was purified by the preparative TLC on SiO_2 plate developed by *n*-pentane–Et_2O (10:3) to give pale yellow needles (**10**), mp 49–52 °C, which were identified with the authentic sample[6] by the comparison of IR and NMR spectra and the mixture melting point.

2,7,9,10,11,12-Hexakis(trifluoromethyl)-1,8-diphosphatetracyclo[6.2.2.0^{2,7}.0^{3,6}]deca-4,9,11-triene (11 and 12). The solution of cerium(IV) ammonium nitrate (14 g) in H_2O–EtOH (7:3, 5 mL) was added dropwise to the solution of **1** (2.23 g) and cyclobutadieneiron tricarbonyl (0.763 g) in acetone (100 mL) at 0 °C for 20 min. After the solution was stirred at room temperature for 3 h, H_2O (100 mL) was added, and the reaction mixture was extracted with Et_2O. After the Et_2O layer was washed with H_2O and dried over Na_2SO_4, Et_2O was evaporated with a vacuum line. The residue was chromatographed over SiO_2 (150 g) in *n*-pentane. The first effluent with *n*-pentane was recrystallized from *n*-pentane to give colorless plates (**11**): 410 mg (23.7%); mp 97–8 °C (in a sealed tube); IR (KBr) $\nu_{C=C}$ 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.00 (2 H, m, >CH), 6.22 (2 H, s, C=CH); ^{19}F NMR ϕ −5.40 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 40.6 Hz, CF_3], −6.06 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 38.4 Hz, CF_3], −6.16 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 33.8 Hz, CF_3]; mass *m/e* 600 (M^+); high mass calcd for $C_{16}H_4F_{18}P_2$ 599.950, found 599.949.

The second effluent was recrystallized from *n*-pentane to give colorless plates (**12**): 560 mg (33.2%); mp 111–112 °C (in a sealed tube); IR (KBr) $\nu_{C=C}$ 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.95 (2 H, b, >CH), 6.00 (2 H, b, C=CH); ^{19}F NMR ($CDCl_3$) ϕ −2.84 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 41.7 Hz, CF_3], −6.04 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 39.5 Hz, CF_3], −6.08 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 39.5 Hz, CF_3]; mass *m/e* 600 (M^+); high mass calcd for $C_{16}H_4F_{18}P_2$ 599.950, found 599.949.

2,5,7,10,11,12-Hexakis(trifluoromethyl)-1,6-diphosphahexacyclo[4.4.2.0^{2,5}.0^{3,9}.0^{4,8}.0^{7,10}]dodec-11-ene (13). The solution of **12** (350 mg) in acetone (5 mL) was sealed in a Pyrex tube (diameter = 7 mm) under vacuum and irradiated with a high-pressure mercury lamp for 16 h. After evaporation of acetone with a vacuum line, the residue was recrystallized from acetone to give colorless plates (**13**): 247 mg (73%); mp 201–203 °C (in a sealed tube); IR (KBr) $\nu_{C=C}$ 1610; ^{1}H NMR [$(CD_3)_2CO$] δ 3.96 (4 H, s); ^{19}F NMR [$(CD_3)_2CO$] ϕ −1.06 [12 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 41.3 Hz, $4CF_3$], −4.80 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 38.6 Hz, $2CF_3$]; mass *m/e* 600 (M^+); high mass, calcd for $C_{16}H_4F_{18}P_2$ (M^+) 599.950, found 599.950.

Similar irradiation of **11** in a Pyrex NMR tube caused no change of the ^{1}H and ^{19}F NMR.

Reaction of 1 wtih 2,3-Dimethylbutadiene. The solution of **1** (1 g) and 2,3-dimethylbutadiene (0.66 g) in CH_3CN (20 mL) was shaken at 100 °C in a stainless steel tube for 5 h. After evaporation of solvent with a vacuum line, the residue was chromatographed over SiO_2 (50 g) in *n*-pentane solution. The first effluent with *n*-pentane was sublimed at 30 °C (15 mmHg) to give colorless needles [1,2-dimethyl-4,5-bis(trifluoromethyl)-1,4-cyclohexadiene]: 120 mg (22.9%); mp 49–50 °C (in a sealed tube); ^{1}H NMR ($CDCl_3$) δ 1.73 (6 H, s, $2CH_3$), 2.97 (4 H, bs, $2CH_2$); ^{19}F NMR −5.0 (s); mass *m/e* 244 (M^+). This compound was identified with the authentic sample obtained by the reaction of hexafluorobutyne-2 and dimethylacetylene.

The second effluent from the SiO_2 column mentioned above was recrystallized from *n*-pentane to give colorless plates: 194 mg (19.1%); mp 119–122 °C (in a sealed tube); IR (KBr) $\nu_{C=C}$ 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.75 (12 H, m, $4CH_3$), 2.08–3.50 (8 H, bm, $4CH_2$); ^{19}F NMR ϕ −3.40 (3 F, m, CF_3), −8.00 to −12.10 (9 F, bm, $3CF_3$); mass *m/e* 556 (M^+); high mass, calcd for $C_{20}H_{20}F_{12}P_2$ (M − 16) 550.085, found 550.085.

These data show that this product consists of 2 mol of dimethylbutadiene, 1 mol of diphosphabenzene, and one oxygen atom, but its structure is not fully assigned.

Thermolysis of the Exo Adduct (11). (a) The solution of **11** (150 mg) in *n*-pentane (0.5 mL) was sealed in a Pyrex tube (diameter = 3 mm) under vacuum and heated at 130 °C for 16 h. The crystals precipitated on cooling were filtered and recrystallized from acetone. Colorless needles, 148 mg (quantitative), were obtained: mp 175–176 °C (in a sealed tube); IR (KBr) $\nu_{C=C(cyclobutene)}$ 1715, $\nu_{C=C}$ 1590 cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 3.32 (2 H, m, >CH), 3.54 [2 H, d, $^1/_2(J_{PH} + J_{PH'})$ = 24 Hz, PCCH]; ^{19}F NMR [$(CD_3)_2CO$] ϕ 2.36 (6 F, s, C=CCF$_3$), −5.66 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 40.6 Hz, $2CF_3$], −6.22 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 40.6 Hz, $2CF_3$]; mass *m/e* 600 (M^+), high mass calcd for $C_{16}H_4F_{18}P_2$ (M^+) 599.950, found 599.949.

(b) The solution of **11** (100 mg) in *n*-pentane (0.5 mL) was sealed in a Pyrex tube (diameter = 3 mm) under vacuum and heated at 180 °C for 3 h. ^{19}F NMR of the reaction mixture showed that equimolar amounts of 1,2-bis(trifluoromethyl)benzene and **3** were formed quantitatively. The former product was identified with the authentic sample by GLC.

Thermolysis of the Endo Adduct (12). The endo adduct (**12**, 70 mg) and *n*-pentane (0.5 mL) were sealed in a Pyrex tube (diameter = 3 mm) under vacuum and heated at 180 °C for 3 h. The crystals precipitated on cooling were collected by filtration and recrystallized from acetone (−78 °C) to give colorless plates (**16**): 52 mg (quantitative); mp over 200 °C; IR (KBr) $\nu_{C=C}$ 1595 cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 2.80 (2 H, m, >CH), 3.00 (2 H, m, >CH); ^{19}F NMR [$(CD_3)_2CO$] ϕ −2.72 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 40.6 Hz, $2CF_3$], −5.73 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 37.2 Hz, $2CF_3$], −5.97 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 37.2 Hz, $2CF_3$], −6.32 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 40.6 Hz, $2CF_3$], −7.38 [6 F, d, $^1/_2(J_{PF} + J_{PF'})$ = 38.6 Hz, $2CF_3$]; mass *m/e* 600 [M^+ − 386, $(CF_3)_4C_4P_2$]. Extremely high volatility prevented determination of the accurate molecular weight. Therefore, the structure of **16** is a speculative one.

Acknowledgment. We express our sincere gratitude to Dr. D. Schonburg of Technische Universitat, Braunschweig, for X-ray analysis of compound **13**.

Registry No. **1**, 2925-91-9; **3**, 62218-19-3; **4**, 19968-19-5; **9**, 63790-89-6; **10**, 63790-90-9; **11**, 62839-77-4; **12**, 62929-10-6; **13**, 62839-78-5; **14**, 71901-72-9; **16**, 71901-73-0; diazomethane, 334-88-3; phenyl azide, 622-37-7; 2,3-dimethylbutadiene, 513-81-5; 1,2-dimethyl-4,5-bis(trifluoromethyl)-1,4-cyclohexadiene, 781-87-3; 1,2-bis(trifluoromethyl)benzene, 433-95-4.

Synthesis of Some Tetrahydrochrysenes as Potential Ultraviolet Laser Dyes[1-3]

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A general synthetic pathway employed in the synthesis of 5,6,11,12-tetrahydrochrysene and six of its benzo- and phenyl-substituted derivatives is described. Development of an efficient synthesis of the required starting materials 2-(3-biphenylyl)ethyl bromide and 6-phenyl-3,4-dihydro-1(2*H*)-naphthalenone is also presented. Preliminary laser performance data of the tetrahydrochrysenes have been included.

A number of *trans*-1,2-diarylethylenes (**1**) which have been synthesized in our laboratory during the past 15 years as liquid scintillator solutes[4] have recently shown promise as potential UV laser dyes when irradiated at 337 nm with

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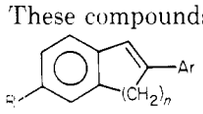
a nitrogen laser[5]. These compounds are all derivatives

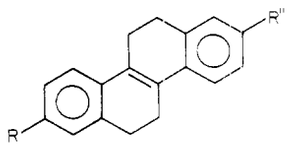


1

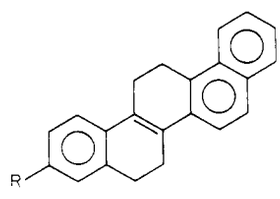
n = 1,2; R = H, phenyl; Ar = phenyl, 1-naphthyl, 2-naphthyl, 4-biphenylyl

of *trans*-stilbene and were designed to have the ethylene double bond as part of a fused ring. Such a structural condition is necessary in the use of these compounds as organic fluors since in solution *trans*-stilbene reverts to the cis isomer[6] when photoexcited rather than efficiently emitting energy in the form of light; the presence of the ring prevents such isomerization, and the excited molecule efficiently emits its energy as light (fluorescence). The wavelength of this emitted light falls in the range of 360–425 nm, depending on the types of aryl groups attached to the ethylene moiety. These systems have short fluorescence lifetimes in the range of 1–8 ns, making them highly desirable as compounds for use as laser dyes.

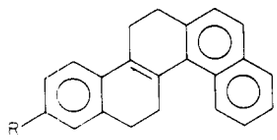
Although many of these compounds were shown to have excellent lasing properties without significant fatigue during prolonged excitation, one of the structural features of the above compounds is the free rotating aryl group attached to the olefinic bond. Taber[7] has shown that coplanarity of the conjugated system is a desirable condition for efficient scintillation in polyaryls, and a logical extension of the *trans*-diarylethylene systems was to synthesize molecules in which free rotation of both aryl groups is restricted, hopefully enhancing the lasing characteristics of these compounds. We have therefore synthesized the tetrahydrochrysene derivatives **2aa**, **2ab**, **2ac**, **2ba**, **2bb**, **2bc**, and **2bd** and have evaluated them as potential UV laser dyes by using a N_2 laser.



2aa, R = R′ = H
2ba, R = H, R″ = C_6H_5
2bd, R = R″ = C_6H_5



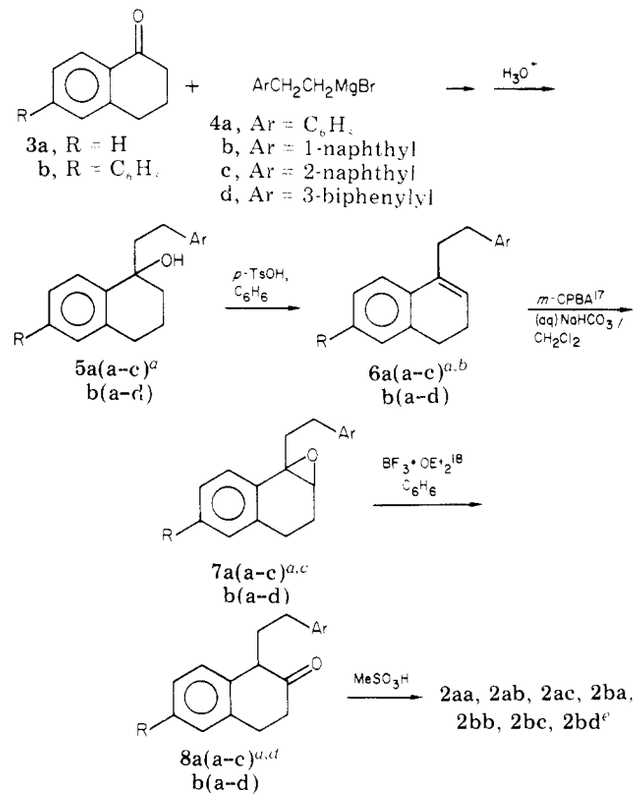
2ab, R = H
2bb, R = C_6H_5



2ac, R = H
2bc, R = C_6H_5

Cahana and co-workers[8] reported the synthesis of **2aa** from 4-phenyl-2-(2-phenylethyl)butanoic acid, but the generality of this approach was not investigated further. Salzer[9] and Mukherji[10] have reported the synthesis of **2aa** and **2ab**, respectively, from **8aa** and **8ab** in unspecified yield. In our hands the synthesis of **8aa** from β-tetralone via alkylation of the sodium enolate,[10] the lithium enolate,[11] the potassium enolate,[12] and the pyrrolidine enamine[13] gave little if any of the desired ketone.

Scheme I



[a] (5-8)aa, R = H, Ar = C_6H_5; (5-8)ab, R = H, Ar = 1-naphthyl; (5-8)ac, R = H, Ar = 2-naphthyl; (5-8)ba, R = Ar = C_6H_5; (5-8)bb, R = C_6H_5, Ar = 1-naphthyl; (5-8)bc, R = C_6H_5, Ar = 2-naphthyl; (5-8)bd, R = C_6H_5, Ar = 3-biphenylyl. [b] Table I. [c] Table II. [d] Table III. [e] Table IV.

A successful synthesis of **8aa** was developed as outlined in Scheme I and applied to the synthesis of **2a(a–c)** from **3a** and **2b(a–d)** from **3b**, respectively. Although the reaction of **4a** with **3a** proceeded smoothly in ether, **4b** and **4c** underwent extensive coupling under these conditions;[14,15] however, formation of the Grignard reagents in THF followed by replacement of the THF with benzene in the reaction with **3a** circumvented this problem.[16]

Although 2-(3-biphenylyl)ethyl bromide (**9**) needed for the preparation of **4d** had been prepared earlier,[19] a shorter

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Table I.[a] 3,4-Dihydronaphthalenes 6a(a-c) and 6b(a-d)

compd	R	Ar	% yield from 3(a or b)	mp, °C	R_f[b]	NMR
6aa	H	phenyl	62[c]	d	0.68	e
6ab	H	1-naphthyl	58[f]	102.5-103.5[g]	0.45	h
6ac	H	2-naphthyl	51[i]	57.5-59.5[g]	0.43	j
6ba	C_6H_5	phenyl	38[c]	68.5-69.5[g]	0.42	k
6bb	C_6H_5	1-naphthyl	60[f]	114-117[l]	0.39	m
6bc	C_6H_5	2-naphthyl	40[i]	106.5-108[l]	0.38	n
6bd	C_6H_5	3-biphenylyl	39[o]	74-78.5[p]	0.39	q

[a] Satisfactory analytical data (±0.25% for C and H) were obtained for all compounds in this table. See Experimental Section for typical procedure. [b] TLC solvent = benzene:cyclohexane (1:2). [c] Grignard prepared (in ether) from 2-phenylethyl bromide (Aldrich), redistilled, bp 97-98 °C (14 mm). [d] Bp 117-118 °C (0.02 mm) [lit.[25] bp 209-212 °C (16 mm)]. [e] ^{1}H NMR ($CDCl_3$) δ 7.31-6.94 (9 H, m), 5.73 (1 H, t, J = 5 Hz), 2.86-1.89 (8 H, m); ^{13}C NMR ($CDCl_3$) 142.08, 136.61, 135.68, 134.61, 128.26, 128.12, 127.48, 126.21, 125.63, 125.03, 122.35, 34.76, 34.61, 28.26, 22.93 ppm. [f] Grignard prepared (in THF) from 2-(1-naphthyl)ethyl bromide, bp 115-116 °C (0.02 mm).[23] [g] Recrystallized from hexanes. [h] ^{1}H NMR ($CDCl_3$) δ 8.12-6.97 (11 H, m), 5.82 (1 H, t, J = 5 Hz), 3.49-1.98 (8 H, m); ^{13}C NMR ($CDCl_3$) 138.19, 136.63, 135.97, 134.68, 133.80, 131.87, 128.57, 127.47, 126.49, 126.41, 126.21, 125.74, 125.51, 125.32, 125.16, 124.91, 123.57, 122.36, 33.64, 31.75, 28.22, 22.94 ppm. [i] Grignard prepared (in THF) from 2-(2-naphthyl)ethyl bromide, mp 59-61.5 °C.[24] [j] ^{1}H NMR ($CDCl_3$) δ 7.88-7.00 (11 H, m), 5.72 (1 H, t, J = 5 Hz), 3.08-1.87 (8 H, m); ^{13}C NMR ($CDCl_3$) 139.39, 136.46, 135.44, 134.47, 133.39, 131.78, 127.48, 127.39, 127.16, 126.45, 126.18, 125.58, 124.94, 124.84, 122.31, 34.61, 34.36, 28.15, 22.80 ppm. [k] ^{1}H NMR ($CDCl_3$) δ 7.67-6.92 (13 H, m), 5.73 (1 H, t, J = 5 Hz), 2.88-1.96 (8 H, m); ^{13}C NMR ($CDCl_3$) 141.83, 140.61, 138.98, 136.87, 135.30, 133.58, 128.38, 128.12, 127.98, 126.72, 126.54, 126.07, 125.50, 124.96, 124.70, 122.67, 34.77, 34.56, 28.46, 23.04 ppm. [l] Recrystallized from ethyl acetate:95% ethanol (1:6). [m] ^{1}H NMR ($CDCl_3$) δ 8.17-7.04 (15 H, m), 5.87 (1 H, t, J = 4 Hz), 3.47-1.89 (8 H, m); ^{13}C NMR ($CDCl_3$) 140.98, 139.39, 137.25, 135.92, 133.97, 133.90, 131.95, 128.70, 128.60, 127.00, 126.82, 126.55, 126.35, 125.89, 125.66, 125.45, 125.31, 125.26, 124.96, 123.72, 122.93, 33.83, 31.97, 28.54, 23.15 ppm. [n] ^{1}H NMR ($CDCl_3$) δ 7.90-7.06 (15 H, m), 5.82 (1 H, t, J = 4.5 Hz), 3.01-2.01 (8 H, m); ^{13}C NMR ($CDCl_3$) 141.03, 139.67, 139.41, 137.26, 135.60, 133.92, 133.69, 132.06, 128.60, 127.72, 127.52, 127.34, 126.98, 126.89, 126.82, 126.35, 125.74, 125.41, 124.97, 124.88, 122.92, 35.08, 34.53, 28.54, 23.12 ppm. [o] Grignard prepared (in THF) from 2-(3-biphenylyl)ethyl bromide (**9**); see Experimental Section. [p] Recrystallized from methanol. [q] ^{1}H NMR ($CDCl_3$) δ 7.92-6.91 (17 H, m), 5.87 (1 H, t, J = 4 Hz), 3.12-1.89 (8 H, m); ^{13}C NMR ($CDCl_3$) 142.61, 141.37, 141.26, 140.98, 139.38, 137.21, 135.65, 133.89, 128.59, 127.30, 127.07, 126.97, 126.89, 126.82, 126.35, 125.35, 124.94, 124.66, 122.92, 35.09, 34.65, 28.56, 23.15 ppm.

Table II.[a] 3,4-Dihydronaphthalene 1,2-Epoxides 7a(a-c) and 7b(a-d)

compd	R	Ar	IR, cm^{-1}	R_f[b]
7aa	H	phenyl	3060, 3030, 2935, 1600, 1495, 1450, 1250 (C-O), 1080, 1045, 905, 760, 705	0.55[c]
7ab	H	1-naphthyl	3030, 2930, 2850, 1570, 1450, 1430, 1260 (C-O), 900, 825, 760	0.62[d]
7ac	H	2-naphthyl	3030, 2930, 1600, 1505, 1495, 1450, 1260 (C-O), 895, 855, 815, 755	0.61
7ba	C_6H_5	phenyl	3050, 2940, 1600, 1500, 1470, 1255 (C-O), 775, 755	0.57
7bb	C_6H_5	1-naphthyl	3060, 2940, 2850, 1600, 1425, 1390, 1265 (C-O), 900, 825, 775, 730	0.64
7bc	C_6H_5	2-naphthyl	3050, 2930, 2850, 1600, 1570, 1480, 1430, 1270 (C-O), 890, 815, 750, 700	0.61
7bd	C_6H_5	3-biphenylyl	3060, 3030, 2940, 2845, 1600, 1475, 1265 (C-O), 900, 830, 760, 740, 700	0.65

[a] See Experimental Section for typical procedure. [b] TLC solvent = ethyl acetate:toluene (1:9) unless otherwise specified. [c] Solvent = ethyl acetate:benzene (1:9). [d] Crude, mp 93-96 °C.

route was developed in the current work via ethyl 3-biphenylacetate (**12**) which was readily obtained through the reaction of 3-phenyl-2-cyclohexenone[20] with the lithium enolate of ethyl acetate[21] followed by dehydration and dehydrogenation of the resulting hydroxy ester **11**. The ketone **3b** was obtained by cyclization of 4-(3-biphenylyl)butanoic acid (**16**) which was available from the bromide **9** via the malonic ester or more readily by desulfurization of 4-(2-dibenzothienyl)butanoic acid (**19**)[22] with Raney nickel alloy in aqueous base.

All of the tetrahydrochrysenes **2** gave UV-absorption, ^{13}C NMR, and ^{1}H NMR spectra (Table IV) consistent with their assigned structures. Each was tested to determine primarily whether they were capable of lasing under pulsed nitrogen laser excitation. The dyes were evaluated in cyclohexane solution except in those cases where solubility limitations required the use of toluene as the solvent. Lasing wavelength ranges and qualitative maximum power output for each dye are reported in Table IV.

Experimental Section

Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected as are reported boiling points. Elemental analyses were performed by Mrs. Ruby Ju of the Department of Chemistry. IR measurements were obtained on a Perkin-Elmer Model 237 spectrophotometer. ^{1}H NMR spectra using Me_4Si as an internal standard were recorded on Varian Model A-60 or EM-360 instruments at 60 MHz or a Varian Model FT-80A instrument at 80 MHz. ^{13}C NMR spectra were obtained on pulse Fourier transform Varian Model XL-100, CFT-20, or FT-80A spectrometers. The ^{13}C chemical shifts, reported as parts per million downfield from Me_4Si, were referenced to the solvent peaks: $CDCl_3$ (76.9 ppm), C_6D_6 (128.0 ppm), or Me_2SO-d_6 (39.6 ppm). Product purity and reaction progress were checked by using analytical thin-layer chromatography using 2.5 × 10 cm Analtech plates coated with silica gel GF. UV-visible

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Table III.[a] 3,4-Dihydro-2(1*H*)-naphthalenones 8a(a-c) and 8b(a-d)

compd	R	Ar	% yield from 6	bp, °C[b] (mmHg)	R_f[c]	NMR/IR
8aa	H	phenyl	94	120-125[d] (0.005)	0.49[e]	*f*
8ab	H	1-naphthyl	93	178-180[g] (0.10)	0.53	*h*
8ac	H	2-naphthyl	93	167-170 (0.005)	0.53	*i*
8ba	C_6H_5	phenyl	99	180-185 (0.01)	0.50	*j*
8bb	C_6H_5	1-naphthyl	85	225-232 (0.02)	0.52	*k*
8bc	C_6H_5	2-naphthyl	81	231-235 (0.005)	0.51	*l*
8bd	C_6H_5	3-biphenylyl	92	232-240 (0.005)	0.55	*m*

[a] Satisfactory analytical data (±0.40% for C and H) were obtained for all compounds in this table. See Experimental Section for typical procedure. [b] Cited temperatures refer to evaporative distillation pot temperatures and do not represent true boiling points. [c] TLC solvent = ethyl acetate:toluene (1:9) unless otherwise specified. [d] Reported[9] bp 210 °C (6 mm). [e] Solvent = ethyl acetate:benzene (1:9). [f] IR (neat) 3060, 3030, 2940, 2850, 1705 (C=O), 1600, 1495, 1450, 1250, 1170, 755, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28-7.09 (9 H, m), 3.44 (1 H, t, J = 6 Hz), 3.23-2.03 (8 H, m). [g] Reported[10] bp 225-230 °C (4 mm). [h] IR (neat) 3055, 3025, 2940, 2855, 1705 (C=O), 1600, 1480, 1450, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00-7.02 (11 H, m), 3.53 (1 H, t, J = 6 Hz), 3.22-2.02 (8 H, m). [i] IR (neat) 3040, 2940, 2855, 1705 (C=O), 1600, 1510, 1460, 1455, 855, 820, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93-7.14 (11 H, m), 3.49 (1 H, t, J = 6 Hz), 3.22-2.12 (8 H, m). [j] IR (neat) 3040, 2940, 1715 (C=O), 1600, 1515, 1480, 780, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.83-6.87 (13 H, m), 3.47 (1 H, t, J = 6 Hz), 3.29-1.93 (8 H, m). [k] IR (neat) 3040, 2940, 1710 (C=O), 1600, 1480, 800, 775, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.05-6.98 (15 H, m), 3.60 (1 H, t, J = 6 Hz), 3.39-2.14 (8 H, m). [l] IR (neat) 3050, 2940, 2850, 1710 (C=O), 1600, 1480, 910, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90-7.06 (15 H, m), 3.52 (1 H, t, J = 6 Hz), 3.31-2.02 (8 H, m). [m] IR (neat) 3055, 3030, 2940, 2850, 1710 (C=O), 1600, 1475, 760, 700, 680; ^1H NMR ($CDCl_3$) δ 7.79-6.85 (17 H, m), 3.54 (1 H, t, J = 6 Hz), 3.33-2.07 (8 H, m).

Table IV.[a] Tetrahydrochrysenes 2a(a-c) and 2b(a-d)

							lasing data		
compd	R	R'	% yield from 8	mp, °C	R_f[b]	NMR/UV	solvent	lasing wavelength, nm	power
2aa	H	H	78	101.5-103[c]	0.45	*d*	cyclohexane	384-421	moderate
2ab	H		91	185-186.5[e]	0.41	*f*	cyclohexane	418-419	very weak
2ac	H		46	150-151[g]	0.42	*h*	cyclohexane	did not lase	
2ba	C_6H_5	H	79	194-196[i]	0.39	*j*	toluene	394-432	moderate
2bb	C_6H_5		75	238-240[k]	0.37	*l*	toluene	416-461	moderate
2bc	C_6H_5		50	211.2-212.2[m]	0.36	*n*	toluene	403-444	strong
2bd	C_6H_5	C_6H_5	82	307-308[o]	0.37	*p*	toluene	410-457	very strong

[a] Satisfactory analytical data (±0.26% for C and H) were obtained for all compounds in this table. See Experimental Section for typical procedure. [b] TLC solvent = benzene:cyclohexane (3:7). [c] Recrystallized from methanol, reported[8,9] mp 105 °C. [d] ^1H NMR ($CDCl_3$) δ 7.31-7.02 (8 H, m), 2.97-2.32 (8 H, m); ^{13}C NMR ($CDCl_3$) 135.70, 135.22, 130.91, 126.79, 126.20, 121.62, 28.14, 24.46 ppm; UV λ_{max} nm (log ε) 339.7 (4.38), 324.0 (4.54), 310.5 (4.42), 243.8 (4.16), 237.0 (4.37), 231.0 (4.29), 206.9 (4.48). [e] Recrystallized from ethyl acetate:ethanol (1:20), reported[10] mp 269-270 °C. [f] ^1H NMR (C_6D_6) δ 8.05-6.98 (10 H, m), 3.21-2.20 (8 H, m); ^{13}C NMR (C_6D_6) 136.48, 135.83, 133.69, 133.45, 132.06, 131.82, 131.34, 131.12, 128.87, 128.29, 128.25, 127.41, 126.19, 125.19, 124.02, 122.35, 121.51, 28.82, 25.33, 24.58, 23.52 ppm; UV λ_{max} nm (log ε) 365.3 (4.35), 347.3 (4.46), 332.0 (4.31), 292.3 (4.63), 280.8 (4.53), 270.3 (4.20), 250.0 (4.23), 241.8 (4.32). [g] Recrystallized from ethanol. [h] ^1H NMR ($CDCl_3$) δ 7.52-6.70 (10 H, m), 2.95-2.11 (8 H, m); ^{13}C NMR ($CDCl_3$) 135.91, 135.62, 134.33, 132.64, 132.43, 131.15, 127.62, 126.95, 126.72, 126.54, 126.30, 125.34, 125.03, 124.67, 121.94, 120.15, 28.76, 28.28, 24.82 ppm; UV λ_{max} nm (log ε) 348.6 (4.44), 331.9 (4.58), 317.7 (4.43), 290.2 (4.21), 278.7 (4.15), 267.9 (3.95), 258.8 (4.12), 247.7 (4.63). [i] Recrystallized from benzene:ethyl acetate (1:9). [j] ^1H NMR ($CDCl_3$) δ 7.73-6.98 (12 H, m), 3.21-2.51 (8 H, m); ^{13}C NMR ($CDCl_3$) 141.03, 139.37, 136.19, 136.04, 135.76, 135.21, 131.35, 131.01, 128.62, 127.11, 127.01, 126.82, 126.57, 126.44, 125.84, 125.09, 122.37, 121.94, 28.49, 28.31, 24.55 ppm; UV λ_{max} nm (log ε) 355 sh (4.34), 339.4 (4.48), 326 sh (4.39), 240.8 (4.13), 235 sh (4.13), 205.2 (4.48). [k] Recrystallized from cyclohexane:ethyl acetate (1:1). [l] ^1H NMR (C_6D_6) δ 8.05-6.73 (14 H, m), 3.27-2.33 (8 H, m); ^{13}C NMR (C_6D_6) 147.62, 141.73, 139.93, 136.36, 135.61, 133.51, 132.17, 131.87, 131.19, 131.14, 128.91, 128.28, 127.71, 127.27, 126.50, 126.30, 126.25, 125.54, 125.25, 124.03, 122.85, 121.55, 28.97, 25.38, 24.48, 23.55 ppm; UV λ_{max} nm (log ε) 379.1 (4.07), 360.9 (4.19), 346.2 (4.05), 301.1 (4.11), 289.0 (4.00), 255.1 (3.76), 247.0 (3.81), 223.2 (4.28), 206.0 (4.27). [m] Recrystallized from benzene:cyclohexane (1:6). [n] ^1H NMR (C_6D_6) δ 7.92-6.91 (14 H, m), 3.02-2.39 (8 H, m); ^{13}C NMR (C_6D_6) 141.69, 140.09, 136.71, 135.72, 135.09, 134.88, 133.72, 133.49, 132.82, 131.83, 128.42, 128.29, 127.70, 127.65, 127.40, 127.29, 126.35, 125.92, 125.57, 125.48, 123.16, 121.04, 28.91, 28.86, 25.18 ppm; UV λ_{max} nm (log ε) 368.0 (4.54), 350.1 (4.66), 337.2 (4.55), 296.0 (4.18), 283.9 (4.09), 273.3 (3.89), 247.0 (4.37), 220.1 (4.64). [o] Recrystallized from benzene. [p] ^1H and ^{13}C NMR spectra could not be obtained for this compound due to its insolubility; UV λ_{max} nm (log ε) 354.7 (4.62), 237.5 (4.27), 200.8 (4.70).

spectra were obtained in cyclohexane solution and recorded on a Cary Model 219 spectrophotometer using 1-cm quartz cells.

To provide an example of the typical procedures used for the synthesis of the tetrahydrochrysenes **2** the synthesis of 5,6,13,14-tetrahydrobenzo[*a*]chrysene (**2ab**) via the 3,4-dihydronaphthalene **6ab**, the 3,4-dihydronaphthalene 1,2-epoxide **7ab**, and the 3,4-dihydro-2(1*H*)-naphthalenone **8ab** is described in detail in this section. Tables I, II, III, and IV provide pertinent information on yields, physical data, analyses, and spectra for all of the compounds **6**, **7**, **8**, and **2**, respectively.

Each of the dyes **2** was tested to determine primarily whether they were capable of lasing under pulsed nitrogen laser excitation. In addition, the wavelength range and estimated power of each dye were determined. The dyes were evaluated in cyclohexane solution except in those cases where toluene was used because of solubility problems in cyclohexane. A 1 mM solution of the dye was placed in a 4-mL quartz cell which was transparent on both sides and ends. The cell was capped and placed within the optical cavity of an AVCO Model C590 pulsed gas laser equipped with a Model 1000 dye module and was irradiated with a narrow pulse of 332-nm nitrogen laser light which spanned the entire length of the cell. A repetition rate of one pulse per second was maintained, and the mirror and diffraction grating alignments were adjusted until lasing was observed. The wavelength range was measured by using a Bausch and Lomb Model 33-86-07 monochromator set at 0.5-mm entrance and exit slit widths. Laser

power at maximum intensity was estimated by comparison with 4,4‴-bis[(2-butyloctyl)oxy]-*p*-quaterphenyl (BBQ).

1-[2-(1-Naphthyl)ethyl]-3,4-dihydronaphthalene (6ab). A 100-mL three-necked round-bottom flask equipped with a magnetic stirrer, an addition funnel, a rubber septum, and a condenser attached to a silica gel drying tube was flame dried and charged with 0.196 g (8.07 mmol) of Mg turnings. A crystal of I_2 was added, and the flask was kept under an atmosphere of dry N_2 at all times. The Mg was covered with 2.4 mL of anhydrous THF, and to the stirred mixture was added dropwise 1.91 g (8.15 mmol) of 2-(1-naphthyl)ethyl bromide,[23] bp 115–116 °C (0.2 mm), in 6 mL of anhydrous THF. The solution was warmed gently to reflux during the addition, and after the complete addition of the bromide, the solution was stirred at reflux for 1 h. The THF was removed while anhydrous benzene was added to keep the reaction volume constant. After the complete addition of the benzene, the solution was cooled in an ice bath, and a solution of 1.17 g (8.00 mmol) of 3,4-dihydro-1(2*H*)-naphthalenone, bp 78–79 °C (0.3 mm), in 18 mL of anhydrous benzene was added dropwise over a 40-min period. After the addition of the ketone, the solution was heated at reflux for 1.3 h. The bright green solution was allowed to cool slowly to ambient temperature and was stirred for an additional 10 h. The reaction mixture was cooled in ice, and the reaction was quenched with 5% HCl and extracted with ether. The organic layer was washed with water and saturated NaCl and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to give a pale green oil. This oil was dissolved in 45 mL of benzene and heated at reflux for 20 min with approximately 0.1 g of *p*-toluenesulfonic acid. After the solution had cooled to ambient temperature, the solution was washed with water and saturated NaCl and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure, affording an amber oil. This oil was dissolved in 4 mL of benzene/cyclohexane (1:2) and chromatographed on a 13 × 2.5 cm column of neutral Woelm alumina. Evaporation of the first 125 mL of eluate under reduced pressure gave a colorless oil, which partially solidified upon standing. This oily solid was subjected to distillation (Kugelrohr, 150–153 °C, 0.005 mm) which afforded **6ab** (1.31 g, 58%) as a colorless solid, mp 97.5–101 °C. Several recrystallizations from hexanes gave an analytical sample as colorless plates, mp 102–103.5 °C. See Table I for analytical and spectral data.

1-[2-(1-Naphthyl)ethyl]-3,4-dihydronaphthalene 1,2-Epoxide (7ab). A solution of 0.57 g (2.0 mmol) of **6ab**, mp 102.5–103.5 °C, in 20 mL of CH_2Cl_2 and 30 mL of aqueous 0.5 M $NaHCO_3$ was introduced into a 125-mL pear-shaped flask equipped with a magnetic stirrer and a thermometer. The vigorously stirred mixture was cooled to 3 °C in an ice bath, and 0.41 g (2.0 mmol) of 85% *m*-chloroperbenzoic acid was added in small portions over a 15-min period.[17] The cold bath was removed, and the mixture was stirred for 4 h. The organic layer was separated, washed with 10% Na_2SO_3, and dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure to give **7ab** (0.57 g, 100%) as a yellow oil which solidified upon standing to give a pale yellow solid, mp 93–96 °C. See Table II for TLC and spectral data.

1-[2-(1-Naphthyl)ethyl]-3,4-dihydro-2(1*H*)-naphthalenone (8ab). A 250-mL round-bottom flask equipped with a magnetic stirrer and a rubber septum was flame dried and flushed with dry N_2. The flask was charged with a solution of 0.55 g (1.83 mmol) of crude **7ab**, mp 93–96 °C, in 25 mL of anhydrous benzene. To this stirred solution was added approximately 0.01 mL of boron trifluoride etherate.[18] After being stirred for 20 min, the solution was washed with water and saturated NaCl and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to give a pale yellow oil. This oil was subjected to evaporative distillation (178–182 °C, 0.15 mm) to afford **8ab** (0.51 g, 93%) as a pale yellow oil which was used directly in the next reaction. See Table III for analytical and spectral data.

5,6,13,14-Tetrahydrobenzo[*a*]chrysene (2ab). A mixture of 0.50 g (1.66 mmol) of **8ab** and 10 mL of methanesulfonic acid, bp 145 °C (0.5 mm), was placed in a 25-mL round-bottom flask equipped with a magnetic stirrer and a silica gel drying tube. The reaction mixture was stirred at ambient temperature for 1.3 h and then poured into a mixture of ice–water to give a colorless solid which was extracted into benzene. The organic layer was washed with water and saturated NaCl and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to afford 0.45 g of a yellow solid, mp 180–185 °C. This solid was dissolved in approximately 10 mL of benzene/cyclohexane (1:2) and chromatographed on a 5 × 2.5 cm column of neutral Woelm alumina. Evaporation of the first 250 mL of eluate under reduced pressure gave **2ab** (0.43 g, 91%) as a colorless solid, mp 184–186.5 °C. An analytical sample was obtained by several recrystallizations from EtOAc/ethanol (1:20) as colorless plates, mp 185–186.5 °C (lit.[10] mp 269–270 °C). See Table IV for analytical spectral and laser data.

Ethyl 3-Biphenylylacetate (12). To a cold (−78 °C) solution of 4.5 g (32 mmol) of *N*-isopropylcyclohexylamine in 20 mL of THF was added in one portion a 20-mL aliquot (32 mmol) of *n*-butyllithium. After being stirred in the cold for 10 min, a solution of 2.82 g (32 mmol) of ethyl acetate in 20 mL of THF was added slowly, followed by an additional 10 min of stirring at −78 °C. To this solution was added over a 45-min period a solution of 5.00 g (29 mmol) of 3-phenyl-2-cyclohexenone (**10**)[20] in 50 mL of THF, and after 15 min of stirring at −78 °C, 4 mL of concentrated HCl in 20 mL of THF was slowly added. The cold bath was removed, and the solution was stirred for several hours, washed three times with 5% HCl, and dried over $MgSO_4$ and the solvent removed under reduced pressure to afford 7.56 g (100%) of ethyl 2-(3-hydroxy-1-phenylcyclohexen-3-yl)acetate (**11**) as a yellow oil: IR (NaCl) 3500 (OH), 1730 (C=O) cm^{-1}.

A mixture of 6.00 g (23 mmol) of the crude hydroxy ester **11** and 0.60 g of 10% palladium/charcoal was heated under an atmosphere of dry N_2 at 260 °C for 2.5 h at which time TLC analysis of the reaction mixture showed the complete disappearance of the ester **11**. The reaction mixture was extracted with benzene and filtered and the solvent removed under reduced pressure to afford a yellow oil which was subjected to evaporative distillation (90–100 °C, 0.02 mm), affording **12** (3.91 g, 71%) as a colorless oil: IR (NaCl) 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70–7.00 (9 H, m), 4.05 (2 H, q, J = 7 Hz), 3.55 (2 H, s), 1.05 (3 H, t, J = 7 Hz); TLC (EtOAc/toluene, (1:9)) R_f 0.49.

2-(3-Biphenylyl)ethanol (13). A 125-mL Erlenmeyer flask equipped with a magnetic stirrer, a Claisen adapter, a dropping funnel, and a reflux condenser attached to a silica gel drying tower was flame dried and flushed with dry N_2. The flask was charged with 1.14 g (30 mmol) of LAH and 50 mL of anhydrous ether and the stirred mixture heated at reflux for 15 min. After the reaction mixture was cooled to below 5 °C in an ice bath, a solution of 10.19 g (42.4 mmol) of **12** in 10 mL of anhydrous benzene and 20 mL of anhydrous THF was added dropwise to the stirred mixture. After the addition of 1 mL of this solution, the cold bath was removed and the rate of addition adjusted to maintain gentle refluxing of the reaction mixture. After the complete addition of the ester, the mixture was heated at reflux for 4 h and then allowed to cool to room temperature. Excess LAH was consumed by the dropwise addition of 15 mL of ethyl acetate, followed by the addition of 150 mL of 15% HCl. The resulting aqueous layer was washed with ethyl acetate, and the combined organic layers were washed with water and saturated NaCl and dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford 8.25 g of a colorless solid, mp 55–59 °C. This solid was crystallized from cyclohexane to give **13** (7.40 g, 88%) as colorless prisms, mp 60.5–62.0 °C. An analytical sample was obtained from several recrystallizations from cyclohexane as colorless plates: mp 60–61 °C; ^1H NMR ($CDCl_3$) δ 7.90–6.80 (9 H, m), 3.72 (2 H, t, J = 6.5 Hz), 2.78 (2 H, t, J = 6.5 Hz), 2.40 (1 H, s); TLC (EtOAc/toluene, (1:9)) R_f 0.15.

Anal. Calcd for $C_{14}H_{14}O$: C, 84.86; H, 7.07. Found: C, 84.97; H, 7.02.

2-(3-Biphenylyl)ethyl Bromide (9). A 25-mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser was charged with a solution of 7.00 g (35.3 mmol) of **13** in 6.0 g of 48% HBr and 3.2 g of concentrated H_2SO_4. The stirred solution was heated at reflux for 16.5 h, an additional 4 mL of 48% HBr added, and the heating at reflux continued for 5 h. After the solution was poured into water, the resulting mixture was extracted with

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a solution of benzene:ether (1:1), the organic phase washed twice with water and once with saturated NaCl and dried over $MgSO_4$, and the solvent removed under reduced pressure to afford an amber oil. This oil was dissolved in benzene and chromatographed on a 12 × 2.5 cm column of neutral Woelm alumina. Evaporation of the first 125 mL of eluate under reduced pressure gave 8.62 g of a pale yellow oil which was subjected to evaporative distillation (110–120 °C, 0.5 mm) to afford **9** (6.83 g, 74%) as a colorless oil. An analytical sample was obtained by fractional distillation of a small sample through a 10-cm Vigreux column to give **9** as a colorless oil: bp 124 °C (0.005 mm); ^1H NMR ($CDCl_3$) δ 7.90–6.60 (9 H, m), A_2B_2 (4 H; δ_A 3.33, d, J_{AB} = 6.3 Hz; δ_B 3.07, d, J_{AB} = 6.3 Hz). A_2B_2 parameters were confirmed by a spin-simulator computer program.

Anal. Calcd for $C_{14}H_{13}Br$: C, 64.41; H, 4.98. Found: C, 64.51; H, 4.65

2-[2-(3-Biphenylyl)ethyl]malonic Acid (15). A 125-mL Erlenmeyer flask equipped with a Claisen head, a dropping funnel, a magnetic stirrer, and a reflux condenser fitted with a $CaCl_2$ drying tube was charged with 30 mL of freshly distilled anhydrous ethanol and 0.23 g (10 mmol) of freshly cut Na metal. After the Na had dissolved, 3.20 g (20 mmol) of freshly distilled diethyl malonate was added dropwise over a 15-min period to the stirred solution. After the solution was stirred for 5 min, 2.61 g (10 mmol) of 2-(3-biphenylyl)ethyl bromide (**9**), bp 133–137 °C (0.025 mm), was added dropwise to the stirred solution over a 25-min period, and the stirred solution was then heated at reflux for 3.75 h. The solution was cooled to ambient temperature and filtered, and the solvent was removed under reduced pressure. The residue was heated at reflux for 3 h with a solution of 2.5 g of KOH in 20 mL of 70% aqueous ethanol. The solution was acidified with aqueous HCl, and a colorless solid was obtained. This was collected, washed with water, and dried at reduced pressure to give **15** (1.72 g, 61%) as colorless plates, mp 137–139 °C dec.

4-(3-Biphenylyl)butanoic Acid (16). A. From 2-[2-(3-Biphenylyl)ethyl]malonic Acid (15). A test tube containing 1.72 g (6 mmol) of **15**, mp 137–139 °C dec, was heated for 1.5 h in an oil bath maintained between 140 and 160 °C. Cooling of the melt afforded a light orange solid which upon crystallization from hexanes containing a trace of ethyl acetate gave **16** (1.16 g, 80%) as colorless plates: mp 110.8–111.5 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 11.60 (1 H, s), 7.77–7.17 (9 H, m), 2.75 (2 H, *t*, *J* = 7 Hz), 2.53–2.27 (2 H, m), 2.10 (2 H, t, *J* = 7 Hz); ^{13}C NMR (Me_2SO-d_6) 174.05, 142.16, 140.27, 128.74, 127.32, 127.20, 126.70, 126.62, 126.52, 124.20, 34.45, 33.10, 26.20.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.90; H, 6.55.

B. From 4-(2-Dibenzothienyl)butanoic Acid (19). 4-(2-Dibenzothienyl)butanoic acid was prepared via 3-(2-dibenzothienoyl)propanoic acid (**18**) in 87% overall yield, according to the method described by Gilman and Jacoby.[22] A 4-L beaker equipped with a magnetic stirrer and a thermometer was charged with 15.0 g (55.5 mmol) of **19**, mp 115–121 °C, and 1.125 L of 10% NaOH. The solution was heated to 50 °C and stirred until the acid had completely dissolved. Approximately 0.5 mL of 2-octanol was added to inhibit foaming. To the stirred solution was added 75 g of Raney nickel alloy in small portions to keep foaming at a minimum and to maintain the reaction temperature at 50–55 °C. Additional portions of 2-octanol were added as needed, and the sides of the beaker were occasionally rinsed with water. After the complete addition of the alloy, the stirred mixture was heated at 66 °C for 3 h to allow the steam distillation of the 2-octanol from the reaction mixture. The beaker was then covered with aluminum foil and the mixture heated at 74 °C for 11 h. After cooling to 40 °C, the mixture was filtered through a Celite pad to remove the Raney nickel and then washed thoroughly with 5% NaOH. The filtrate was cooled in an ice bath and acidified carefully with 1.1 L of concentrated HCl. This resulted in a colorless precipitate which was collected, washed thoroughly with water, and air-dried for several hours, followed by drying at 55 °C under reduced pressure to afford **16** (12.93 g, 97%) as a colorless solid: mp 103–107 °C. Recrystallization of a small sample from hexanes containing a trace of ethyl acetate gave **16** as colorless plates, mp 110.5–112 °C.

6-Phenyl-3,4-dihydro-1(2*H*)-naphthalenone (3b). A. Cyclization of 16 with Methanesulfonic Acid. A mixture of 0.85 g (3.5 mmol) of **16**, mp 110.8–111.5 °C, and 8 mL of methanesulfonic acid, bp 145 °C (0.5 mm), was placed in a 25-mL round-bottom flask equipped with a magnetic stirrer and $CaCl_2$ drying tube. The mixture was stirred for 15 h at ambient temperature. Analysis of the reaction mixture (TLC) showed that the cyclization was incomplete, so 3 mL of additional methanesulfonic acid was added, and the mixture was stirred for an additional 6 h. The reaction mixture was poured into a mixture of ice and water to give a colorless solid which was collected, washed with water, and dried under reduced pressure to give 0.75 g of a colorless solid, mp 113–115 °C. Crystallization from hexanes containing a trace of ethyl acetate afforded **3b** (0.6 g, 76%) as colorless plates, mp 112.5–114 °C. Recrystallization of a small sample from cyclohexane gave **3b** as colorless plates: mp 112.5–113.5 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 8.26–7.30 (8 H, m), 2.94 (2 H, t, *J* = 6 Hz), 2.61 (2 H, t, *J* = 6 Hz), 2.34–1.88 (2 H, m); ^{13}C NMR ($CDCl_3$) 195.15, 145.52, 145.29, 144.42, 139.35, 130.95, 128.43, 127.76, 126.73, 124.88, 38.73, 29.48, 22.94; IR (KBr) 3030, 2940, 2870, 1665 (C=O), 1555, 1350, 1325, 1275, 1230, 1180, 1125, 1020, 895, 830, 770, 750, 700 cm^{-1}; TLC (EtOAc/toluene (1:9)) R_f 0.43.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.69; H, 6.12.

B. Cyclization of 16 with Anhydrous Hydrogen Fluoride. A 600-mL polyethylene beaker was charged with 12.9 g (53.8 mmol) of **16**, mp 103–107 °C. To this was added 130 mL of anhydrous hydrogen fluoride. The mixture was stirred occasionally over a 1-h period with a polyethylene stirring rod and then allowed to stand for 24 h. The residue was treated with 5% $NaHCO_3$ and extracted with benzene. The layers were separated, and the organic layer was washed with water and saturated NaCl and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave a violet solid which was dissolved in 15 mL of benzene and chromatographed on a 33 × 2.5 cm column of neutral Woelm alumina. Evaporation of the first 240 mL of eluate under reduced pressure afforded an off-white solid which was crystallized from 95% ethanol to give **3b** (8.11 g, 68%) as colorless plates, mp 112.5–114.5 °C.

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