme (52 mL) and BF_3·Et_2O (14 mL) in diglyme (15 mL)] for 23 h under conditions identical with those described for **5a**. After decomposition of the excess diborane with water (5 mL), the organoborane was oxidized with 3 N NaOH (8 mL) and 30% H_2O_2 (8 mL) for 1 h with stirring and heating to 35–40 °C. The organic material was extracted with Et_2O–ethyl acetate by the procedure described earlier to afford the crude triol **17b**: 298 mg (32%); mp 147–153 °C. Crystallization of a part of this material from Et_2O afforded the pure triol **17b**: mp 161 °C; IR (Nujol) 3250, 1615, 1590, 1460 cm^{-1}; UV 278 nm (log ϵ 3.5). A solution of crude **17b** (120 mg, 0.43 mmol) in acetone (10 mL) was oxidized by dropwise addition of Jones reagent (1 mL, 2.67 mmol) in two lots as described for **17a**. The total stirring time was 3 h. The reaction mixture was diluted with water and extracted with ethyl acetate. The ethyl acetate extract was washed with water, NaOH (2%), and water and dried (Na_2SO_4). Removal of the solvent gave a negligible amount of a brown liquid which was rejected. The basic aqueous washing on acidification (6 N HCl) and extraction with ethyl acetate afforded a white solid, 85 mg (65%). Crystallization from THF–petroleum ether afforded the pure acid **18b**, mp 220 °C. Anal. Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 64.19; H, 5.87.

The acid **18b** (60 mg, 0.2 mmol) was esterified with CH_2N_2–Et_2O to afford the diester **19b**: 62 mg (94%); colorless liquid; IR (film) 1730, 1710, 1615, 1590, 1490, 1460 cm^{-1}; UV 250 nm (log ϵ 4.2); mass spectrum, *m/e* 346 (M^+), 314, 287, 228, 227, 149; NMR (CCl_4) 1.01–1.45 (m, 4 H, methylenes), 1.60 (s, 3 H, CCH_3), 1.90–2.10 (m, 2 H, methylenes), 3.66 (s, 6 H, 2 $COOCH_3$), 3.70 (s, 1 H, COCH), 3.83 (s, 3 H, OCH_3), 7.03–7.26 (m, 3 H, Ar H) ppm.

Registry No. 4a, 74741-03-0; **4b**, 76403-71-9; **5a**, 76403-72-0; **5b**, 76403-73-1; **6a**, 76403-74-2; **6b**, 76403-75-3; **7a**, 76403-76-4; **8a**, 76403-77-5; **9a**, 76403-78-6; **9b**, 76403-79-7; **10a**, 76403-80-0; **10b**, 76403-81-1; **11a**, 76403-82-2; **12a**, 76403-83-3; **17a**, 76403-84-4; **17b**, 76403-85-5; **18a**, 76403-86-6; **18b**, 76403-87-7; **19a**, 76403-88-8; **19b**, 76403-89-9.

Electrochemical Reduction of Bis(α-bromocyclopropyl) Ketone

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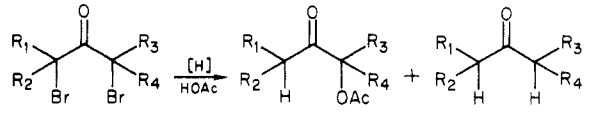
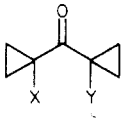
Received November 28, 1980

Reduction of α,α′-dibromo ketones (**1**) in acetic acid affords as major products α-acetoxy ketones (**2**) when the



1 **2** **3**

α-carbons bear at least three alkyl substituents; if the latter condition is not fulfilled, the so-called "parent" ketone (**3**) predominates. Reduction may be effected both electrochemically[1] or by finely dispersed mercury.[2] Although product distributions are somewhat different in the two reduction methods, they are on the whole fairly similar.[3,4] In the course of exploring the scope of this reductive acetoxylation process, we had occasion to examine the reduction of bis(α-bromocyclopropyl) ketone (**4**).[5] We describe the anomalous behavior of **4** under our reduction conditions.



4, X = Y = Br
5, X = Br; Y = H
6, X = Y = H

Although α,α′-dibromo ketones are generally reduced in 0.25 to 2 days by ultrasonically dispersed mercury,[2] **4** was recovered (95%) after 8 days. The electrochemical reduction of **4** was also exceptional. Controlled-potential reduction of **4** in acetic acid/1.0 M sodium acetate (HOAc/NaOAc) at −0.80 V (SCE) afforded a mixture of α-bromocyclopropyl cyclopropyl ketone (**5**; 76%) dicyclopropyl ketone (**6**; 14%), and unreacted **4** (10%). Electrolytic reduction of **4** in 9:1 dimethylformamide

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