bicarbonate. The mixture was extracted with ethyl acetate, and the organic phase was washed with brine, dried (Na_2SO_4), filtered, and evaporated to dryness. The residue was purified by column chromatography on silica gel using ethyl acetate–hexane (1:15), to give 106 mg (63%) of **17** as a glass: IR ($CHCl_3$), 1633, 1600 (C=C), 841 ($SiMe_3$) cm^{-1}; MS, *m/z* 604 (M$^+$),[14] 584 (10), 452 (4), 131 (78), 77 (100); UV λ_{max} (ethanol) 243 (ϵ 15330), 268 nm (15790); ^{1}H NMR δ 0.08 (s, 6 H, $SiMe_2$), 0.10 (s, 9 H, $SiMe_3$), 0.56 (s, 3 H, CH_3), 0.88 (s, 9 H, CMe_3), 0.93 (d, *J* = 7 Hz, 3 H, $CHCH_3$), 1.20 (s, 6 H, CMe_2), 2.51 (m, 1 H), 2.82 (br d, *J* = 13 Hz, CH of CH_2), 4.16 (br m, 1 H, CHO), 5.09 (s, 1 H, olefinic CH), 5.10 (dm, *J* = 48 Hz, 1 H, CHF), 5.36 (s, 1 H, olefinic CH), 6.03 (d, *J* = 12 Hz, 1 H, olefinic CH), 6.35 (d, *J* = 12 Hz, 1 H, olefinic CH); exact mass calcd for $C_{36}H_{65}O_2FSi_2$ 604.4507, found 604.4503.

1α-Fluoro-25-hydroxycholecalciferol (18). To a solution of 101 mg (0.167 mmol) of **17** in 10 mL of dry tetrahydrofuran was added 0.83 mL (0.83 mmol) of a 1 M solution of tetrabutylammonium fluoride in tetrahydrofuran, and the mixture was stirred at 20 °C for 15 h under argon. After dilution with 20 mL of water, the mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried (Na_2SO_4), and evaporated to dryness. The crude product obtained was purified by column chromatography on silica gel using ethyl acetate–hexane (1:1.3) as the eluent, to afford 63 mg (90%) of 1α-fluoro-25-hydroxycholecalciferol (**18**) as a foamy glass: $[\alpha]^{25}_D$ +80.7° (*c* 0.15, MeOH); IR ($CHCl_3$), 3610 (OH), 1644, 1600 (C=C) cm^{-1}; MS, *m/z* 418 (M$^+$),[14] 398 (15), 380 (42), 362 (28), 347 (6), 59 (100); UV λ_{max} (ethanol) 240 (ϵ 13620), 268 nm (13390); ^{1}H NMR δ 0.55 (s, 3 H, CH_3), 0.94 (d, *J* = 7 Hz, 3 H, $CHCH_3$), 1.22 (s, 6 H, CMe_2), 2.19 (m, 1 H), 2.31 (m, 1 H), 2.63 (dm, *J* = 13 Hz, 1 H), 2.82 (br d, *J* = 13 Hz, 1 H), 4.23 (br s, 1 H, CHO), 5.11 (s, 1 H, olefinic CH), 5.14 (dm, *J* = 48 Hz, 1 H, CHF), 5.40 (s, 1 H, olefinic), 6.03 (d, *J* = 12 Hz, 1 H, olefinic CH), 6.42 (d, *J* = 12 Hz, 1 H, olefinic CH); exact mass calcd for $C_{27}H_{43}O_2F$ 418.3247, found 418.3242.

[[(1α,3β,5*Z*,7*E*,22*E*)-3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-1-fluoro-9,10-secoergosta-5,7,10(19),22-tetraen-25-yl]oxy]trimethylsilane (20). In a manner analogous to the preparation of **17**, when 102 mg (0.217 mmol) of 1α-fluoro A-ring synthon **15** was coupled with 54.7 mg (0.150 mmol) of **19**,[5] 46 mg (50%) of **20** was obtained as a glass: MS, *m/z* 616 (M$^+$),[14] 596 (3), 581 (1), 539 (1), 506 (2), 464 (2), 131 (100); ^{1}H NMR δ 0.08 (s, 6 H, $SiMe_2$), 0.10 (s, 9 H, $SiMe_3$), 0.56 (s, 3 H, CH_3), 0.88 (s, 6 H, CMe_3), 0.94 (d, *J* = 7 Hz, 3 H, $CHCH_3$), 1.01 (d, *J* = 7 Hz, 3 H, $CHCH_3$), 1.11 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3), 2.50 (m, 1 H, CH of CH_2), 2.83 (br d, *J* = 13 Hz, 1 H, CH of CH_2), 4.16 (br m, 1 H, CHO), 5.08 (s, 1 H, olefinic CH), 5.10 (dm *J* = 48 Hz, 1 H, CHF), 5.20 (s, 1 H, olefinic CH), 5.15–5.36 (m, 3 H, olefinic CH), 6.01 (d, *J* = 12 Hz, 1 H, olefinic CH), 6.33 (d, *J* = 12 Hz, 1 H, olefinic CH).

1α-Fluoro-25-hydroxyergocalciferol (21). In a manner analogous to the preparation of **18**, when 44 mg (0.071 mmol) of **20** was reacted with tetrabutylammonium fluoride in tetrahydrofuran, 28 mg (91%) of **21** was obtained as a glass: $[\alpha]^{25}_D$ +98.5° (*c* 0.13, MeOH); IR ($CHCl_3$) 3605 (OH), 1650, 1600 (C=C) cm^{-1}; MS, *m/z* 410 (M$^+$ – HF),[14] 392 (76), 374 (7), 269 (40), 251 (30), 59 (100); UV λ_{max} (ethanol) 242 (ϵ 15320), 269 nm (15100); ^{1}H NMR δ 0.56 (s, 3 H, CH_3), 1.00 (d, *J* = 7 Hz, 3 H, $CHCH_3$), 1.04 (d, *J* = 7 Hz, 3 H, $CHCH_3$) 1.13 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 2.63 (dm, *J* = 13 Hz, 1 H, CH of CH_2), 2.83 (dm, *J* = 13 Hz, 1 H, CH of CH_2), 4.23 (br s, 1 H, CHO), 5.11 (s, 1 H, olefinic CH), 5.14 (dm, *J* = 48 Hz, 1 H, CHF), 5.26–5.43 (m, 3 H, olefinic CH), 6.03 (d, *J* = 12 Hz, 1 H, olefinic CH), 6.41 (d, *J* = 12 Hz, 1 H, olefinic CH); exact mass calcd for $C_{28}H_{43}O_2F$ 430.3247, found 430.3219.

Acknowledgment. We thank the staff of the Physical Chemistry Department of Hoffmann-La Roche Inc. for the determination of physical and analytical data.

Registry No. **1**, 81506-17-4; **2**, 123836-51-1; **3**, 123836-52-2; **4**, 123836-53-3; **5**, 123836-54-4; **6**, 123836-55-5; **7**, 123836-56-6; **8**, 123836-57-7; **9**, 123836-58-8; **10**, 123836-59-9; **11**, 123836-60-2; **12**, 123930-10-9; **13**, 123836-61-3; **14**, 123836-62-4; **15**, 123836-63-5; **16**, 81506-41-4; **17**, 123836-64-6; **18**, 95586-94-0; **19**, 95716-69-1; **20**, 123836-65-7; **21**, 123836-66-8; $ClCO_2CH_2CCl_3$, 17341-93-4.

Benz[*f*]indene

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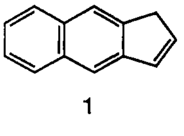
A convenient route to benz[*f*]indene (**1**) has been developed in which 2-methylnaphthalene is brominated sequentially in the α-position and the methyl group followed by application of a standard malonic ester route to propionic acid **10**. Cyclization of **10** via the acid chloride gave **11** (76%). Simultaneous reduction of the carbonyl group and hydrogenolysis of the aryl bromide linkage of **11** gave secondary alcohol **12** in 55.4% yield. Sulfuric acid dehydration of **12** gave **1** (85%). Less successful routes to **1** involved dithionite reduction of unsaturated sulfones **6**. Dihydro derivative **7** could be synthesized in 72% yield by magnesium/methanol reduction of **5b**.

Curiously, benz[*f*]indene (**1**) is only fleetingly referenced in the chemical literature. Although this relatively simple and potentially very useful isomer of fluorene has been cited only as a constituent of tobacco smoke,[1] the ultraviolet spectrum and melting point determined on a sample contaminated with 3% of its dihydro derivative are recorded in a UV handbook.[2]



1

Our interest in **1** relates to its possible use as a building block in the development of modified base-sensitive amino-protecting groups of the FMOC type.[3] In the present paper we describe a reliable route to hydrocarbon **1**. Retroanalytically, it is clear that benz[*f*]indene is po-

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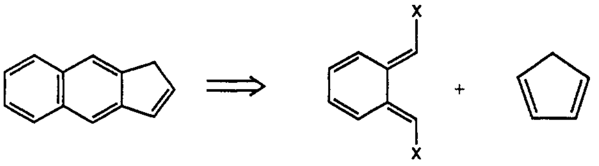
[1] Severson, R. F.; Snook, M. E.; Arrendale, R. F.; Chortyk, O. T. *Anal. Chem.* **1976**, *48*, 1866.

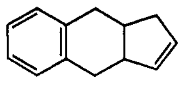
[2] *Ultraviolet Atlas of Organic Compounds*; Plenum Press: New York, 1966; Vol. 4, Spectrum E1/40. We are indebted to Dr. O. T. Chortyk for pointing out this reference. The submitter of the sample for UV analysis, Dr. E. A. Johnson, National Institute for Biological Standards and Control, Blanche Lane, South Mimms, Potters Bar, Hertfordshire, U.K., has kindly informed us that the sample in question was synthesized by the oxidation of benz[*f*]indane (Johnson, E. A. *J. Chem. Soc.* **1962**, 994) by means of dichlorodicyanoquinone and had mp 162–163 °C after recrystallization from ethanol and sublimation in vacuo. We learned of this work only after completion of the present study.

[3] Carpino, L. A. *Acc. Chem. Res.* **1987**, *20*, 401.

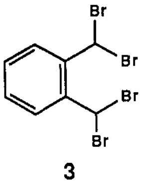
Scheme I



tentially available in a few steps via a Diels–Alder process (Scheme I). In fact, the tetrahydro derivative **2** was obtained in 1961 by Alder and Fremery[4] in this way (40%) from *o*-xylylene dibromide, cyclopentadiene, and zinc metal. Having investigated a similar approach to **1** using tetrabromide **3**[5] without success, we switched our attention to more classical approaches.

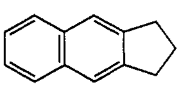


2



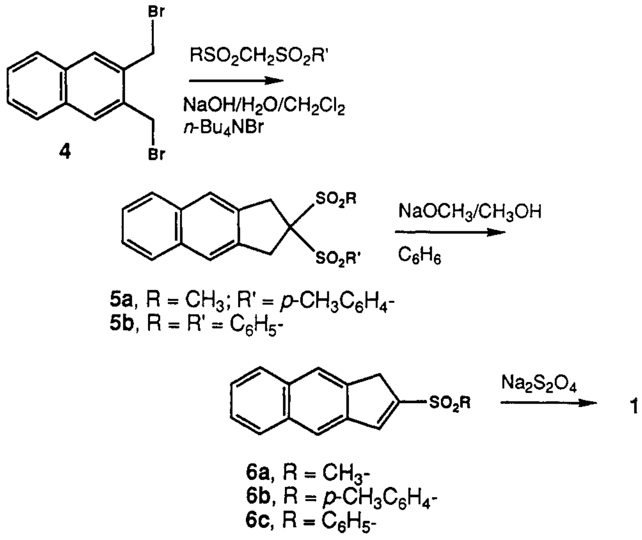
3

A route to **1** suitable for small quantities involved dithionite[6] reduction (49%) of a mixture of the two unsaturated sulfones **6a,b** obtained via sulfinate elimination from **5a** under carefully defined conditions (Scheme II). Similarly, **6c** obtained from **5b** gave **1** in 60% yield. These methods, however, proved difficult to scale up for large quantities due to the present lack of a large-scale commercial source of bis(alkyl- or arylsulfonyl)methanes. Disulfone **5b**, on treatment with magnesium metal in methanol,[7] gave benz[*f*]indan (**7**) in nearly quantitative yield, but attempts to dehydrogenate **7** via heating with sulfur[8] or Pd/C[9] or via bromination/dehydrobromination techniques[10] were unsuccessful.

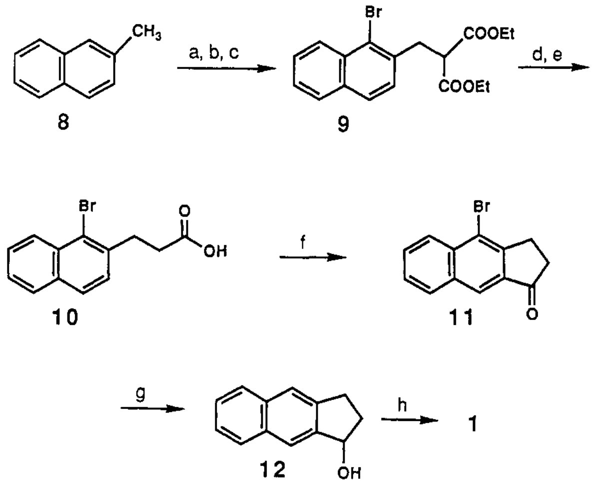


7

Scheme II



Scheme III[a]



[a] (a) Br_2, Fe/I_2, CCl_4 (90.5%); (b) NBS, Bz_2O_2, CCl_4 (91.6%); (c) NaOEt, EtOH, $CH_2(COOEt)_2$ (86.2%); (d) 5 N NaOH, reflux for 2 h, then 5 N HCl (58.7%); (e) 6 N HCl, reflux for 16 h (74%); (f) $SOCl_2$, CH_2Cl_2, then $AlCl_3$ (76%); (g) $LiAlH_4$, THF, reflux for 8 days (55.4%); (h) 10% H_2SO_4, reflux for 24 h (85%).

Finally, a viable large-scale route to **1** was developed on the basis of Friedel–Crafts chemistry from 2-methylnaphthalene (**8**) (Scheme III). To avoid cyclization into the α-position,[11] **8** is first brominated in the presence of an electrophilic catalyst, and then the methyl group is brominated, to give 1-bromo-2-(bromomethyl)naphthalene. Although a multistep process, all reactions of Scheme III are easy to carry out and readily scaled up for large-scale work. Some of these reactions had been reported previously[12] up to the stage of bromo ketone **11** although with little, if any, experimental detail. Slow addition of the arylmethyl bromide to malonate anion in freshly prepared ethanolic sodium ethoxide was required in the synthesis of **9** to avoid formation of significant amounts of the corresponding arylmethyl ethyl ether. Meyer and Sieglitz[12] state that the acid chloride derived from **10**, upon treatment with aluminum chloride in carbon disulfide solution, gave **11** in poor yield ("Ausbeute schlecht"). In our hands, in the more convenient solvent methylene dichloride, the overall yield for this step was 76%.

Following cyclization, the protecting α-bromo substituent was removed at the same time as the carbonyl group was reduced by extended treatment with lithium aluminum hydride.[13] Short-time treatment with the hydride reagent gave the intermediate 4-bromobenz[*f*]indan-1-ol along with the desired alcohol. Overall, the yield of benz[*f*]indene from 2-methylnaphthalene was 12–16%. For very large scale work, a shorter route to **1** will probably be required. In view of the recent conversion of **1** to benz[*f*]indene-3-methanol, a key intermediate in the synthesis of BIMOC-protected amino acids,[14] further study of simpler routes to this hydrocarbon, possibly including

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(4) Alder, K.; Fremery, M. *Tetrahedron* **1961**, *14*, 190.

(5) Cava's technique of generating the *o*-xylylene involving treatment of **3** with sodium iodide was used. See: Cava, M. P.; Deana, A. A.; Muth, K. *J. Am. Chem. Soc.* **1959**, *81*, 6458.

(6) Bremner, J.; Julia, M.; Launay, M.; Stacino, J.-P. *Tetrahedron Lett.* **1982**, 3265.

(7) Brown, A. C.; Carpino, L. A. *J. Org. Chem.* **1985**, *50*, 1749.

(8) Weiss, R. In *Organic Syntheses*; Horning, E. C., Ed.; John Wiley and Sons: New York, 1955; Collect. Vol. III, p 729.

(9) House, H. O.; Bashe, K. W., II *J. Org. Chem.* **1967**, *32*, 784.

(10) Carpino, L. A.; Göwecke, S. *J. Org. Chem.* **1964**, *29*, 2824.

(11) Compare: (a) Koelsch, C. F.; Scheiderbauer, R. A. *J. Am. Chem. Soc.* **1943**, *65*, 2311. (b) Maréchal, E.; Chaintrou, G. *Bull. Soc. Chim. Fr.* **1967**, 987.

(12) Meyer, F.; Sieglitz, A. *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 1835.

(13) Karabatsos, G. J.; Shone, R. L. *J. Org. Chem.* **1968**, *33*, 619.

(14) Carpino, L. A.; Cohen, B. J.; Lin, Y.-Z.; Stephens, K. E.; Jr.; Triolo, S. A. *J. Org. Chem.*, following paper in this issue.

methods based on intermediates such as **6a–c**, is to be encouraged.

Experimental Section

Instrumentation and General Procedures. Melting points were obtained in open capillary tubes by using a Mel-Temp apparatus and are uncorrected. Infrared spectra were determined on Perkin-Elmer Model 237B or 1310 spectrometers and ^{1}H NMR spectra on Perkin-Elmer R-12 (60 MHz) or Varian XL-200 (200 MHz) or XL-300 (300 MHz) instruments with Me_4Si as internal standard. ^{13}C NMR spectra were recorded on a Varian Model XL-300 spectrometer at 75 MHz. TLC was performed on aluminum-backed Merck silica gel 60 F_{254} plates, spots being visualized by UV light. Elemental analyses were carried out by the University of Massachusetts Microanalytical Laboratory under the direction of Greg Dabkowski.

1-Bromo-2-(bromomethyl)naphthalene. To a solution of 103 g of 1-bromo-2-methylnaphthalene [bp 98–120 °C (0.5 mm), prepared in 90% yield by the method of Adams and Binder[15]] and 82 g of *N*-bromosuccinimide in 1030 mL of CCl_4 was added 0.54 g of dibenzoyl peroxide. The reaction mixture was refluxed with stirring for 3 h. After another 0.54 g of dibenzoyl peroxide was added, the mixture was refluxed for 3 h. The solution was allowed to stand at room temperature overnight, and the resulting suspension was brought to the boiling point and filtered while hot. Concentration of the filtrate gave 139 g (99.4%) of the bromide as a light yellow solid, mp 104–107 °C, which was recrystallized from CCl_4 to give 128 g (91.6%) of pure 1-bromo-2-(bromomethyl)naphthalene as colorless crystals: mp 106.5–107.5 °C (lit.[12] mp 107–108 °C); ^{1}H NMR ($CDCl_3$) δ 4.80 (s, 2, CH_2Br), 7.3–8.4 (m, 6, aryl).

Diethyl 2-[(1-Bromo-2-naphthyl)methyl]malonate (9). To a solution of NaOEt prepared from 9.66 g of sodium and 210 mL of dry EtOH was added 63.76 mL of diethyl malonate, and the reaction mixture was refluxed for 2 h. To the resulting yellow solution was added in small portions 126 g of 1-bromo-2-(bromomethyl)naphthalene, and the reaction mixture was refluxed for 16 h. Distillation of ethanol from an oil bath (100–110 °C) through a simple Claisen head gave a yellow suspension, to which were added 350 mL of CH_2Cl_2 and 350 mL of H_2O. The aqueous layer was extracted twice with 120-mL portions of CH_2Cl_2, and the combined organic layer was washed three times with 100-mL portions of H_2O, dried ($MgSO_4$), and evaporated to give 152 g (95.6%) of the ester as a yellow solid, mp 60–65 °C. Recrystallization from acetic acid gave 137 g (86.2%) of the pure diester as a colorless solid: mp 77–79 °C (lit.[12] mp 79–80 °C); ^{1}H NMR ($CDCl_3$) δ 1.20 (t, 6, CH_3), 3.40–3.60 (m, 2, $ArCH_2$), 4.15 (q, 4, OCH_2), 4.65 (s, 1, CH), 7.3–8.4 (m, 6, aryl).

β-(1-Bromo-2-naphthyl)propionic Acid (10). To a solution of 160 g of **9** in 239 mL of methanol was added 538 mL of 5 N NaOH solution. The mixture was refluxed for 135 min and cooled by means of an ice bath to 0 °C. To the reaction mixture was added 320 mL of ice water, and the resulting precipitate was collected by filtration and washed several times with small portions of ice water. To the ice-cold, stirred filtrate was added dropwise 5 N HCl solution until the solution was weakly acidic. The precipitate was filtered and washed several times with small portions of water. Drying gave 86 g (63.1%) of the crude diacid as a light yellow solid, mp 154–157 °C. Recrystallization from water gave 80 g (58.7%) of the pure diacid as colorless crystals: mp 157–159 °C; ^{1}H NMR (acetone-d_6) δ 3.50–3.75 (m, 2, $ArCH_2$), 3.85–4.20 (m, 1, CH), 7.45–8.50 (m, 6, aryl). A suspension of 47.5 g of the crude malonic acid in 968 mL of 6 N HCl solution was refluxed for 16 h. The mixture was cooled by means of an ice bath to 0 °C, treated with 650 mL of CH_2Cl_2, and stirred for 15 min. The aqueous layer was extracted twice with 100-mL portions of CH_2Cl_2. The combined extracts were washed three times with 100-mL portions of water, dried ($MgSO_4$), and evaporated to give 30.3 g (74%) of yellow solid, mp 116–119 °C, which was recrystallized from alcohol to give 28 g (68%) of the acid as colorless crystals: mp 123–124 °C (lit.[12] mp 125 °C); ^{1}H NMR ($CDCl_3$) δ 2.70 (t, 2, CH_2CO), 3.20 (t, 2, $ArCH_2$), 7.25–8.35 (m, 6, aryl), 10.35 (br, 1, COOH).

β-(1-Bromo-2-naphthyl)propionyl Chloride. To a solution of 40.16 g of **10** in 802 mL of CH_2Cl_2 was added 19.3 mL of thionyl chloride. The mixture was refluxed for 4 h and cooled to room temperature, and the solvent was evaporated from a water bath (40–50 °C) with a rotary evaporator (10 mm), to give a red-brown residue. In order to remove traces of thionyl chloride, small portions of CH_2Cl_2 were added and the solution was reevaporated three times. Eventually the crude acid chloride was obtained as a red-brown oil. The crude product was used immediately for the next step without further purification: ^{1}H NMR ($CDCl_3$) δ 2.55–2.90 (m, 2, CH_2COCl), 3.05–3.40 (m, 2, $ArCH_2$), 7.25–8.35 (m, 6, aryl); IR (neat) 1805 cm^{-1} (C=O).

4-Bromobenz[*f*]indan-1-one (11). To an ice-cold, stirred solution of the above crude β-(1-bromo-2-naphthyl)propionyl chloride in 802 mL of dry CH_2Cl_2 was added 26.11 g of anhydrous $AlCl_3$ carefully. The reaction mixture was refluxed for 2 h, cooled to room temperature, and treated carefully, with stirring, with 900 mL of ice/water followed by 75 mL of concentrated HCl. The brown precipitate was filtered and washed five times with small portions of CH_2Cl_2. The aqueous layer was separated and extracted twice with 100-mL portions of CH_2Cl_2. The combined CH_2Cl_2 extracts were washed three times with small portions of H_2O, dried ($MgSO_4$), and evaporated from a water bath (50–60 °C) with a rotary evaporator (7 mm) to give 30.1 g (80.1%) of the crude ketone as a yellow solid, mp 146–149 °C, which could be recrystallized from acetic acid to give 28.5 g (76%) of the pure ketone as colorless crystals: mp 149–151 °C (lit.[12] mp 152 °C); ^{1}H NMR ($CDCl_3$) δ 2.60–2.80 (m, 2, CH_2CO), 3.00–3.25 (m, 2, $ArCH_2$), 7.30–8.35 (m, 5, aryl); IR (KBr) 1700 cm^{-1} (C=O).

Benz[*f*]indan-1-ol (12). To an ice-cold solution of 22 g of **11** in 150 mL of dry THF was added carefully in small portions 16.1 g of $LiAlH_4$. Subsequently, another 270 mL of the dry THF was added to the suspension, and the mixture was refluxed for 8 days. The reaction mixture was cooled to 0 °C by means of an ice bath and treated dropwise with 50 mL of ice/water followed by 1080 mL of 10% H_2SO_4 solution. The mixture was extracted three times with 100-mL portions of ether, and the combined ether extracts were washed three times with 150-mL portions of H_2O, dried ($MgSO_4$), and evaporated from a water bath (60–70 °C) with a rotary evaporator (10 mm) to give 9.2 g (59.3%) of the crude alcohol as a light yellow solid, mp 135–139 °C. Recrystallization from benzene (45 mL) gave 8.6 g (55.4%) of pure alcohol **12** as colorless crystals: mp 139–141 °C; ^{1}H NMR ($CDCl_3$) δ 1.80 (br, 1, OH), 1.95–2.70 (m, 2, CH_2), 2.85–3.25 (m, 2, $ArCH_2$), 5.20–5.45 (m, 1, CHO), 7.35–7.95 (m, 6, aryl); IR (KBr) 3500–2650 cm^{-1} (OH).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.76; H, 6.48.

Benz[*f*]indene (1). A solution of 8.6 g of benz[*f*]indan-1-ol in 250 mL of 10% H_2SO_4 was refluxed for 24 h. After cooling to room temperature, the reaction mixture was extracted with three 150-mL portions of a mixture of benzene and hexane (1:2). The extracts were washed three times with 100-mL portions of water, dried ($MgSO_4$), and evaporated to give 7.6 g (98%) of a colorless solid, mp 160–163 °C. Recrystallization from 340 mL of 95% ethanol gave 6.6 g (85%) of the hydrocarbon as colorless crystals: mp 163–164 °C; ^{1}H NMR ($CDCl_3$) δ 3.40–3.55 (m, 2, CH_2), 6.45–6.70 (m, 1, H_2), 6.80–7.05 (m, 1, H_3), 7.20–8.00 (m, 6, aryl); ^{13}C NMR (75 MHz, $CDCl_3$) 38.5 (ring CH_2's), 119, 122, 124.4, 124.8, 127.6, 131.7, 131.9, 133, 135.8, 141.4, 141.5, 143.8 (vinyl and aryl).

Anal. Calcd for $C_{13}H_{10}$: C, 93.94; H, 6.06. Found: C, 93.85; H, 6.23.

(Methylsulfonyl)methyl *p*-Tolyl Sulfone. To a stirred solution of 10.5 g of (methylthio)methyl *p*-tolyl sulfone[16] in 120 mL of HOAc and 43.5 mL of Ac_2O was added very slowly and carefully 15 mL of 30% H_2O_2. After 3 h at room temperature, an additional 15 mL of 30% H_2O_2 was added slowly to the reaction mixture. The mixture was stirred at room temperature for 70 min and diluted with water. The precipitated solid was filtered, washed three times with small portions of water, and recrystallized from HOAc to give 8.8 g (73%) of pure sulfone as snow-white crystals: mp 159–161 °C (lit.[17] mp 158 °C); ^{1}H NMR ($CDCl_3$) δ

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(15) Adams, R.; Binder, L. O. *J. Am. Chem. Soc.* **1941**, *63*, 2771.

(16) Ogura, K.; Yahata, N.; Watanabe, J.; Takahashi, K.; Iida, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3543.

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2.45 (s, 3, $SO_2C_6H_4CH_3$), 3.25 (s, 3, SO_2CH_3), 4.6 (s, 2, CH_2), 7.35–7.95 (m, 4, aryl).

2-(Methylsulfonyl)-2-(*p*-tolylsulfonyl)benz[*f*]indan (5a). To a stirred mixture of 3.14 g of 2,3-bis(bromomethyl)naphthalene[18] in 40 mL of 40% aqueous NaOH solution and 50 mL of CH_2Cl_2 was added 2.48 g of (methylsulfonyl)methyl *p*-tolyl sulfone followed by a catalytic amount of tetrabutylammonium bromide. The resulting suspension was stirred at room temperature for 1 h and treated with 150 mL of water and the CH_2Cl_2 layer separated. The aqueous solution was extracted with three 150-mL portions of CH_2Cl_2. The combined extracts were washed with three 100-mL portions of water, dried ($MgSO_4$), decolorized with charcoal, and evaporated from a water bath (35 °C) with a rotary evaporator (10 mm) to provide 3.5 g (87.5%) of crude sulfone **5a**, mp 249–252 °C. Because the sulfone had very low solubility in commonly used organic solvents, it could be purified simply by washing several times with acetone and hexane, to give 3 g (75%) of the indane sulfone as a white solid: mp 252–254 °C; IR (KBr) 1340, 1150 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.30 (s, 3, $SO_2C_6H_4CH_3$), 3.40 (s, 3, SO_2CH_3), 4.05 (s, 4, $ArCH_2$), 7.25–8.00 (m, 10, aryl).

Anal. Calcd for $C_{21}H_{20}O_4S_2$: C, 62.98; H, 5.03; S, 16.01. Found: C, 62.90; H, 4.84; S, 15.86.

Benz[*f*]indene (1) from 2-(Methylsulfonyl)-2-(*p*-tolylsulfonyl)benz[*f*]indan (5a). To a suspension of 5 g of **5a** in 300 mL of benzene was added a solution of 12.5 g of sodium methoxide in 360 mL of MeOH. The mixture was refluxed with stirring for 30 min and evaporated from a water bath (50 °C) with a rotary evaporator (10 mm). With stirring, the resulting residue was treated with 400 mL of CH_2Cl_2 and 400 mL of H_2O for 10 min. The organic layer was washed with three 150-mL portions of water, dried ($MgSO_4$), decolorized with charcoal, and evaporated to give 1.8 g of a yellow solid, the NMR spectrum of which showed that it was a mixture (about 1:1) of sulfones **6a** and **6b**: ^1H NMR ($CDCl_3$) δ 2.40 (s, 3, $SO_2C_6H_4CH_3$), 3.10 (s, 3, SO_2CH_3), 3.75 (m, 2, CH_2Ar), 3.95 (m, 2, CH_2Ar), 7.0–7.8 (m, 7, aryl, vinyl). Without further treatment, this mixture was reduced to **1**. To 8.3 g of a similarly prepared mixture of **6a** and **6b** in 620 mL of DMF and 620 mL of water were added 20 g of $Na_2S_2O_4$ and 19.5 g of $NaHCO_3$. The reaction mixture was refluxed for 7 h, treated with an additional 20 g of $Na_2S_2O_4$, and refluxed for another 21 h. The mixture was cooled to room temperature and treated with 600 mL of water and the resulting suspension extracted with three 100-mL portions of benzene. The combined extracts were washed with three 100-mL portions of water, dried over anhydrous $MgSO_4$, and evaporated, to give 3 g (61%) of the crude hydrocarbon as a pale yellow solid, which could be recrystallized from 120 mL of 95% EtOH, to afford 2.4 g (49%) of pure benz[*f*]indene as colorless crystals, mp 163–164 °C, identified by comparison of its melting point and spectral data with similar data obtained from the sample previously synthesized by elimination of water from benz[*f*]indan-1-ol (**12**).

2,2-Bis(phenylsulfonyl)benz[*f*]indan (5b). Sulfone **5b** was prepared by reaction of dibromide **4**[18] and bis(phenylsulfonyl)methane[19] by the same procedure used for synthesis of sulfone **5a**. The crude product could be recrystallized from ethyl acetate to give the sulfone (75%) as colorless crystals: mp 226–227.5 °C; IR (KBr) 1310, 1130 cm^{-1} (SO_2); ^1H NMR (DMSO-d_6) δ 4.1 (s, 4, $ArCH_2$), 7.6–8.1 (m, 16, aryl).

Anal. Calcd for $C_{25}H_{20}S_2O_4$: C, 66.94; H, 4.49; S, 14.30. Found: C, 66.44; H, 4.25; S, 13.81.

2-(Phenylsulfonyl)benz[*f*]indene (6c). Sulfone **6c** was synthesized from **5b** by the same procedure as was used for the synthesis of sulfone mixture **6a** and **6b**. The crude product was recrystallized from acetonitrile to give the sulfone (58%) as colorless crystals: mp 268–269 °C; IR (KBr) 1280, 1120 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 3.75 (m, 2, $ArCH_2$), 7.35–8.15 (m, 12, aryl, vinyl). Reduction by the same method described for **6a**/**6b** gave benz[*f*]indene in 60% yield.

Benz[*f*]indan (7). A. From 2,2-Bis(phenylsulfonyl)benz[*f*]indan (5b). To 100 mL of refluxing MeOH was added 2 g of Mg metal followed by 1.3 g of **5b**. The resulting suspension was refluxed for 2 h and an additional 1 g of Mg metal added. After refluxing for another 2 h, the reaction mixture was treated with an additional 1.5 g of Mg metal and refluxed for a final 1-h period. The solvent was evaporated from a water bath (40 °C) with a rotary evaporator (10 mm), and the resulting residue was treated with 200 mL of 20% aqueous H_2SO_4 solution. The aqueous solution was extracted twice with 50-mL portions of CH_2Cl_2. The combined CH_2Cl_2 extracts were washed once with 50 mL of 10% Na_2CO_3 solution and twice with 50-mL portions of water, dried over $MgSO_4$, and evaporated to give 0.45 g (93%) of pale yellow solid, which was recrystallized from 80% EtOH to give 0.35 g (72%) of pure benz[*f*]indane as colorless crystals: mp 86–88 °C (lit.[20] mp 84–86 °C); ^1H NMR ($CDCl_3$) δ 1.95–2.35 (m, 2, CH_2), 2.80–3.20 (t, 4, $ArCH_2$), 7.1–7.85 (m, 6, aryl, ArH).

B. From Benz[*f*]indene (1). To a solution of 200 mg of benz[*f*]indene (**1**) in 30 mL of MeOH/THF (1:1) was added 50 mg of 10% Pd/C, and the mixture was shaken in a Parr apparatus at a pressure of 38 psi over a period of 1.5 h. The reaction mixture was filtered to remove catalyst and the filtrate evaporated to afford 200 mg of crude hydrocarbon **7**, which was recrystallized from 80% EtOH to give 190 mg (94%) of pure **7** as colorless crystals, mp 86–88 °C. The IR and ^1H NMR spectral data of the product were identical with analogous data obtained from the sample prepared from sulfone **5b**.

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Registry No. **1**, 268-40-6; **4**, 38998-33-3; **5a**, 123332-14-9; **5b**, 123332-20-7; **6a**, 123332-15-0; **6b**, 123332-19-4; **6c**, 123332-21-8; **7**, 1624-26-6; **9**, 123332-17-2; **9** diacid derivative, 123332-16-1; **10**, 68125-21-3; **11**, 68106-95-6; **12**, 123332-18-3; **21**, 64399-25-3; 1-bromo-2-methylnaphthalene, 2586-62-1; 1-bromo-2-(bromomethyl)naphthalene, 37763-43-2; diethyl malonate, 105-53-3; β-(1-bromo-2-naphthyl)propionyl chloride, 68106-94-5; (methylthio)methyl *p*-tolyl sulfone, 59662-65-6; bis(phenylsulfonyl)methane, 3406-02-8.

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