confirmed by ^1H NMR in the presence of Eu(dcm)$_3$.[11] The methyl signal of the major enantiomer appeared at higher field than that of minor enantiomer.

Reaction of (*S*)-(*Z*)-1-Phenyl-3-(trimethylsilyl)-1-butene (4) with MCPBA. In a similar manner to that described for (*R*)-(*E*)-1, 2.80 g (13.7 mmol) of (*S*)-(*Z*)-**4** ([α]$^{20}_D$ +65.5° (*c* 1.5, benzene), 44% ee)[12] was treated with 3.25 g (15.1 mmol) of 80% MCPBA and 1.26 g (15.0 mmol) of sodium bicarbonate in 100 mL of dichloromethane at 0 °C for 1.5 h. To the residue obtained by removal of the solvent under reduced pressure were added 60 mL of acetic acid and 20 mL of water, and the mixture was stirred at room temperature for 1.5 h. Ether was added and the solution was washed with 20% sodium hydroxide (4 × 50 mL) and aqueous sodium thiosulfate, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to give 1.82 g of crude (*E*)-1-phenyl-2-buten-1-ol (**5**), which was contaminated with 30–40% of (*E*)-4-phenyl-3-buten-2-ol (**2**). The alcohol (*E*)-**5** was purified by silica gel medium-pressure liquid chromatography (MPLC) (ethyl acetate/hexane = 1/1). It was observed that (*E*)-**5** was isomerized slowly into (*E*)-**2** during the chromatographic separation. (*E*)-**5**: [α]$^{20}_D$ +12.5° (*c* 2.1, chloroform); ^1H NMR (CCl_4) δ 1.72 (d, J = 5 Hz, 3 H), 1.56–1.92 (broad s, 1 H), 4.97–5.16 (m, 1 H), 5.40–5.80 (m, 2 H), 7.04–7.46 (m, 5 H). ^1H NMR in the presence of Eu(dcm)$_3$[11] indicated that the enantiomeric purity of (*E*)-**5** was 35%, the ortho phenyl proton of the major enantiomer appearing at higher field than that of the minor one.

Hydrogenation (50 atm) of (*E*)-**5** in the presence of 10% Pd-C in benzene for 13 h gave quantitatively (*S*)-1-phenylbutan-1-ol (**6**) with [α]$^{27}_D$ −14.3° (*c* 4.52, benzene) (lit.[13] [α]$^{27}_D$ −45.93° (*c* 6.1, benzene) for (*S*)-**6**).

Reaction of (*S*)-3-(Trimethylsilyl)cyclopentene (7) with MCPBA. To a mixture of 1.02 g (7.30 mmol) of (*S*)-**7** (22–25% ee) and 0.646 g (7.69 mmol) of sodim bicarbonate in 10 mL of dichloromethane was added at 0 °C a solution of 1.66 g (7.67 mmol) of 80% MCPBA in 25 mL of dichloromethane. The mixture was stirred at room temperature for 14 h, and the solvent was evaporated. Ether (40 mL) was added and the solution was washed with 20% sodium hydroxide (2 × 30 mL) and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave 1.79 g (78% yield) of 1-hydroxy-2-(trimethylsilyl)-3-[(*m*-chlorobenzoyl)oxy]cyclopentane (**8**). An analytically pure sample was obtained by preparative TLC on silica gel (chloroform): [α]$^{20}_D$ −6.6° (*c* 1.1, CCl_4); ^1H NMR ($CDCl_3$) δ 0.07 (s, 9 H), 1.32 (t, J = 3 Hz, 1 H, d upon spin-decoupling at 4.08 or 5.15), 1.65–2.10 (broad m, 4 H), 4.08 (q, J = 3 Hz, 1 H, t upon spin-decoupling at 1.32), 5.15 (q, J = 3 Hz, 1 H, t upon spin-decoupling at 1.32), 7.10–7.47, 7.64–7.92 (m, 4 H). ^1H NMR in the presence of Eu(dcm)$_3$ showed that the enantiomeric purity of **8** was around 30%. Anal. Calcd for $C_{15}H_{21}O_3ClSi$: C, 57.56; H, 6.76. Found: C, 57.42; H, 6.79.

To a solution of 0.818 g (2.61 mmol) of **8** in 10 mL of methanol was added 0.7 mL of 30% aqueous potassium hydroxide, and the mixture was allowed to reflux for 6 h. Methanol was evaporated and 10 mL of water was added. The mixture was extracted with ether (4 × 10 mL), and the combined ether extracts were washed with 20% sodium hydroxide and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure afforded 0.447 g (98% yield) of 1,3-dihydroxy-2-(trimethylsilyl)cyclopentane. An analytical sample was obtained as colorless needles, mp 83.0–83.5 °C, by recrystallization from hexane: ^1H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 1.28 (broad s, 1 H), 1.75–1.90 (broad d, 4 H), 2.75 (broad s, 2 H), 4.17 (broad s, 2 H). Anal. Calcd for $C_8H_{18}O_2Si$: C, 55.12; H, 10.41. Found: C, 55,36; H, 10.67.

A mixture of 91 mg (0.52 mmol) of the diol, 0.11 mL (1.2 mmol) of acetic anhydride, 0.18 mL (4.3 mmol) of triethylamine, and 2 mg of 4-(*N*,*N*-dimethylamino)pyridine in 0.5 mL of THF was stirred at room temperature for 14 h. Ether was added and the solution was washed with water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was passed through a short silica gel column to give 121 mg (90% yield) of 1,3-diacetoxy-2-(trimethylsilyl)cyclopentane (**9**): ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H), 1.53 (t, J = 3 Hz, 1 H, s upon spin-decoupling at 5.10), 1.80–1.98 (m, 4 H), 2.09 (s, 6 H), 5.10 (q, J = 3 Hz, 2 H, t upon spin-decoupling at 1.53).

A solution of 1 M tetrabutylammonium fluoride in THF (4 mL, 4.0 mmol) was added to 1.05 g (3.34 mmol) of **8**. After stirring at room temperature for 26 h, 20 mL of ether was added. The solution was washed successively with water and 20% sodium hydroxide, dried over anhydrous sodium sulfate, and evaporated. Distillation (~100 °C (17 mm), bath temperature) followed by preparative GLC (Silicone DC550) gave 0.11 g (36% yield) of (*S*)-2-cyclopentenol[17] (**10**): [α]$^{21}_D$ −13.2° (*c* 1.6, CCl_4). ^1H NMR in the presence of Eu(dcm)$_3$[11] showed that the enantiomeric purity of (*S*)-**10** was ~19%, the methine proton of the *S* isomer appearing at higher field than that of the *R* isomer.

Registry No. (*R*)-(*E*)-**1**, 82570-93-2; (*R*)-(*Z*)-**1**, 82570-94-3; (*S*)-(*E*)-**2**, 81176-43-4; (*R*)-(*Z*)-**2**, 92075-80-4; (*S*)-**3**, 22148-86-3; (*R*)-**3**, 39516-03-5; (*S*)-(*Z*)-**4**, 88133-09-9; (*S*)-(*E*)-**5**, 92075-81-5; (*S*)-**6**, 22135-49-5; (*S*)-**7**, 89576-21-6; (1*S*,2*R*,3*R*)-**8**, 91948-47-9; **9**, 91948-49-1; (*S*)-**10**, 6426-28-4; MCPBA, 937-14-4; (*E*)-1-phenyl-3-[(trimethylsilyl)oxy]-1-butene, 92075-82-6; (*Z*)-1-phenyl-3-[(trimethylsilyl)oxy]-1-butene, 92075-83-7; 1,3-dihydroxy-2-(trimethylsilyl)cyclopentane, 91948-48-0.

Synthesis of Biological Markers in Fossil Fuels. 2. Synthesis and ^{13}C NMR Studies of Substituted Indans and Tetralins

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Unambiguous syntheses of all possible methyl, ethyl, *n*-propyl, and *n*-butyl derivatives of indan and tetralin were developed using the Kumada coupling procedure involving the reaction of aryl or vinyl halides with Grignard reagents in the presence of [1,3-bis(diphenylphosphino)propyl]nickel(II) chloride. An analysis of the ^{13}C NMR spectra of these compounds was also completed.

Partially aromatized steranes[1] such as 5,17-dimethyl-18,19-dinorcholesta-8,11,13-triene[2] (**1**) represent an unusual but interesting family of biomarkers.[3] These "molecular fossils" are potentially useful probes for addressing prob-

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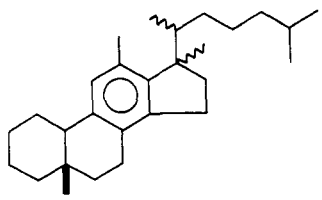

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lems of source, maturation, migration, and biodegradation of crude oils.[4] In connection with synthetic efforts directed toward aromatized steranes, we required unambiguous ^{13}C NMR data for indans and tetralins which comprise the principal structural subunits of biomarkers such as **1**. The occurrence of these compounds in various coal, shale, and petroleum derived fuels[5-7] also makes their study of interest to fossil fuel chemists. We now report a comprehensive study of the synthesis and ^{13}C NMR data for all monosubstituted indans and tetralins possessing methyl, ethyl, *n*-propyl, and *n*-butyl substituents and the resolution of various ambiguities in ^{13}C NMR assignments in the literature.[8]

The following routes provide access to various substituted indans and tetralins as well as many of their dehydro derivatives. Condensation of 1-indanone (**2**) with various Grignard reagents, dehydration of the intermediate alcohols, and hydrogenation of the resulting alkenes[9] **3** furnish 1-alkylindans[10,11] **4**. Alkylation of 1-indanone (**2**), reduction of the monoalkylated ketone **5**, dehydration to the 2-alkylidenes **6**, and hydrogenation furnish the 2-alkylindans[12] **7** in poor overall yields. A preferable route involves the coupling of 2-bromoindene (**8**) with Grignard reagents mediated by [1,3-bis(diphenylphosphino)propyl]nickel(II) chloride[13] and subsequent hydrogenation of the alkenes **6** to secure the 2-alkylindans **7**. Preparation of 4-alkylindans[14] involves the conversion of 2-bromobenzyl bromide to 4-bromoindanone (**9**), the reduction of **9** to 7-bromo-1*H*-indene (**10**), the coupling of **10** with various Grignard reagents mediated by $NiCl_2[dppp]_2$, and finally reduction of the 7-alkyl-1*H*-indenes **11** to secure the 4-alkylindans **12**. A similar sequence originating with 4-bromobenzyl bromide and proceeding via 6-bromoindanone (**13**), 5-bromo-1*H*-indene (**14**), and 5-alkyl-1*H*-indenes **15** provides the 5-alkylindans[15,20] **16**.

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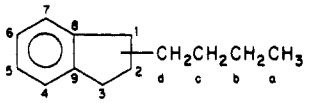
Table I. ^{13}C NMR Data[a] for Substituted Indans

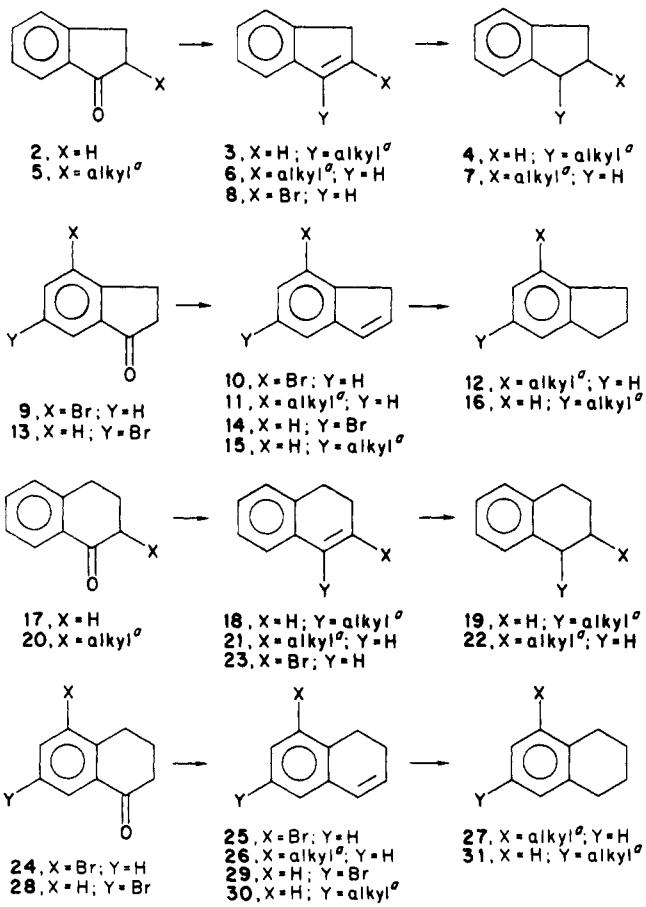


	C1	C2	C3	C4	C5	C6	C7	C8	C9	a (CH_3)	b (CH_2)	c (CH_2)	d (CH_2)
indan[b]	33.0	25.4	33.0	124.4	126.2	124.0	144.0						
1-methyl (**4a**)	39.4	34.8	31.4	129.3	126.1	126.1	123.1	148.6	143.7	19.9			
1-ethyl (**4b**)	46.5	31.6	31.4	124.4	125.9	126.2	123.6	147.85	144.1	12.0	27.7		
1-propyl (**4c**)	44.7	32.2	31.5	124.3	125.9	126.1	123.5	147.8	144.0	14.4	20.8	37.4	
1-butyl (**4d**)	44.8	32.2	31.7	124.3	125.9	126.1	123.5	147.8	144.0	14.1	23.0	30.0	34.8
2-methyl (**7a**)	41.1	34.4	41.1	124.4	126.0	126.0	124.4	143.7	143.7	20.7			
2-ethyl (**7b**)	39.0	42.0	39.0	124.4	126.0	126.0	124.4	143.7	143.7	12.7	28.6		
2-propyl (**7c**)	39.3	40.0	39.3	124.3	125.9	125.9	124.3	143.6	143.6	14.3	21.5	38.1	
2-butyl (**7d**)	39.4	40.2	39.4	124.3	125.9	125.9	124.3	143.7	143.7	14.1	22.9	30.7	35.5
4-methyl (**12a**)	33.1	24.7	31.4	133.7	126.8	126.2	126.7	143.8	142.9	19.2			
4-ethyl (**12b**)	33.1	24.9	31.0	139.9	125.1	126.4	121.8	144.0	142.3	14.4	26.5		
4-propyl (**12c**)	33.1	24.9	31.2	138.4	126.8	126.2	121.8	144.0	142.5	14.1	23.4	35.7	
4-butyl (**12d**)	33.1	24.9	31.2	138.6	125.9	126.2	121.8	144.0	142.4	14.0	22.7	32.4	33.3
5-methyl (**16a**)	32.8	25.6	32.4	125.1	135.5	126.7	124.0	141.1	144.3	21.2			
5-ethyl (**16b**)	32.8	25.6	32.5	124.1	142.2	125.6	123.8	141.4	144.3	16.0	28.7		
5-propyl (**16c**)	32.8	25.6	32.5	124.4	140.5	126.3	124.0	141.4	144.2	13.9	24.9	38.0	
5-butyl (**16d**)	32.8	25.6	32.5	124.4	140.8	126.2	124.0	141.3	144.2	14.0	22.5	34.1	35.6

[a] Central signal of $CDCl_3$ set at 77.00 ppm. [b] Agrawal, P. K.; Schneider, H. J.; Malik, M. S.; Rastogi, S. N. *Org. Magn. Res.* **1983**, *21*, 146.

Condensation of 1-tetralone (**17**) with various Grignard reagents, dehydration of the intermediate alcohols, and hydrogenation of the resulting alkenes **18** furnish 1-alkyltetralins[21,22] **19**. Once again, alkylation of 1-tetralone (**17**), reduction of the monoalkylated ketone **20**, dehydration to 2-alkyl-3,4-dihydronaphthalenes **21**, and hydrogenation furnish 2-alkyltetralins[23] **22** in poor overall yields. However, coupling of 2-bromo-3,4-dihydronaphthalene (**23**) with Grignard reagents in the presence of $NiCl_2[dppp]_2$ and subsequent hydrogenation of the alkenes **21** provide 2-alkyltetralins **22** in excellent overall yield. Preparation of 5-alkyltetralins involves the conversion of 2-bromobenzyl bromide to 5-bromotetralone[24a] (**24**), the reduction of **24** to 5-bromo-3,4-dihydronaphthalene (**25**), the coupling of **25** with various Grignard reagents to furnish 5-alkyl-3,4-dihydronaphthalenes **26**, and, finally, the reduction of **26** to secure the 5-alkyltetralins[25] **27**. Preparation of 6-al-

Scheme I



[a] Letter designations specify alkyl groups as follows: a = CH_3, b = C_2H_5, c = n-C_3H_7, d = n-C_4H_9.

(15) An alternate route to 5-alkylindans **16** utilizing 5-haloindans was briefly explored. The direct bromination[16] of indan furnished mixtures of 4-bromoindan and, principally, 5-bromoindan which were inseparable[17] by distillation[18] or by chromatography. A similar approach involving the nitration of indan[19] and reduction of the nitroindan mixture did furnish pure 5-aminoindan by crystallization, but the Sandmeyer reaction of this material furnished 5-bromoindan contaminated with an inseparable by-product.

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(17) Purification can be achieved by using a sulfonation–desulfonation procedure: Eigenman, G.; Zollinger, H. *Helv. Chim. Acta* **1965**, *48*, 1795.

(18) (a) Borsche, W.; Pommer, M. *Chem. Ber.* **1921**, *59*, 102. (b) Lindner, J.; Bruhin, J. *Ibid.* **1927**, *60*, 435.

(19) Borsche, W.; John, G. *Chem. Ber.* **1924**, *57*, 656.

(20) An alternate route to 5-alkylindans **16** involves the Diels–Alder reactions of 1-cyclopentene-1,2-dicarboxylic acid anhydride and olefins: Skvarchenko, V. R.; Chervoneva, L. A.; Pastukhova, I. S.; Levina, R. Y. *J. Gen. Chem. USSR (Engl. Transl.)* **1959**, *29*, 2140.

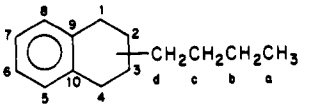
(21) (a) Karo, W.; McLaughlin, R. L.; Hipsher, H. F. *J. Am. Chem. Soc.* **1953**, *75*, 3233. (b) Nazarov, I. N.; Burmistrova, M. S. *Zh. Obshch. Khim.* **1950**, *20*, 1304. (c) Nelson, N. A.; Ladbury, J. E.; Hsi, R. S. P. *J. Am. Chem. Soc.* **1958**, *80*, 6633. (d) Delobelle, J.; Fetizon, M. *Bull. Soc. Chim. Fr.* **1961**, 1632.

(22) Alternate routes to 1-alkyltetralins **19** involve the following. (a) Friedel–Crafts cyclizations: Roblin, R. O., Jr.; Davidson, D.; Bogert, M. T. *J. Am. Chem. Soc.* **1935**, *57*, 151. Baddeley, G. Williamson, R. *J. Chem. Soc.* **1956**, 4647. Heck, R.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 3105. (b) Benzylic alkylations of tetralin: Kutz, W. M.; Nickels, J. E.; McGovern, J. J.; Corson, B. B. *J. Am. Chem. Soc.* **1948**, *70*, 4026. Closson, R. D.; Napolitano, J. P.; Ecke, G. G.; Kolka, A. J. *J. Org. Chem.* **1957**, *22*, 646. Friedlin, L. K.; Nazarova, N. M. *Neftekhimiya* **1961**, *1*, 619. Russey, W. E.; Haenel, M. W. *Tetrahedron Lett.* **1981**, *22*, 4065. (c) Partial hydrogenation of 1-alkylnaphthalenes: Hipsher, H. F.; Wise, P. H. *J. Am. Chem. Soc.* **1954**, *76*, 1747.

(23) Alternate routes to 2-alkyltetralins **22** involve Friedel–Crafts cyclizations: (a) Barry, J.; Kagan, H.-B.; Snatzke, G. *Tetrahedron* **1971**, *27*, 4737. (b) Christol, H.; Jacquier, R.; Mosseron, M. *Bull. Soc. Chim. Fr.* **1958**, 248.

(24) (a) Uyeo, S.; Mizutani, T.; Yoshitake, A.; Ito, A. *Yakugaku Zasshi* **1964**, *84*, 458; *Chem. Abstr.* **1964**, *61*, 4286h. (b) Newman, M. S.; Seshadri, S. *J. Org. Chem.* **1962**, *27*, 76.

Table II. ^{13}C NMR Data[a] for Substituted Tetralins



	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	a (CH_3)	b (CH_2)	c (CH_2)	d (CH_2)
tetralin[b]	29.6	23.6	23.6	29.6	129.4	125.8	125.8	129.4	137.1	137.1				
1-methyl (**19a**)	32.4	30.0	22.8	31.5	129.0	125.4	125.6	128.0	142.1	139.8	20.4			
1-ethyl (**19b**)	39.2	26.9	19.9	29.4	129.0	125.4	125.3	128.6	141.3	137.1	11.9	29.8		
1-propyl (**19c**)	37.3	27.4	19.8	29.8	129.0	125.4	125.3	128.6	141.7	137.0	14.3	20.6	39.3	
1-butyl (**19d**)	37.6	27.5	19.8	29.8	129.0	125.4	125.3	128.5	141.6	136.9	14.1	23.0	29.6	36.7
2-methyl (**22a**)	38.1	29.3	31.5	29.3	129.0	125.3	125.4	128.9	136.7	136.9	22.0			
2-ethyl (**22b**)	36.0	35.9	29.2	29.2	129.1	125.3	125.4	128.8	136.9	137.0	11.5	29.3		
2-propyl (**22c**)	36.2	33.9	29.5	29.2	129.1	125.3	125.4	128.8	137.0	137.0	14.3	20.0	38.8	
2-butyl (**22d**)	36.3	34.2	29.6	29.2	129.1	125.3	125.4	128.8	136.9	137.0	14.1	23.0	29.2	36.3
5-methyl (**27a**)	30.1	23.5	22.9	26.7	136.5	127.0	125.1	126.9	137.1	135.5	19.5			
5-ethyl (**27b**)	30.2	23.5	22.9	25.9	142.2	125.3	125.1	126.9	137.1	134.8	14.3	25.6		
5-propyl (**27c**)	30.2	23.5	22.9	26.1	140.8	126.1	125.1	126.9	137.2	134.9	14.4	23.1	34.9	
5-butyl (**27d**)	30.2	23.5	22.9	26.1	141.0	126.1	125.1	126.9	137.2	134.8	14.1	22.9	32.4	32.5
6-methyl (**31a**)	29.3	23.4	23.3	29.0	129.7	134.7	126.2	129.4	134.0	136.8	20.9			
6-ethyl (**31b**)	39.4	23.4	23.4	29.0	128.5	141.3	125.1	129.1	134.3	136.9	15.8	28.5		
6-propyl (**31c**)	29.4	23.4	23.3	29.0	128.9	139.7	125.6	129.1	134.3	136.8	14.0	24.7	37.7	
6-butyl (**31d**)	29.4	23.4	23.3	29.0	129.0	139.9	125.6	129.0	134.2	136.8	14.0	22.5	33.9	35.3

[a] Central signal of $CDCl_3$ set at 77.00 ppm. [b] Reference 8e.

Table III. Substituent Parameters for Alkyl Chains in Substituted Indans and Tetralins

	α-effects			β-effects		γ-effects
	CH_2CH_3	$CH_2CH_2CH_3$	$CH_2CH_2CH_2CH_3$	$CH_2CH_2CH_3$	$CH_2CH_2CH_3CH_2$	$CH_2CH_2CH_2CH_3$
cyclopentane	+8.4	+9.4	+8.6	+9.7	+3.2[a]	−2.7
1-indan (**4a**)	+7.6	+8.8	+8.6	+9.7	+9.2	−2.6
2-indan (**7**)	+7.9	+8.8	+8.6	+9.5	+9.2	−2.6
cyclohexane	+7.3	+8.8	+9.0	+9.6	+9.3	−2.5
1-tetralin (**19**)	+9.4	+8.7	+8.7	+9.5	+9.0	−2.6
2-tetralin (**22**)	+7.3	+8.5	+8.5	+9.5	+9.6	−2.5
benzene	+8.0	+8.4	+8.9	+9.2	+8.8	−2.5
4-indan (**12**)	+7.3	+9.0	+8.6	+9.2	+9.0	−2.4
5-indan (**16**)	+7.5	+8.9	+8.6	+9.3	+9.2	−2.4
5-tetralin (**27**)	+6.1	+8.8	+8.5	+9.3	+9.3	−2.4
6-tetralin (**31**)	+7.4	+8.9	+8.5	+9.2	+9.2	−2.4

[a] We suspect that this value is taken from ref 27b may be in error.

kyltetralins involves the conversion of bromobenzene to 7-bromotetralone[24b] (**28**), reduction of **28** to 7-bromo-3,4-dihydronaphthalene (**29**), coupling of **29** with various Grignard reagents to furnish 7-alkyl-3,4-dihydronaphthalenes **30**, and, finally, the hydrogenation of **30** to secure the 6-alkyltetralins[26] **31**.

Guided by the substituent parameters calculated from published data[27] for alkylcyclopentanes, alkylcyclohexanes, and alkylbenzenes, we assigned the ^{13}C NMR spectra of indans (Table I) and tetralins (Table II) substituted in all possible positions with methyl, ethyl, *n*-propyl, and *n*-butyl groups. In some cases, we resolved conflicting assignments by using distortionless enhancement polarization transfer (DEPT) experiments,[28] but in a few cases, we were unable to distinguish similar carbon types differing by only a few tenths of a ppm. In addition, the ^{13}C NMR data for various indenes and 1,2-dihydronaphthalenes were analyzed and these data are recorded in the Experimental Section.

As shown in Table III, the α-, β-, and γ-substituent parameters for the appended alkyl chains parallel those values obtained in other systems.[29] The only significant deviation from the pattern of values in Table III is the unusually high α-effect for 1-methyltetralin (**19a**) which may reflect the presence of an axially oriented conformer as recently suggested by Grant.[5e] However, the source of the low α-effect for 5-methyltetralin (**27a**) remains unclear although unfavorable steric interaction of the C-5 methyl and *o*-methylene may distort this system relative to isomeric systems.

The substituent parameters for the alicyclic carbons in this series are summarized in Table IV. The diminished α-effect of an axial methyl group in cyclohexane relative

(25) Alternate syntheses of 5-alkyltetralins **27** involve the following. (a) Selective reductions of 1-alkylnaphthalenes: Huckel, W.; Jennewein, C.-M. *Chem. Ber.* **1962**, *95*, 350. Demole, E.; Enggist, P. *Helv. Chim. Acta* **1978**, *61*, 1335. Gaudemar-Bardone, F.; Gaudemar, M. *Synthesis* **1979**, 463. Russey, W. E.; Haenel, M. W. *Tetrahedron Lett.* **1981**, *22*, 4065. (b) Acid-catalyzed rearrangements: Bakuzis, P.; Magalhaes, G. C.; Martins, H.; Bakuzis, M. L. F. *J. Org. Chem.* **1974**, *39*, 2427.

(26) Alternate syntheses of 6-alkyltetralins **31** involve the following. (a) Friedel–Crafts cyclizations: Ando, T.; Yamawaki, J.; Saito, Y.; Takai, Y.; Yamataka, H. *Bull. Chim. Soc. Jpn.* **1980**, *53*, 2348. Jacques, J.; Horeau, A. *Bull. Soc. Chim. Fr.* **1956**, 1631. Bongue-Boma, R.; Rinaudo, J.; Bonnier, J.-M. *Bull. Soc. Chim. Fr.* **1982**, 52. (b) Selective hydrogenation of 2-alkylnaphthalenes: Fu, P. P.; Evans, F. E.; Miller, D. W.; Freeman, J. P.; Yang, S. K. *Org. Prep. Proced. Int.* **1982**, *14*, 169. (c) Trimerization of acetylenes: Vasil'ev, V. Y.; Rekhsfel'd, V. O. *Tr. Khim. Metall. Inst., Akad. Nauk Kaz. SSR* **1972**, *18*, 29; *Chem. Abstr.* **1973**, *79*, 18461s. (d) Friedel–Crafts acylation/reduction: Horii, Z.; Yamamura, S.; Hakusui, H.; Nishikado, T.; Momose, T. *Chem. Pharm. Bull.* **1968**, *16*, 2456.

(27) (a) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972. (b) Adams, J. Q.; Lindeman, L. P. *Am. Chem. Soc., Div. Pet. Chem., Prepr.* **1972**, *17*, C4-C18; *Chem. Abstr.* **1974**, *80*, 26465g.

(28) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323.

(29) (a) Gorenstein, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 2254. (b) Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *Ibid.* **1970**, *92*, 7107. (c) Seidman, K.; Maciel, G. E. *Ibid.* **1977**, *99*, 659. (d) Beierbeck, H.; Saunders, J. K. *Can. J. Chem.* **1976**, *54*, 2985.

Table IV. Substituent Parameters for Alicyclic Carbons in Substituted Indans and Tetralins

	α-effects		β-effects					γ-effects							
compd	C-1	C-2	C-1	C-2	C-3	C-8	C-9	C-1	C-2	C-3	C-4	C-7	C-8	C-9	C-10
cyclopentane[a]															
1-methyl	+9.5			+9.5						+0.1					
1-ethyl			+7.5						−2.4						
1-*n*-propyl								−2.3							
indan															
1-methyl (**4a**)	+6.4			+9.4		+4.6				−1.6		−0.9		−0.3	
1-ethyl (**4b**)			+7.1						−3.2				−1.1		
1-*n*-propyl (**4c**)								−1.8							
2-methyl (**7a**)		+9.0	+8.1		+8.1								−0.3	−0.3	
2-ethyl (**7b**)				+7.6				−2.1		−2.1					
2-*n*-propyl (**7c**)									−2.0						
cyclohexane[a]															
1-methyl	+6.4			+9.1						−0.2					
1-ethyl			+6.4						−2.8						
1-*n*-propyl								−2.2							
tetralin															
1-methyl (**19a**)	+2.8			+6.4			+5.0			−0.8			−1.4		−0.3
1-ethyl (**19b**)			+6.8						−3.1					−0.8	
1-*n*-propyl (**19c**)								−1.9							
2-methyl (**22a**)		+5.7	+8.5		+7.9						−0.3			−0.4	
2-ethyl (**22b**)				+6.6				−2.1		−2.3					
2-*n*-propyl (**22c**)									−2.0						

[a] Reference 27b.

Table V. Substituent Parameters for Aromatic Carbons in Substituted Indans and Tetralins

	α-effects				β-effects								γ-effects									
compd	C-1	C-4	C-5	C-6	C-1	C-2	C-4	C-5	C-6	C-7	C-9	C-10	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
benzene																						
1-Me	+9.1					+0.6									−0.2							
1-Et					+6.3									−1.2								
1-*n*-Pr													−1.6									
indan																						
4-Me (**12a**)		+9.3						+0.6			−1.1				−1.6			0.0		−1.1		
4-Et (**12b**)							+6.2										−1.7				−0.6	
4-*n*-Pr (**12c**)																−1.5						
5-Me (**16a**)			+9.3				+0.7		+0.5										0.0		+0.3	
5-Et (**16b**)								+6.7								−1.0		−1.1				
5-*n*-Pr (**16c**)																	−1.7					
tetralin																						
5-Me (**27a**)			+7.1						+1.2		−1.6					−2.9			−0.7		0.0	
5-Et (**27b**)								+5.7										−1.7				−0.7
5-*n*-Pr (**27c**)																	−1.4					
6-Me (**31a**)				+8.9				+0.3		+0.4										−0.4		−0.3
6-Et (**31b**)									+6.6								−1.2		−1.1			
6-*n*-Pr (**31c**)																		−1.6				

[a] Reference 27b.

to an equatorial methyl group[30] is consistent with the low α-effect at C-1 in 1-methyltetralin (**19a**) in which an axial conformer is present to a significant degree. It is more difficult to evaluate whether a similar decline of the α-effect to 6.4 ppm at C-1 for 1-methylindan (**4a**) is significant relative to the larger α-effect of 9.5 ppm observed for methylcyclopentane.[27] Little significant variation in β-effects relative to cyclopentane and cyclohexane analogues was noted except for 1-methyltetralin (**19a**) in which the β-effect at C-2 was slightly lower (6.4 ppm) than the β-effect at C-2 in methylcyclohexane[30] (9.1 ppm). Similarly, β-effects at the bridgehead aromatic carbons were diminished significantly. The only significant γ-effects were noted for ethyl and *n*-propyl substituents on alicyclic C-1 and C-2 carbons.

The magnitude of the α-effect of a methyl group attached to the aromatic ring of indans or tetralins parallels the α-effects observed in toluene as shown in Table V. 5-Methyltetralin (**27a**) and 6-methyltetralin (**31a**) display a somewhat smaller α-effect than expected and this diminished value may, as pointed out earlier, reflect steric

(30) Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1972**, *94*, 5318.

interaction within the system. It is also apparent for methyl-substituted indans and tetralins that the value of the β-effect on an aromatic carbon when the substituent is an ethyl group is about 6.4 ppm. Again, 5-methyltetralin (**27a**) and 5-ethyltetralin (**27b**) exhibit slightly higher and lower β-effects, respectively, than related systems. The values of the β-effect on bridgehead carbons is approximately −1.0 ppm. Finally, the γ-effect of various alkyl groups on the aromatic carbons is fairly consistent: the methyl group, regardless of its position, produces a small diamagnetic shift, whereas the ethyl and propyl groups produce a somewhat larger diamagnetic shift ranging from −1.2 to −1.7 ppm. γ-Effects at the bridgehead carbons are generally −0.3 ppm or less.

Experimental Section

Infrared spectra were determined on a Beckman Microlab 600 spectrometer. The abbreviation TF denotes thin film. NMR spectra were determined on a JEOL 270 MHz NMR spectrometer. Mass spectra were determined on either a Varian MAT CH5 or a VG-ZAB-1F mass spectrometer. Melting points were determined by using a Thomas-Hoover melting point apparatus and are uncorrected.

General Procedure for the Preparation of 1-Alkylindans 4 from 1-Indanone (2). 1-Methylindan (4a). To a solution of 10 mL of 3 M (1.5 equiv) methylmagnesium iodide in tetrahydrofuran at 0 °C under a nitrogen atmosphere was added 2.64 g (20 mmol) of 1-indanone (**2**) in 50 mL of tetrahydrofuran over a 20-min period followed by the addition of 10 mL of anhydrous hexamethylphosphoramide. The reaction was stirred at 25 °C for 8–12 h, quenched with 50 mL of 15% aqueous hydrochloric acid solution at −78 °C, and stirred an additional 10 h at 25 °C to complete the dehydration of the intermediate alcohol. The solution was extracted with ether, washed with brine, and dried over anhydrous magnesium sulfate. The crude product was chromatographed on Merck silica gel 60 with hexane to afford 2.4 g (94%) of 1-methyl-3*H*-indene (**3a**): NMR ($CDCl_3$) δ 1.52 (s, 3, CH_3), 3.12–3.44 (m, 2, CH_2), 6.2–6.28 (m, 1, vinylic H), 7.16–7.34 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 139.9 (C-1), 128.6 (C-2), 37.6 (C-3), 123.5 (C-4), 124.5 (C-5 or 6), 126.0 (C-5 or 6), 118.8 (C-7), 146.1 (C-8), 144.3 (C-9), 13.0 (CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 130 (M^+, 34), 115 ($M^+ - CH_3$, 64), 77 (41); exact mass spectrum calcd for $C_{10}H_{10}$ 130.0783, found 130.0780.

A mixture of 1.3 g (10 mmol) of 1-methyl-3*H*-indene (**3a**) and 23 mg (0.1 mmol) of platinum oxide in 5 mL of tetrahydrofuran was hydrogenated at 20–30 psi for 10–15 h. The mixture was filtered through a pad of Celite 545, and the pad was washed thoroughly with additional tetrahydrofuran. The crude product was chromatographed on Merck silica gel 60 with hexane to afford 1.4 g (95%) of 1-methylindan (**4a**): IR ref 31; ^1H NMR ($CDCl_3$) δ 1.28[32] (d, *J* = 7 Hz, 3, CH_3), 1.52–2.4 (m, 2, C-2 CH_2), 2.78–3.28 (m, 3, benzylic H), 7.08–7.32 (m, 4, aromatic H); mass spectrum ref 33; exact mass spectrum calcd for $C_{10}H_{12}$ 132.0939, found 132.0934.

Summary of Yields and Spectral Data for 1-Alkyl-3*H*-indenes 3. 1-Ethyl-3*H*-indene (3b): 85%; ^1H NMR ($CDCl_3$) δ 1.26 (t, *J* = 7 Hz, 3, CH_2CH_3), 2.52 (q, *J* = Hz, 2, CH_2CH_3), 3.27 (m, 2, benzylic H), 6.16 (m, 1, vinylic H), 7.13–7.43 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 144.0 (C-1), 126.6 (C-2), 37.6 (C-3), 123.7 (C-4), 124.4 (C-5 or 6), 125.9 (C-5 or 6), 118.8 (C-7), 146.2 (C-8), 144.0 (C-9), 20.8 (CH_2CH_3), 31.8 (CH_2CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 144 (M^+, 47), 129 ($M^+ - CH_3$, 100), 115 ($M^+ - C_2H_5$, 40); exact mass spectrum calcd for $C_{11}H_{12}$ 144.0939, found 144.0939.

1-*n*-Propyl-3*H*-indene (3c): 90%; IR and ^1H NMR ref 34; ^{13}C NMR ($CDCl_3$) δ 144.5 (C-1), 127.6 (C-2), 37.6 (C-3), 123.7 (C-4), 124.4 (C-5 or 6) 125.9 (C-5 or 6), 118.9 (C-7), 145.6 (C-8), 144.5 (C-9), 14.2 ($CH_2CH_2CH_3$), 21.2 ($CH_2CH_2CH_3$), 29.9 ($CH_2CH_2CH_3$); mass spectrum (70 eV), *m/e* (relative intensity) 158 (M^+, 37), 129 ($M^+ - C_2H_5$, 100), 115 ($M^+ - C_3H_7$, 23); exact mass spectrum calcd for $C_{12}H_{14}$ 158.1096, found 158.1093.

1-*n*-Butyl-3*H*-indene (3d): 81%; ^1H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7 Hz, 3, $(CH_2)_3CH_3$), 1.36–1.72 (m, 4, $CH_2(CH_2)_2CH_3$), 2.50–2.58 (m, 2, $CH_2(CH_2)_2CH_3$), 3.25–3.32 (m, 2, benzylic H), 6.14–6.22 (m, 1, vinylic H), 7.11–7.43 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 144.5 (C-1), 127.5 (C-2), 37.6 (C-3), 123.6 (C-4), 124.4 (C-5 or 6), 125.9 (C-5 or 6), 118.9 (C-7), 145.6 (C-8), 144.6 (C-9), 14.0 ($CH_2CH_2CH_2CH_3$), 22.7 ($CH_2CH_2CH_2CH_3$), 27.4 (CH_2CH_2-CH_2CH_3), 30.2 ($CH_2CH_2CH_2CH_3$); mass spectrum (70 eV), *m/e* (relative intensity) 172 (M^+, 21), 143 ($M^+ - C_2H_5$, 22), 130 ($M^+ - C_3H_6$, 100), 129 ($M^+ - C_3H_7$, 64), 115 ($M^+ - C_4H_9$, 29); exact mass spectrum calcd for $C_{13}H_{16}$ 172.1252, found 172.1254.

Summary of Yields and Spectral Data for 1-Alkylindans 4. 1-Ethylindan (4b): IR, ^1H NMR, and mass spectrum ref 35.

1-*n*-Propylindan (4c): 84%; IR and ^1H NMR ref 34; mass spectrum (70 eV), *m/e* (relative intensity) 160 (M^+, 16), 117 ($M^+ - C_3H_7$, 100); exact mass spectrum calcd for $C_{12}H_{16}$ 160.1252, found 160.1247.

1-*n*-Butylindan (4d): 94%; ^1H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7 Hz, 3, CH_3), 2.72–3.14 (m, 3, benzylic H), 7.08–7.28 (m, 4, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 174 (M^+, 14), 117 ($M^+ - C_4H_9$, 100); exact mass spectrum calcd for $C_{13}H_{18}$ 174.1409, found 174.1411.

General Procedure for the Preparation of 2-Alkylindans 7 from 1-Indanone (2). 2-Methylindan (7a). To a solution of 2.6 g (25.7 mmol) of diisopropylamine in 100 mL of tetrahydrofuran at −78 °C under a nitrogen atmosphere was added 16 mL of 1.6 M *n*-butyllithium in hexane. The reaction mixture was allowed to stir at 25 °C for 0.5 h. To the lithium diisopropylamide solution was added 3.8 g (28.8 mmol) of 1-indanone in 50 mL of tetrahydrofuran. After stirring at −78 °C for 1.5 h, the enolate was quenched with 19.35 g (13.5 mmol, 4.68 equiv) of methyl iodide, and the mixture was stirred an additional 4 h at −78 °C and then allowed to warm to 25 °C. The reaction was quenched with 50 mL of 15% hydrochloric acid solution, extracted with ether, washed with brine, and dried over anhydrous magnesium sulfate. The crude product was chromatographed on Merck silica gel 60 with 1:6 ethyl acetate:hexane to afford 2.33 g (55%) of 2-methylindanone (**5a**): ^1H NMR ($CDCl_3$) δ 1.30 (d, *J* = 7.25 Hz, 3, CH_3), 2.60–2.72 (m, 2, benzylic H), 3.28–3.40 (m, 1, $CHCH_3$), 7.38–7.80 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 209.3 (C-1), 34.9 (C-2), 41.9 (C-3), 127.3 (C-4), 123.9 (C-5), 126.5 (C-6), 134.6 (C-7), 153.4 (C-8), 136.3 (C-9), 16.2 (CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 146 (M^+, 70), 131 ($M^+ - CH_3$, 100), 117 (26), 115 (26); exact mass spectrum calcd for $C_{10}H_{10}O$ 147.0731, found 147.0724.

To a solution of 0.58 g (4 mmol) of 2-methylindanone (**5a**) in 30 mL of 2:1 tetrahydrofuran–methanol was added 222 mg (6 mmol) of sodium borohydride. The reaction was stirred at 25 °C for ca. 4 h and quenched with 15% hydrochloric acid solution. The product was extracted with ether, washed with brine, and dried over anhydrous magnesium sulfate. The solvent was removed, and the residue was dissolved in 10 mL of benzene containing 66 mg (0.34 mmol) of *p*-toluenesulfonic acid monohydrate. The mixture was refluxed for 1 h. The product was diluted with ether, washed successively with 10% sodium bicarbonate solution and brine, and dried over anhydrous magnesium sulfate. The product was chromatographed on Merck silica gel 60 with hexane to afford 439 mg (84%) of 2-methyl-1*H*-indene (**6a**): ^1H NMR ref 36; ^{13}C NMR ($CDCl_3$) δ 42.6 (C-1), 145.9 (C-2), 127.1 (C-3), 119.7 (C-4), 123.2 (C-5 or 6), 126.1 (C-5 or 6), 123.4 (C-7), 143.3 (C-8), 145.9 (C-9), 16.7 (CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 130 (M^+, 100), 115 (70); exact mass spectrum calcd for $C_{10}H_{10}$ 130.0782, found 130.0782.

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A mixture of 0.48 g (10 mmol) of 2-methyl-1*H*-indene (**6a**) and 8.5 mg (0.037 mmol, 0.10 equiv) of platinum oxide in 5 mL of tetrahydrofuran was hydrogenated at 20–30 psi for 10–15 h. The mixture was filtered through Celite 545, and the pad was washed thoroughly with additional tetrahydrofuran. The crude product was chromatographed on Merck silica gel 60 with hexane to give 0.43 g (95%) of 2-methylindan (**7a**): ^{1}H NMR ($CDCl_3$) δ 1.13 (d, J = 6 Hz, 3, CH_3), 2.40–2.60 (m, 3, C-2 H and benzylic H), 2.92–3.12 (m, 2, benzylic H), 7.04–7.24 (m, 4, aromatic H); mass spectrum ref 37.

General Procedure for the Preparation of 2-Alkylindans 7 from 2-Bromo-1*H*-indene (8). The procedure described for the preparation of 4-alkylindanes 12 from 7-bromo-1*H*-indene (**10**) was repeated with 2-bromo-1*H*-indene (**8**).

Summary of Yields and Spectral Data for 2-Alkylindanones 5. 2-Ethylindanone (5b): 40%; ^{1}H NMR ($CDCl_3$) δ 0.76 (t, J = 7.25 Hz, 3, CH_2CH_3), 1.44–1.60 (m, 1, CH_2CH_3), 2.52–2.64 (m, 1, benzylic H), 2.72–2.88 (m, 1, benzylic H), 3.24–3.40 (m, 1, $CHCH_2$), 7.28–7.80 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 208.7 (C-1), 29.8 (C-2), 48.7 (C-3), 127.2 (C-4), 123.7 (C-5), 126.9 (C-6), 134.5 (C-7), 153.7 (C-8), 136.9 (C-9), 11.6 (CH_2CH_3), 24.4 ($CHCH_3$).

2-*n*-Propylindanone (5c): 22%; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 7 Hz, 3, $CH_2CH_2CH_3$), 1.32–1.60 (m, 3), 1.8–2.04 (m, 1), 2.6–2.88 (m, 2), 3.24–3.36 (m, 1) 7.32–7.80 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 208.8 (C-1), 32.7 (C-2), 47.1 (C-3), 127.1 (C-4), 123.6 (C-5), 126.3 (C-6), 134.4 (C-7), 153.6 (C-8), 136.6 (C-9), 13.9 ($CH_2CH_2CH_3$), 33.4 ($CH_2CH_2CH_3$).

Summary of Yields and Spectral Data for 2-Alkyl-1*H*-indenes 6. 2-Ethyl-1*H*-indene (6b): 98% from **8**; 70% from **5b**; ^{1}H NMR ($CDCl_3$) δ 1.19 (t, J = 7.25 Hz, 3, CH_2CH_3), 2.47 (q, J = 7.25, 2, CH_2CH_3), 3.27 (s, 2, benzylic H), 6.47 (m, 1, vinylic H), 7.04–7.40 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 40.9 (C-1), 152.3 (C-2), 126.2 (C-3), 119.8 (C-4), 123.2 (C-5 or 6), 125.2 (C-5 or 6), 123.5 (C-7), 143.0 (C-8), 145.7 (C-9), 13.2 (CH_2CH_3), 24.3 (CH_2CH_3); mass spectrum ref 38; exact mass spectrum calcd for $C_{11}H_{12}$ 144.0939, found 144.0931.

2-*n*-Propyl-1*H*-indene (6c): 99% from **8**; 70% from **5c**; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, J = 7 Hz, 3, $CH_2CH_2CH_3$), 1.58–1.76 (m, 2), 2.43 (t, J = 7 Hz, 2, $CH_2CH_2CH_3$), 3.27 (s, 2, benzylic H), 6.48 (s, 1), 7.04–7.40 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 40.9 (C-1), 150.7 (C-2), 126.2 (C-3), 119.8 (C-4), 123.3 (C-5 or 6), 126.1 (C-5 or 6), 123.5 (C-7), 143.1 (C-8), 145.7 (C-9), 13.9 ($CH_2CH_2CH_3$), 22.2 ($CH_2CH_2CH_3$), 33.3 ($CH_2CH_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 158 (M^+, 26), 129 (100), 115 (9), 69 (65); exact mass spectrum calcd for $C_{12}H_{14}$ 158.1095, found 158.1094.

2-*n*-Butyl-1*H*-indene (6d): 97% from **8**; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7 Hz, 3, $CH_2CH_2CH_3$), 1.28–1.44 (m, 2, $CH_2CH_2CH_2CH_3$), 1.32–1.64 (m, 2, $CH_2CH_2CH_2CH_3$), 2.45 (t, J = 7 Hz, 2, $CH_2CH_2CH_2CH_3$), 3.28 (s, 2, benzylic H), 6.48 (s, 1), 7.04–7.40 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 41.0 (C-1), 150.9 (C-2), 126.2 (C-3), 119.8 (C-4), 123.3 (C-5 or 6), 126.1 (C-5 or 6), 123.4 (C-7), 143.1 (C-8), 145.7 (C-9), 13.9 ($CH_2CH_2CH_2CH_3$), 22.5 ($CH_2CH_2CH_2CH_3$), 30.9 ($CH_2CH_2CH_2CH_3$), 31.2 ($CH_2CH_2CH_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 172 (M^+, 24), 129 (100), 130 (35), 115 (10), 89 (27); exact mass spectrum calcd for $C_{13}H_{16}$ 172.1252, found 172.1224.

Summary of Yields and Spectral Data for 2-Alkylindans 7. 2-Ethylindan (7b): 98%; IR and ^{1}H NMR ref 39; mass spectrum (70 eV), m/e (relative intensity) 146 (M^+, 62), 131 (52), 117 (100); exact mass spectrum calcd for $C_{11}H_{14}$ 146.1095, found 146.1086.

2-*n*-Propylindan (7c): 97%; IR and ^{1}H NMR ref 39; mass spectrum (70 eV), m/e (relative intensity) 160 (M^+, 67), 131 (64), 117 (100), 104 (63); exact mass spectrum calcd for $C_{12}H_{16}$ 160.1252, found 160.1245.

2-*n*-Butylindan (7d): 97%; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7 Hz, 3, $CH_2CH_2CH_2CH_3$), 1.28–1.60 (m, 6), 2.36–2.52 (m, 1, C-2 H), 2.52–2.64 (m, 2, benzylic H), 2.96–3.12 (m, 2, benzylic H), 7.08–7.28 (m, 4, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 174 (M^+, 53), 117 (100), 104 (79); exact mass spectrum calcd for $C_{13}H_{18}$ 174.1409, found 174.1403.

2-Bromo-1*H*-indene (8): mp 37–38 °C; ^{1}H NMR ($CDCl_3$) δ 3.54 (s, 2, benzylic H), 6.88 (s, 1, vinylic H), 7.08–7.46 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 132.9 (C-1), 124.7 (C-2), 45.4 (C-3), 123.11 (C-4), 124.8 (C-5), 126.5 (C-6), 120.1 (C-7), 143.9 (C-8), 142.5 (C-9); mass spectrum (70 eV), m/e (relative intensity) 196 (M^+ + 2, 12), 194 (M^+, 14), 131 (55), 115 (100); exact mass spectrum calcd for C_9H_7Br 193.9732, found 193.9738.

4-Bromoindanone (9). The procedure of Holliman[40] was repeated with some modifications. To a solution of 1.94 g (0.084 mol) of sodium in 60 mL of anhydrous ethanol was added 26.08 g (0.163 mol) of diethyl malonate followed by 12.45 g (0.05 mol) of 2-bromobenzyl bromide. The mixture was refluxed for 3.5 h. The mixture was concentrated and diluted with water. The reaction was extracted with ether, washed successively with dilute hydrochloric acid solution and half-saturated brine, and dried over anhydrous magnesium sulfate. The product was distilled to afford 10.5 g (64%) of diethyl 2-(2-bromobenzyl)malonate: bp 200 °C (20 mm) (lit.[40] bp 115–120 °C (0.004 mm)); ^{1}H NMR ($CDCl_3$) δ 1.19 (t, J = 6.6 Hz, 3, CH_2CH_3), 1.19 (t, J = 7.3 Hz, 3, CH_2CH_3), 3.33 (d, J = 7 Hz, 2), 3.84 (t, J = 7 Hz, 1), 4.14 (q, J = 6.6 Hz, 2, CH_2CH_3), 4.15 (q, J = 7.3 Hz, 2, CH_2CH_3), 7.04–7.56 (m, 3, aromatic H). A mixture of 5 g (0.015 mol) of diethyl 2-(2-bromobenzyl)malonate and 5 g (0.089 mol, 6 equiv) of potassium hydroxide in 50 mL of 1:2:3 of HOAc–water–tetrahydrofuran was stirred at 25 °C for ca. 12 h. The product was diluted with water, acidified with 15% hydrochloric acid solution, saturated with sodium chloride, extracted with ethyl acetate, and dried over anhydrous magnesium sulfate. The solvent was evaporated to afford 3.7 g (89%) of 2-(2-bromobenzyl)malonic acid: mp 154–155 °C (lit.[40] mp 139–140 °C). To effect decarboxylation, 3.5 g (12.5 mmol) of 2-(2-bromobenzyl)malonic acid was heated at 165 °C until evolution of carbon dioxide ceased (ca. 10 min). The product was crystallized from petroleum ether to afford 2.45 g (81%) of 3-(2-bromophenyl)propionic acid: mp 96–99 °C (lit.[40] mp 97–98.5 °C); ^{1}H NMR (acetone-d_6) δ 2.63 (t, J = 7 Hz, 2, CH_2CO_2H), 3.04 (t, J = 7 Hz, 2, $CH_2CH_2CO_2H$), 7.08–7.64 (m, 4, aromatic H). To 2 g (8.5 mmol) of 3-(2-bromophenyl)propionic acid was added 10 mL of thionyl chloride. The solution was refluxed for 45 min, and excess thionyl chloride was removed. To the crude acid chloride was added 40 mL of carbon disulfide and 1.5 g of aluminum chloride. The mixture was refluxed for 3 h. The product was diluted with a cold hydrochloric acid solution, extracted with ethyl acetate, and dried over anhydrous magnesium sulfate. The product was chromatographed on Merck silica gel 60 with 1:3 ethyl acetate–hexane to afford 1.71 g (93%) of 4-bromoindanone (**9**): mp 95 °C (from petroleum ether) (lit.[40] mp 94 °C); ^{1}H NMR ($CDCl_3$) δ 2.71 (t, J = 6 Hz, 2, C-2 CH_2), 3.05 (t, J = 6 Hz, 2, benzylic H), 7.2–7.76 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 205.8 (C-1), 26.9 (C-2), 36.0 (C-3), 122.2 (C-4), 137.2 (C-5), 129.0 (C-6), 122.5 (C-7), 154.6 (C-8), 139.0 (C-9).

7-Bromo-1*H*-indene (10). To a solution of 530 mg (2.5 mmol) of 4-bromoindanone[40] (**9**) in 20 mL of ethanol was added 75.6 mg (2 mmol) of sodium borohydride. The reaction was stirred at 25 °C for 2 h. The mixture was concentrated, diluted with 15% hydrochloric acid solution, saturated with sodium chloride, and extracted with ether. The ether solutions were dried over anhydrous magnesium sulfate. The product was chromatographed on Merck silica gel 60 with 1:3 ethyl acetate–hexane to afford 520 mg (98%) of 4-bromoindanol: mp 70–72 °C; ^{1}H NMR ($CDCl_3$) δ 1.8–1.96 (m, 1), 2.36–2.52 (m, 1), 2.56–3.04 (m, 2), 3.4–4.0 (m, 1, OH), 5.12–5.24 (m, 1, $CHOH$), 7.04–7.4 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 75.9 (C-1), 29.3 (C-2), 36.01 (C-3), 131.2 (C-4), 127.4 (C-5), 120.2 (C-6), 126.4 (C-7), 147.1 (C-8), 142.1 (C-9).

A mixture of 7 g (32.8 mmol) of 4-bromoindanol and 624 mg (3.28 mmol) of *p*-toluenesulfonic acid monohydrate in 150 mL of benzene was refluxed for 1 h. The mixture was washed successively with 10% sodium bicarbonate solution and brine. The benzene solution was dried over anhydrous magnesium sulfate. The product was chromatographed on Merck silica gel 60 with hexane to afford 5.8 g (92%) of 7-bromo-1*H*-indene (**10**): ^{1}H NMR

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($CDCl_3$) δ 3.20–3.40 (m, 2, benzylic H), 6.52–6.60 (m, 1, vinylic H), 6.76–6.84 (m, 1, vinylic H), 7.24–7.56 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 124.0 (C-1), 124.9 (C-2), 38.7 (C-3), 135.8 (C-4), 131.2 (C-5), 120.17 (C-6), 127.2 (C-7), 146.9 (C-8), 142.2 (C-9); mass spectrum (70 eV), *m/e* (relative intensity) 195 (M^++2, 21), 193 (M^+, 18), 115 (M^+ – Br, 100); exact mass spectrum calcd for C_9H_7Br 193.9731, found 193.9697.

General Procedure for the Preparation of 4-Alkylindans 12 from 7-Bromo-1*H*-indene (10). 4-Methylindan (12a). To a solution of 975 mg (4 mmol) of 7-bromo-1*H*-indene (**10**) and 21 mg (0.04 mmol) [1,3-bis(diphenylphosphino)propyl]nickel(II) chloride in 8 mL of anhydrous ether under a nitrogen atmosphere was added 1.4 mL of 2.85 M (4 mmol) methylmagnesium bromide in ether. The reaction was refluxed for 22 h. The mixture was quenched with 15% hydrochloric acid solution and extracted with ether. The ether solution was washed with brine and dried over anhydrous magnesium sulfate. The product was chromatographed on Merck silica gel 60 with hexane to afford 624 mg (96%) of 7-methyl-1*H*-indene (**11a**): ^1H NMR ($CDCl_3$) δ 2.33 (s, 3, CH_3), 3.23 (m, 2, benzylic H), 6.46–6.56 (m, 1, vinylic H), 6.80–6.88 (m, 1, vinylic H), 6.92–7.28 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 37.9 (C-1), 132.3 (C-2), 132.8 (C-3), 118.6 (C-4), 125.7 (C-5 or 6), 126.5 (C-5 or 6), 133.6 (C-7), 142.3 (C-8), 144.4 (C-9), 18.6 (CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 130 (100), 115 (78); exact mass spectrum calcd for $C_{10}H_{10}$ 130.0783, found 130.0788.

A mixture of 500 mg (3.84 mmol) of 7-methyl-1*H*-indene (**11a**) and 8.7 mg (0.038 mmol) of platinum oxide in 2 mL of tetrahydrofuran was hydrogenated at 20 psi for 10–15 h. The mixture was filtered through a pad of Celite, and the pad was washed thoroughly with additional tetrahydrofuran. The crude product was chromatographed on Merck silica gel 60 with hexane to give 496 mg (98%) of 4-methylindan (**12a**): IR ref 41; ^1H NMR ($CDCl_3$) δ 1.98–2.08 (m, 2, C-2 CH_2), 2.24[42] (s, 3, CH_3), 2.81 (t, *J* = 7 Hz, 2, benzylic H), 2.90 (t, *J* = 7 Hz, 2, benzylic H) 6.84–7.04 (m, 1, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 132 (M^+, 45), 117 (M^+ – CH_3, 100); exact mass spectrum calcd for $C_{10}H_{12}$ 132.0936, found 132.0936.

Summary of Spectral Data for 7-Alkyl-1*H*-indenes 11. 7-Ethyl-1*H*-indene (11b): 98%; ^1H NMR ($CDCl_3$) δ 1.26 (t, *J* = 7 Hz, 3, CH_2CH_3), 2.70 (q, *J* = 7 Hz, 2, CH_2CH_3), 3.29 (m, 2, benzylic H), 6.48–6.56 (m, 1, vinylic H), 6.84–6.92 (m, 1, vinylic H), 7.0–7.32 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 37.5 (C-1), 132.4 (C-2), 135.5 (C-3), 118.7 (C-4), 123.9 (C-5 or 6), 126.7 (C-5 or 6), 139.0 (C-7), 141.6 (C-8), 144.6 (C-9), 14.2 (CH_2CH_3), 26.1 (CH_2CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 144 (M^+, 52), 129 (M^+ – CH_3, 100), 115 (40); exact mass spectrum calcd for $C_{11}H_{12}$ 144.0939, found 144.0934.

7-*n*-Propyl-1*H*-indene (11c): 99%; ^1H NMR ($CDCl_3$) δ 0.96 (t, *J* = 7 Hz, 3, $CH_2CH_2CH_3$), 1.56–1.76 (m, 2, $CH_2CH_2CH_3$), 2.65 (t, *J* = 7 Hz, 2, $CH_2CH_2CH_3$), 3.30 (m, 2, benzylic H), 6.46–6.56 (m, 1, vinylic H), 6.84–6.92 (m, 1, vinylic H), 6.96–7.28 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 37.7 (C-1), 132.4 (C-2), 133.5 (C-3), 118.7 (C-4), 124.8 (C-5 or 6), 126.6 (C-5 or 6), 137.5 (C-7), 141.9 (C-8), 144.6 (C-9), 14.2 ($CH_2CH_2CH_3$), 23.2 ($CH_2CH_2CH_3$), 35.3 ($CH_2CH_2CH_3$); mass spectrum (70 eV), *m/e* (relative intensity) 158 (M^+, 34), 129 (M^+ – C_2H_5, 100) 115 (M^+ – C_3H_7, 15); exact mass spectrum calcd for $C_{12}H_{14}$ 158.1096, found 158.1105.

7-*n*-Butyl-1*H*-indene (11d): 98%; ^1H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7 Hz, 3, $CH_2CH_2CH_2CH_3$), 1.25–1.44 (m, 1, $CH_2CH_2CH_2CH_3$), 1.56–1.68 (m, 2, $CH_2CH_2CH_2CH_3$), 2.67 (t, *J* = 7 Hz, 2, $CH_2CH_2CH_2CH_3$), 3.3 (m, 2, benzylic H), 6.44–6.56 (m, 2, vinylic H), 6.8–6.9 (m, 1, vinylic H), 6.96–7.28 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 37.6 (C-1), 132.4 (C-2), 133.4 (C-3), 118.6 (C-4), 124.7 (C-5 or 6), 126.6 (C-5 or 6), 137.8 (C-7), 141.8 (C-8), 144.6 (C-9), 14.0 ($CH_2CH_2CH_2CH_3$), 22.7 ($CH_2CH_2CH_2CH_3$), 32.2 ($CH_2CH_2CH_2CH_3$), 32.9 ($CH_2CH_2CH_2CH_3$); mass spectrum (70 eV), *m/e* (relative intensity) 172 (M^+, 39), 129 (M^+ – C_3H_7, 100), 115 (M^+ – C_4H_9, 15); exact mass spectrum calcd for $C_{13}H_{16}$ 172.1252, found 172.1262.

Summary of Yields and Spectral Data for 4-Alkylindans 12. 4-Ethylindan[43] (12b): 97%; ^1H NMR ($CDCl_3$) δ 1.19 (t, *J* = 8 Hz, 3, CH_2CH_3), 1.96–2.08 (m, 2, C-2 CH_2), 2.58 (q, *J* = 8 Hz, 2, CH_2CH_3), 2.76–2.96 (m, 4, benzylic H), 6.92–7.12 (m, 3, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 146 (M^+, 37), 131 (M^+ – CH_3, 41), 117 (M^+ – C_2H_5, 100); exact mass spectrum calcd for $C_{11}H_{14}$ 146.1096, found 146.1098.

4-*n*-Propylindan (12c): 97%; ^1H NMR ($CDCl_3$) δ 0.95 (t, *J* = 7 Hz, 3, $CH_2CH_2CH_3$), 1.48–1.68 (m, 2, $CH_2CH_2CH_3$), 1.96–2.08 (m, 2, C-2 CH_2), 2.54 (t, *J* = 7 Hz, 2, $CH_2CH_2CH_3$), 2.76–2.96 (m, 4, benzylic H), 6.88–7.12 (m, 3, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 160 (M^+, 32), 131 (M^+ – C_2H_5, 100), 117 (M^+ – C_3H_7, 41); exact mass spectrum calcd for $C_{12}H_{16}$ 160.1252, found 160.1252.

4-*n*-Butylindan (12d): 97%; ^1H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7 Hz, 3, $CH_2CH_2CH_2CH_3$), 1.28–1.44 (m, 2, $CH_2CH_2CH_2CH_3$), 1.48–1.60 (m, 2, $CH_2CH_2CH_2CH_3$), 1.96–2.10 (m, 2, C-2 CH_2), 2.55 (t, *J* = 7 Hz, 2, $CH_2CH_2CH_2CH_3$), 2.76–2.96 (m, 4, benzylic H), 6.88–7.12 (m, 3, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 174 (M^+, 31), 131 (M^+ – C_3H_7, 100), 117 (M^+ – C_4H_9, 41); exact mass spectrum calcd for $C_{13}H_{18}$ 174.1409, found 174.1417.

6-Bromoindanone (13). The procedure[40] described for the preparation of 4-bromoindanone (**9**) was repeated with 35 g (0.14 mol) of 4-bromobenzyl bromide and 73 g (0.45 mol) of diethyl malonate to furnish 34.2 g (74%) of diethyl 2-(4-bromobenzyl)-malonate: bp 176 °C (4 mm); ^1H NMR ($CDCl_3$) δ 1.21 (t, *J* = 7 Hz, 6, CH_2CH_3), 3.12–3.24 (m, 2, benzylic H), 3.58–3.64 (m, 1, $CH(CO_2C_2H_5)_2$), 4.13 (q, *J* = 7 Hz, 4, CH_2CH_3), 7.0 (d, *J* = 7.9 Hz, 2, aromatic H), 7.39 (d, *J* = 7.9 Hz, 2, aromatic H). The saponification procedure was repeated with 5 g (0.015 mol) of diethyl 2-(4-bromobenzyl)malonate and 5 g (0.089 mol) of potassium hydroxide to afford 4.02 g (95%) of 2-(4-bromobenzyl)malonic acid: mp 148–150 °C (from petroleum ether). The decarboxylation procedure was repeated at 165 °C to afford 14.3 g (85%) of 3-(4-bromophenyl)propionic acid: mp 132–135 °C (from petroleum ether); ^1H NMR (acetone-d_6) δ 2.61 (t, *J* = 7 Hz, 2, $CH_2CH_2CO_2H$), 2.88 (t, *J* = 7 Hz, 2, $CH_2CH_2CO_2H$), 7.12–7.48 (m, 4, aromatic H). The Friedel–Crafts cyclization was repeated with 23.5 g (0.1 mol) of 3-(4-bromophenyl)propionic acid, 45 mL of thionyl chloride, and 18.6 g of aluminum trichloride in 0.5 L of carbon disulfide to afford 19.7 g (91%) of 6-bromoindanone (**13**): mp 109–110 °C (from hexane); ^1H NMR ($CDCl_3$) δ 2.64–2.76 (m, 2, C-2 CH_2), 3.04–3.16 (m, 2, benzylic H), 7.32–7.84 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 205.7 (C-1), 25.5 (C-2), 36.4 (C-3), 137.2 (C-4), 128.2 (C-5), 121.4 (C-6), 126.5 (C-7), 153.5 (C-8), 138.7 (C-9).

5-Bromo-1*H*-indene (14). The procedure described for the preparation of 7-bromo-1*H*-indene (**10**) was repeated with 6-bromoindanone (**13**). The reduction was repeated with 4.4 g (20.8 mmol) of 6-bromoindanone (**13**) and 770 mg (20.8 mmol) of sodium borohydride to afford 3.95 g (89%) of 6-bromoindanol: mp 84–86 °C (from hexane); ^1H NMR ($CDCl_3$) δ 1.81–1.96 (m, 1), 2.36–2.52 (m, 1), 2.56–3.04 (m, 2), 3.4–4.0 (m, 1, OH), 5.12–5.24 (m, 1, CHOH), 7.04–7.4 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 75.9 (C-1), 29.3 (C-2), 36.01 (C-3), 131.2 (C-4), 127.4 (C-5), 120.2 (C-6), 126.4 (C-7), 147.1 (C-8), 142.1 (C-9). The dehydration was repeated with 4.26 g (20 mmol) of 6-bromoindanol and 380 mg (2 mmol) of *p*-toluenesulfonic acid monohydrate to afford 3.89 (97%) of 5-bromo-1*H*-indene (**14**): mp 41 °C; ^1H NMR ($CDCl_3$) δ 3.24–3.48 (m, 2, benzylic H), 6.52–6.60 (m, 1, vinylic H), 6.84–6.92 (m, 1, vinylic H), 7.08–7.32 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 127.6 (C-1), 119.9 (C-2), 40.7 (C-3), 118.8 (C-4), 134.5 (C-5), 131.9 (C-6), 128.1 (C-7), 146.1 (C-8), 143.7 (C-9); mass spectrum (70 eV), *m/e* (relative intensity) 195 (M^++2, 16), 193 (M^+, 17) 115 (M^+ – Br, 100); exact mass spectrum calcd for C_9H_7Br 193.9731, found 193.9724.

General Procedure for the Preparation of 5-Alkylindans 16 from 5-Bromo-1*H*-indene (14). The procedure described for the preparation of 4-alkylindans **12** was repeated with 5-bromo-1*H*-indene (**14**) to afford 5-alkylindans **16**.

Summary of Yields and Spectral Data for 5-Alkyl-1*H*-indenes 15. 5-Methyl-1*H*-indene (15a): 93%; ^1H NMR ($CDCl_3$) δ 2.37 (s, 3, CH_3), 3.32 (m, 2, benzylic H), 6.48–6.56 (m, 1, vinylic H), 6.8–6.88 (m, 1, vinylic H), 7.0 (d, *J* = 7 Hz, 1, aromatic H),

(41) Munavalli, S.; Ourisson, G. *Bull. Soc. Chim. Fr.* **1964**, 2822.
(42) Gaude, D.; Barrelle, M.; Apparu, M. *Bull. Soc. Chim. Fr.* **1977**, 758.
(43) Bruce, W. F.; Kahn, S. J. *J. Am. Chem. Soc.* **1938**, *60*, 1017.

7.19 (s, 1, aromatic H), 7.32 (d, J = 7 Hz, 1, aromatic H); ^{13}C NMR ($CDCl_3$) δ 38.6 (C-1), 131.9 (C-2), 134.3 (C-3), 121.6 (C-4), 135.7 (C-5), 125.3 (C-6), 123.3 (C-7), 140.6 (C-8), 145.0 (C-9), 21.4 (CH_3); mass spectrum (70 eV), m/e (relative intensity) 130 (M^+, 100), 115 ($M^+ - CH_3$, 76); exact mass spectrum calcd for $C_{10}H_{10}$ 130.0782, found 130.0777.

5-Ethyl-1*H*-indene (15b): 96%; ^{1}H NMR ($CDCl_3$) δ 1.23 (t, J = 7 Hz, 3, CH_2CH_3), 2.65 (q, J = 7 Hz, 2, CH_2CH_3), 3.3 (m, 2, benzylic H), 6.48–6.56 (m, 1, vinylic H), 6.8–6.88 (m, 1, vinylic H), 7.0 (d, J = 7 Hz, 1, aromatic H), 7.21 (s, 1, aromatic H), 7.33 (d, J = 7 Hz, 1, aromatic H); ^{13}C NMR ($CDCl_3$) δ 38.6 (C-1), 132.0 (C-2), 134.2 (C-3), 120.4 (C-4), 142.3 (C-5), 124.2 (C-6), 123.4 (C-7), 140.9 (C-8), 145.1 (C-9), 16.1 (CH_2CH_3), 28.9 (CH_2CH_3); mass spectrum (70 eV), m/e (relative intensity) 144 (M^+, 51), 129 ($M^+ - CH_3$, 100), 115 ($M^+ - C_2H_5$, 30); exact mass spectrum calcd for $C_{11}H_{12}$ 144.0939, found 144.0931.

5-*n*-Propyl-1*H*-indene (15c): 98%; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7 Hz, 3, $CH_2CH_2CH_3$), 1.56–1.72 (m, 2, $CH_2CH_2CH_3$), 2.6 (t, J = 7 Hz, 2, $CH_2CH_2CH_3$), 3.30 (m, 2, benzylic H), 6.48–6.56 (m, 1, vinylic H), 6.76–6.84 (m, 1, vinylic H), 6.97 (d, J = 7 Hz, 1, aromatic H), 7.19 (s, 1, aromatic H), 7.32 (d, J = 7 Hz, 1, aromatic H); ^{13}C NMR ($CDCl_3$) δ 38.6 (C-1), 132.0 (C-2), 134.2 (C-3), 121.0 (C-4), 140.7 (C-5), 124.9 (C-6), 123.3 (C-7), 140.9 (C-8), 145.0 (C-9), 13.9 ($CH_2CH_2CH_3$), 24.9 ($CH_2CH_2CH_3$), 38.1 ($CH_2CH_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 158 (M^+, 28), 129 ($M^+ - C_2H_5$, 100), 115 ($M^+ - C_3H_7$, 9); exact mass spectrum calcd for $C_{12}H_{14}$ 158.1095, found 158.1093.

5-*n*-Butyl-1*H*-indene (15d): 98%; ^{1}H NMR ($CDCl_3$) δ (t, J = 7 Hz, 3, $CH_2CH_2CH_2CH_3$), 1.28–1.42 (m, 2, $CH_2CH_2CH_2CH_3$), 1.52–1.66 (m, 2, $CH_2CH_2CH_2CH_3$), 2.63 (t, J = 7 Hz, 2, $CH_2CH_2CH_2CH_3$), 3.33 (m, 2, benzylic H), 6.48–6.56 (m, 1, vinylic H), 6.80–6.88 (m, 1, vinylic H), 7.00 (d, J = 7 Hz, 1, aromatic H), 7.21 (s, 1, aromatic H), 7.35 (d, J = 7 Hz, 1, aromatic H); ^{13}C NMR ($CDCl_3$) δ 38.6 (C-1), 132.0 (C-2), 134.2 (C-3), 121.0 (C-4), 141.0 (C-5), 124.8 (C-6), 123.3 (C-7), 140.9 (C-8), 145.0 (C-9), 14.0 ($CH_2CH_2CH_2CH_3$), 22.4 ($CH_2CH_2CH_2CH_3$), 34.1 ($CH_2CH_2CH_2CH_3$), 35.7 ($CH_2CH_2CH_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 172 (M^+, 27), 129 ($M^+ - C_3H_7$, 100), 115 ($M^+ - C_4H_9$, 9); exact mass spectrum calcd for $C_{13}H_{16}$ 172.1252, found 172.1247.

Summary of Yields and Spectral Data for 5-Alkylindans

16. 5-Methylindan (16a): 90% from **14**; ^{1}H NMR ($CDCl_3$) δ 1.96–2.08 (m, 2, C-2 CH_2), 2.30 (s, 3, CH_3), 2.85 (t, J = 7 Hz, 2, benzylic H), 6.93 (d, J = 7 Hz, 1, aromatic H), 7.03 (s, 1, aromatic H), 7.13 (d, J = 7 Hz, 1, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 132 (M^+, 46), 117 ($M^+ - CH_3$, 100); exact mass spectrum calcd for $C_{10}H_{12}$ 132.0939, found 132.0946.

5-Ethylindan (16b): 97% from **14**; ^{1}H NMR ($CDCl_3$) δ 1.21 (t, J = 7 Hz, 3, CH_2CH_3), 1.96–2.08 (m, 2, C-2 CH_2), 2.60 (q, J = 7 Hz, 2, CH_2CH_3), 2.76–2.92 (m, 4, benzylic H), 6.96 (d, J = 7 Hz, 1, aromatic H), 7.06 (s, 1, aromatic H), 7.16 (d, J = 7 Hz, 1, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 146 (M^+, 54), 131 ($M^+ - CH_3$, 100), 117 ($M^+ - C_2H_5$, 99); exact mass spectrum calcd for $C_{11}H_{14}$ 146.1095, found 146.1089.

5-*n*-Propylindan (16c): 96% from **14**; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7 Hz, 3, $CH_2CH_2CH_3$), 1.96–2.12 (m, 2, C-2 CH_2), 2.53 (t, J = 7 Hz, 2, $CH_2CH_2CH_3$), 2.80–2.92 (m, 4, benzylic H), 6.93 (d, J = 7.9 Hz, 1, aromatic H), 7.03 (s, 1, aromatic H), 7.11 (d, J = 7.9 Hz, 1, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 160 (M^+, 22), 131 ($M^+ - C_2H_5$, 100), 117 ($M^+ - C_3H_7$, 12); exact mass spectrum calcd for $C_{12}H_{16}$ 160.1251, found 160.1520.

5-*n*-Butylindan (16d): 97% from **14**; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7 Hz, 3, $CH_2CH_2CH_2CH_3$), 1.28–1.34 (m, 2, $CH_2CH_2CH_2CH_3$), 1.52–1.64 (m, 2, $CH_2CH_2CH_2CH_3$), 1.96–2.12 (m, 2, C-2 CH_2), 2.56 (t, J = 7.9 Hz, 2, $CH_2CH_2CH_2CH_3$), 2.80–2.92 (m, 4, benzylic H), 6.93 (d, J = 7.25 Hz, 1, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 174 (M^+, 23), 131 ($M^+ - C_3H_7$, 100), 117 ($M^+ - C_4H_9$, 15); exact mass spectrum calcd for $C_{13}H_{18}$ 174.1409, found 174.1424.

General Procedure for the Preparation of 1-Alkyltetralins 19 from 1-Tetralone (17). The procedure described for the preparation of 1-alkylindans **4** from 1-indanone (**2**) was repeated with 1-tetralone (**17**).

Summary of Yields and Spectral Data for 1-Alkyl-3,4-dihydronaphthalenes

18. 3,4-Dihydro-1-methylnaphthalene (18a): 91% from **17**; ^{1}H NMR ($CDCl_3$) δ 2.02 (s, 3, CH_3), 2.12–2.32 (m, 2, C-3 CH_2), 2.7–2.80 (m, 2, benzylic H), 5.80–5.88 (m, 1, vinylic H), 7.04–7.28 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 136.0 (C-1), 127.3 (C-2), 23.2 (C-3), 28.3 (C-4), 126.3 (C-5, 6, or 7), 126.6 (C-5, 6, or 7), 125.3 (C-5, 6, or 7), 122.5 (C-8), 135.5 (C-9), 131.9 (C-10), 19.3 (CH_3); mass spectrum (70 eV), m/e (relative intensity) 144 (M^+, 51), 129 ($M^+ - CH_3$, 100), 115 (18); exact mass spectrum calcd for $C_{11}H_{12}$ 144.0939, found 144.0928.

1-Ethyl-3,4-dihydronaphthalene (18b): 91% from **17**; ^{1}H NMR ($CDCl_3$) δ 1.13 (t, J = 7 Hz, 3, CH_2CH_3), 2.16–2.32 (m, 2, C-3 CH_2), 2.44 (q, J = 7 Hz, 2, CH_2CH_3), 2.64–2.8 (m, 2, benzylic H), 5.8–5.88 (m, 1, vinylic H), 7.04–7.28 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 137.9 (C-1), 127.4 (C-2), 23.0 (C-3), 28.4 (C-4), 126.3 (C-5, 6, or 7), 126.4 (C-5, 6, or 7), 123.3 (C-5, 6, or 7), 122.4 (C-8), 136.6 (C-9), 135.0 (C-10), 12.9 (CH_2CH_3), 25.3 (CH_2CH_3); mass spectrum (70 eV), m/e (relative intensity) 158 (M^+, 27), 129 ($M^+ - C_2H_5$, 100), 115 (19); exact mass spectrum calcd for $C_{11}H_{14}$ 158.1096, found 158.1096.

3,4-Dihydro-1-*n*-propylnaphthalene (18c): 85% from **17**; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7 Hz, 3, CH_3), 2.64–2.76 (m, 2, benzylic H), 5.76–5.84 (m, 1, vinylic H), 7.04–7.28 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 136.7 (C-1), 127.4 (C-2), 23.1 (C-3), 28.5 (C-4), 126.2 (C-5, 6, or 7), 126.4 (C-5, 6, or 7), 124.7 (C-5, 6, or 7), 122.6 (C-8), 136.3 (C-9), 135.0 (C-10), 14.0 ($CH_2CH_2CH_3$), 21.5 ($CH_2CH_2CH_3$), 34.8 ($CH_2CH_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 172 (M^+, 26), 129 ($M^+ - C_3H_7$, 100), 115 (15); exact mass spectrum calcd for $C_{13}H_{16}$ 172.1253, found 172.1260.

1-*n*-Butyl-3,4-dihydronaphthalene (18d): 70% from **17**; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7 Hz, 3, CH_3), 2.64–2.72 (m, 2, benzylic H), 5.76–5.84 (m, 1, vinylic H), 7.04–7.26 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 136.7 (C-1), 127.4 (C-2), 23.1 (C-3), 28.5 (C-4), 126.2 (C-5, 6, or 7), 126.4 (C-5, 6, or 7), 124.5 (C-5, 6, or 7), 122.6 (C-8), 136.6 (C-9), 135.0 (C-10), 14.0 ($CH_2CH_2CH_2CH_3$), 22.7 ($CH_2CH_2CH_2CH_3$), 23.1 ($CH_2CH_2CH_2CH_3$), 30.7 ($CH_2CH_2CH_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 186 (M^+, 25), 144 (100), 129 ($M^+ - C_4H_9$, 86), 115 (17); exact mass spectrum calcd for $C_{14}H_{18}$ 186.1408, found 186.1407.

Summary of Yields and Spectral Data for 1-Alkyltetralins

19. 1-Methyltetralin (19a): 94% from **18a**; IR ref 44; ^{1}H NMR ref 45; mass spectrum ref 46.

1-Ethyltetralin (19b): 92% from **18b**; IR ref 44; ^{1}H NMR and mass spectrum ref 47.

1-*n*-Propyltetralin (19c): 96% from **18c**; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7 Hz, 3, CH_3), 2.64–2.84 (m, 3, benzylic H), 7.04–7.24 (m, 4, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 174 (M^+, 12), 131 ($M^+ - C_3H_7$, 100), 115 (7); exact mass spectrum calcd for $C_{13}H_{18}$ 174.1409, found 174.1425.

1-*n*-Butyltetralin (19d): 93% from **18d**; IR ref 44; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7 Hz, 3, CH_3), 2.6–2.92 (m, 3, benzylic H), 7.04–7.28 (m, 4, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 188 (M^+, 11), 145 ($M^+ - C_3H_7$, 52), 131 ($M^+ - C_4H_9$, 100), 117 (41), 115 (21); exact mass spectrum calcd for $C_{14}H_{20}$ 188.1564, found 188.1561.

General Procedure for the Preparation of 2-Alkyltetralins 22 from 1-Tetralone (17). The procedure described for the preparation of 2-alkylindans **7** from 1-indanone (**2**) was repeated with 1-tetralone (**17**).

General Procedure for the Preparation of 2-Alkyltetralins 22 from 3-Bromo-1,2-dihydronaphthalene (23). The procedure described for the preparation of 4-alkylindans **12** from 7-bromo-1*H*-indene (**10**) was repeated with 3-bromo-1,2-dihydronaphthalene (**23**).

Summary of Yields and Spectral Data for 2-Alkyltetralones

20. 2-Methyltetralone[48] (20a): 41%; ^{1}H NMR ($CDCl_3$) δ 1.26 (d, J = 7.3 Hz, 3, CH_3), 1.72–1.92 (m, 1), 2.08–2.22

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(m, 1), 2.48–2.60 (m, 1), 2.88–3.08 (m, 2, benzylic H), 7.16–8.04 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 200.6 (C-1), 31.1 (C-2), 28.8 (C-3), 42.6 (C-4), 128.6 (C-5), 126.4 (C-6), 127.3 (C-7), 133.0 (C-8), 144.1 (C-9), 132.2 (C-10), 15.4 (CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 160 (M^+, 61), 145 ($M^+ - CH_3$, 19), 118 (100); exact mass spectrum calcd for $C_{11}H_{12}O$ 160.0889, found 160.0896.

2-Ethyltetralone (20b): 41%; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, *J* = 7 Hz, 3, CH_3), 1.46–1.64 (m, 1), 1.8–2.04 (m, 2) 2.12–2.28 (m, 1), 2.30–2.44 (m, 1), 2.88–3.0 (m, 2, benzylic H), 7.16–8.08 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 200 (C-1), 27.7 (C-2), 28.3 (C-3), 48.8 (C-4), 128.6 (C-5), 126.4 (C-6), 127.3 (C-7), 132.9 (C-8), 143.9 (C-9), 132.5 (C-10), 11.4 (CH_2CH_3), 22.3 (CH_2CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 174 (M^+, 21), 146 (100), 145 ($M^+ - C_2H_5$, 23), 118 (46); exact mass spectrum calcd for $C_{12}H_{14}O$ 174.1044, found 174.1022.

2-*n*-Propyltetralone (20c): 20%; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, *J* = 7 Hz, 3, $CH_2CH_2CH_3$), 1.24–1.56 (m, 3), 1.8–1.96 (m, 2), 2.16–2.32 (m, 1), 2.40–2.56 (m, 1), 2.92–3.04 (m, 2, benzylic H), 7.20–8.08 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 200.3 (C-1), 31.5 (C-2), 28.2 (C-3), 47.2 (C-4), 128.6 (C-5), 126.4 (C-6), 127.4 (C-7), 133.0 (C-8), 143.9 (C-9), 132.7 (C-10), 14.1 ($CH_2CH_2CH_3$), 20.1 ($CH_2CH_2CH_3$), 28.1 ($CH_2CH_2CH_3$).

2-*n*-Butyltetralone (20d): 16%; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7 Hz, 3, $CH_2CH_2CH_2CH_3$), 1.24–1.60 (m, 5), 1.80–2.04 (m, 2), 2.16–2.30 (m, 1), 2.34–2.56 (m, 1), 2.96–3.08 (m, 2, benzylic H), 7.20–8.08 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 200.3 (C-1), 29.0 (C-2), 28.2 (C-3), 47.3 (C-4), 128.5 (C-5), 126.3 (C-6), 127.3 (C-7), 132.9 (C-8), 143.8 (C-9), 132.4 (C-10), 13.9 ($CH_2CH_2CH_2CH_3$), 22.7 ($CH_2CH_2CH_2CH_3$), 28.1 ($CH_2CH_2CH_2CH_3$), 29.1 ($CH_2CH_2CH_2CH_3$).

Summary of Yields and Spectral Data for 2-Alkyl-3,4-dihydronaphthalenes 21. 3,4-Dihydro-2-methylnaphthalene (21a): 98% from **23**; 81% from **20a**; ^{1}H NMR($CDCl_3$) δ 1.89 (s, 3, CH_3), 2.16–2.24 (m, 2), 2.72–2.84 (m, 2, benzylic H), 6.2 (s, 1, vinylic H), 6.88–7.16 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 127.1 (C-1), 138.2 (C-2), 28.8 (C-3), 28.0 (C-4), 125.8 (C-5, 6, or 7), 125.0 (C-5, 6, or 7), 126.3 (C-5, 6, or 7), 122.6 (C-8), 135.0 (C-9), 134.0 (C-10), 22.4 (CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 144 (M^+, 51), 129 ($M^+ - CH_3$, 100), 115 (18); exact mass spectrum calcd for $C_{11}H_{12}$ 144.0939, found 144.0928.

2-Ethyl-3,4-dihydronaphthalene (21b): 98% from **23**; 74% from **20b**; ^{1}H NMR ref 49; ^{13}C NMR ($CDCl_3$) δ 127.0 (C-1), 143.7 (C-2), 30.2 (C-3), 28.2 (C-4), 125.9 (C-5, 6, or 7), 125.3 (C-5, 6, or 7), 126.3 (C-5, 6, or 7), 120.9 (C-8), 135.0 (C-9), 134.3 (C-10), 12.1 (CH_2CH_3), 27.4 (CH_2CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 158 (M^+, 44), 143 ($M^+ - CH_3$, 26), 129 ($M^+ - C_2H_5$, 100), 115 (13); exact mass spectrum calcd for $C_{12}H_{14}$ 158.1096, found 158.1096.

3,4-Dihydro-2-*n*-propylnaphthalene (21c): 97% from **23**; 72% from **20c**; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7 Hz, 3, $CH_2CH_2CH_3$), 1.44–1.60 (m, 2), 2.08–2.28 (m, 4), 2.77 (t, *J* = 8 Hz, 2, benzylic H), 6.19 (s, 1, vinylic H), 6.94–7.16 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 127.1 (C-1), 142.1 (C-2), 39.5 (C-3), 28.2 (C-4), 125.9 (C-5, 6, or 7), 125.2 (C-5, 6, or 7), 126.3 (C-5, 6, or 7), 122.2 (C-8), 135.0 (C-9), 134.4 (C-10), 13.8 ($CH_2CH_2CH_3$), 20.7 ($CH_2CH_2CH_3$), 27.2 ($CH_2CH_2CH_3$); mass spectrum (70 eV), *m/e* (relative intensity) 172 (M^+, 39), 143 (100), 129 (45), 115 (10); exact mass spectrum calcd for $C_{13}H_{16}$ 172.1253, found 172.1255.

2-*n*-Butyl-3,4-dihydronaphthalene (21d): 97% from **23**; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7 Hz, 3, $CH_2CH_2CH_2CH_3$), 1.24–1.64 (m, 4), 2.12–2.28 (m, 4), 2.77 (t, *J* = 8 Hz, 2, benzylic H), 6.19 (s, 1, vinylic H), 6.86–7.22 (m, 4, aromatic H); ^{13}C NMR ($CDCl_3$) δ 127.1 (C-1), 142.4 (C-2), 37.5 (C-3), 28.2 (C-4), 125.9 (C-5, 6, or 7), 125.2 (C-5, 6, or 7), 126.3 (C-5, 6, or 7), 122.0 (C-8), 135.0 (C-9), 134.3 (C-10), 14.0 ($CH_2CH_2CH_2CH_3$), 22.4 ($CH_2CH_2CH_2CH_3$), 27.3 ($CH_2CH_2CH_2CH_3$), 29.3 ($CH_2CH_2CH_2CH_3$); mass spectrum (70 eV), *m/e* (relative intensity) 186 (M^+, 67), 143 (100), 130 (14), 129 (66), 128 (50), 115 (15); exact mass spectrum calcd for $C_{14}H_{18}$ 186.1408, found 186.1384.

Summary of Yields and Spectral Data for 2-Alkyltetralins 22. 2-Methyltetralin (22a): 98% from **21a**; ^{1}H NMR ref 50; mass spectrum (70 eV), *m/e* (relative intensity) 146 (M^+, 100), 118 (14), 117 (19); exact mass spectrum calcd for $C_{11}H_{14}$ 146.1096, found 146.1097.

2-Ethyltetralin (22b): 97% from **21b**; ^{1}H NMR ref 49; mass spectrum (70 eV), *m/e* (relative intensity) 160 (M^+, 79) 131 ($M^+ - C_2H_5$, 100), 129 (22), 117 (25), 115 (24); exact mass spectrum calcd for $C_{12}H_{16}$ 160.1240, found 160.1240.

2-*n*-Propyltetralin (22c): 98% from **21c**; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7 Hz, 3, $CH_2CH_2CH_3$), 1.28–1.98 (m, 6), 2.32–2.44 (m, 1), 2.76–2.92 (m, 4), 7.0–7.12 (m, 4, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 174 (M^+, 19), 131 (66), 117 (100); exact mass spectrum calcd for $C_{13}H_{18}$ 174.1408, found 174.1392.

2-*n*-Butyltetralin (22d): 98% from **21d**; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7 Hz, 3, $CH_2CH_2CH_2CH_3$), 1.28–1.96 (m, 8), 2.32–2.48 (m, 1), 2.72–2.96 (m, 4), 7.0–7.2 (m, 4, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 188 (M^+, 60), 131 (75), 117 (18), 104 (100); exact mass spectrum calcd for $C_{14}H_{20}$ 188.1525, found 188.1545.

3-Bromo-1,2-dihydronaphthalene (23). The procedure described for the preparation of 7-bromo-1*H*-indene (**10**) was repeated with 2-bromo-1-tetralone.[51] The reduction was repeated with 4.5 g (0.02 mol) of 2-bromo-1-tetralone and 0.55 g (0.014 mol) of sodium borohydride in 100 mL of 1:1 ethanol–THF to afford 3.76 g (83%) of 2-bromo-1-tetralol: mp 62–64 °C (from hexane). The dehydration procedure was repeated with 2.27 g (10 mmol) of 2-bromo-1-tetralol and 190 mg (1 mmol) of *p*-toluenesulfonic acid in 40 mL of benzene to afford 2 g (96%) of 3-bromo-1,2-dihydronaphthalene (**23**): ^{1}H NMR ($CDCl_3$) δ 2.72 (t, *J* = 8.5 Hz, 2, allylic H), 2.90 (t, *J* = 8.5 Hz, 2, benzylic H), 6.75 (s, 1, vinylic H), 6.91–7.24 (m, 4, aromatic H); mass spectrum (70 eV), *m/e* (relative intensity) 210 ($M^+ + 2$, 34), 208 (M^+, 37), 129 (100), 127 (26); exact mass spectrum calcd for $C_{10}H_9Br$ 207.9888, found 207.9866.

5-Bromotetralone (24). The procedure of Uyeo[24a] was repeated with some modifications. To a refluxing solution of 32.6 g (0.52 mol) of potassium cyanide in 150 mL of 95% ethanol and 65 mL of water was added 49 g (0.195 mol) of *o*-bromobenzyl bromide over 0.5 h. The mixture was refluxed for an additional 45 min, and 500 mL of ice water was added. The crystalline *o*-bromobenzyl cyanide was collected and recrystallized from 70% aqueous ethanol to afford 32 g (86%) of *o*-bromobenzyl cyanide. A mixture of 30 g (0.15 mol) of *o*-bromobenzyl cyanide, 325 mL of sulfuric acid, and 430 mL of water was refluxed for 4 h. The reaction mixture was poured over ice, and the precipitate was collected. The crude product was dissolved in a 15% solution of sodium hydroxide, and the solution was extracted with ethyl ether. The aqueous layer was acidified with 15% hydrochloric acid, and the precipitated product was collected and dried in vacuo to afford 29.8 g (91%) of *o*-bromophenylacetic acid: mp 103–105 °C. To a mixture of 4 g (0.108 mol) of lithium aluminum hydride in 80 mL of anhydrous ether was added 18 g (0.08 mol) of *o*-bromophenylacetic acid in 80 mL of ether over 0.5 h. The mixture was refluxed for 1 h, quenched with ethyl acetate, and diluted with 15% aqueous hydrochloric acid. The layers were separated and the aqueous portion was extracted several times with ether. The combined ether solutions were washed with brine and dried over anhydrous magnesium sulfate. The crude product was chromatographed on Merck silica gel 60 1:2 with ethyl acetate–hexanes to afford 14.1 g (84%) of 2-(*o*-bromophenyl)ethanol. To a mixture of 17.75 mL of 48% hydrobromic acid and 5.1 mL of sulfuric acid was added 17.9 g (0.09 mol) of 2-(*o*-bromophenyl)-ethanol. An additional 3 mL of sulfuric acid was added dropwise. The mixture was refluxed for 3 h and then poured on to ice. The product was extracted with ether, washed successively with water, 5% sodium bicarbonate solution, brine, and finally dried over anhydrous magnesium sulfate. The crude product was distilled to afford 19.4 g (72%) of 2-(*o*-bromophenyl)ethyl bromide: bp 116–118 °C (7 mm). To a solution of 1.4 g (0.06 mol) of sodium in 35 mL of anhydrous ethanol was added 19.7 g (0.12 mol) of diethyl malonate followed by 11 g (0.041 mol) of 2-(*o*-bromophenyl)ethyl bromide. The mixture was refluxed for 7 h and was

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poured on to ice. The product was extracted with ether, washed successively with dilute hydrochloric acid solution and half-saturated brine, and dried over anhydrous magnesium sulfate. The crude product was chromatographed on Merck silica gel 60 with 1:6 ethyl acetate–hexane to afford 9 g (63%) of diethyl 2-(2-(*o*-bromophenyl)ethyl)malonate. A mixture of 9 g (0.03 mol) of diethyl 2-(2-(*o*-bromophenyl)ethyl)malonate and 5 g (0.09 mol) of potassium hydroxide in 20 mL of 50% aqueous ethanol was refluxed for 6 h. The mixture was diluted with water and acidified with 15% hydrochloric acid solution. A colorless precipitate was collected to afford 7.32 g (98%) of 2-(2-(*o*-bromophenyl)ethyl)-malonic acid: mp 156–158 °C dec. This material was used in the next step without further purification. To effect decarboxylation, 7.5 g (0.026 mol) of 2-(2-(*o*-bromophenyl)ethyl)malonic acid was heated at 170 °C until evolution of carbon dioxide ceased (ca. 20 min). The product was recrystallized from hexane to afford 6 g (95%) of 4-(*o*-bromophenyl)butyric acid: mp 88–89 °C (lit.[24a] mp 87 °C). To 6 g (0.024 mol) of 4-(*o*-bromophenyl)butyric acid was added 60 mL of excess thionyl chloride. The solution was refluxed for 45 min, and the thionyl chloride was removed under reduced pressure. To the crude acid chloride was added 120 mL of carbon disulfide and 4.75 g of aluminum trichloride. The mixture was refluxed for 3 h. The reaction mixture was diluted with a cold hydrochloric acid solution and extracted with ethyl acetate. The ethyl acetate solution was dried over magnesium sulfate. The product was chromatographed on Merck silica gel 60 with 1:6 ethyl acetate–hexane to afford 4.75 g (85%) of 5-bromotetralone (**24**): mp 49–50 °C (from hexane) (lit.[24a] mp 47–48 °C).

5-Bromo-3,4-dihydronaphthalene (25). The procedure described for the preparation of 7-bromo-1*H*-indene (**10**) was repeated with 5-bromotetralone[24a] (**24**). The reduction was repeated with 4.7 g (0.02 mol) of **24** and 0.55 g (0.014 mol) of sodium borohydride in 50 mL of 1:1 ethanol–THF to afford 4.22 g (89%) of 5-bromotetralol. The dehydration procedure was repeated with 4 g (17.6 mmol) of 5-bromotetralol and 0.33 g (1.75 mmol) of *p*-toluenesulfonic acid in 40 mL of benzene to afford 3.53 g (96%) of 5-bromo-3,4-dihydronaphthalene (**25**): ^{1}H NMR ($CDCl_3$) δ 2.28–2.44 (m, 2), 2.90 (t, J = 8 Hz, 2, benzylic H), 5.96–6.12 (m, 1, vinylic H), 6.37 (d, J = 9 Hz, 1 vinylic H), 6.88–7.08 (m, 2, aromatic H), 7.32–7.35 (m, 1, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 210 (M^+ + 2, 23), 208 (M^+, 26), 129 (100), 127 (20); exact mass spectrum calcd for $C_{10}H_9Br$ 207.9888, found 207.9868.

General Procedure for the Preparation of 5-Alkyltetralins 27 from 5-Bromo-3,4-dihydronaphthalene (25). The procedure described for the preparation of 4-alkylindans **12** from 7-bromo-1*H*-indene (**10**) was repeated with 5-bromo-3,4-dihydronaphthalene (**25**).

Summary of Yields and Spectral Data for 5-Alkyl-3,4-dihydronaphthalenes 26. 3,4-Dihydro-5-methylnaphthalene (26a): 98% from **25**; ^{1}H NMR ($CDCl_3$) δ 2.55 (s, 3, CH_3), 2.28–2.32 (m, 1, C-2 vinylic H), 6.42 (d, J = 10 Hz, 1, C-1 vinylic H), 6.85–7.08 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 128.9 (C-1 or 2), 128.1 (C-1 or 2), 23.3 (C-3 or 4), 23.0 (C-3 or 4), 134.9 (C-5), 125.8 (C-6 or 7), 127.8 (C-6 or 7), 124.0 (C-8), 133.8 (C-9), 133.5 (C-10), 19.3 (CH_3); mass spectrum (70 eV), m/e (relative intensity) 144 (M^+, 78), 129 (100), 115 (13); exact mass spectrum calcd for $C_{11}H_{12}$ 144.0940, found 144.0943.

5-Ethyl-3,4-dihydronaphthalene (26b): 97% from **25**; ^{1}H NMR ($CDCl_3$) δ 1.17 (t, J = 7 Hz, 3, CH_2CH_3), 2.24–2.36 (m, 2), 2.62 (q, J = 7 Hz, 2, CH_2CH_3), 2.76 (t, J = 8 Hz, 2, benzylic H), 5.96–6.06 (m, 1, C-2 vinylic H), 6.42 (d, J = 10 Hz, 1, C-1 vinylic H), 6.84–7.16 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 128.3 (C-1 or 2), 127.9 (C-1 or 2), 23.2 (C-3 or 4), 23.0 (C-3 or 4), 140.9 (C-5), 126.0 (C-6 or 7), 127.4 (C-6 or 7), 124.1 (C-8), 134.0 (C-9), 132.9 (C-10), 14.8 (CH_2CH_3), 26.0 (CH_2CH_3); mass spectrum (70 eV), m/e (relative intensity) 158 (M^+, 47), 143 (28), 129 (100), 115 (13); exact mass spectrum calcd for $C_{12}H_{14}$ 158.1096, found 158.1110.

3,4-Dihydro-5-*n*-propylnaphthalene (26c): 98% from **25**; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, J = 7 Hz, 3, $CH_2CH_2CH_3$), 1.28–1.64 (m, 2, $CH_2CH_2CH_3$), 2.24–2.36 (m, 2), 2.61 (t, J = 8 Hz, 2, $CH_2CH_2CH_3$), 2.76 (t, J = 8 Hz, 2, benzylic H), 5.96–6.06 (m, 1, C-2 vinylic H), 6.42 (d, J = 10 Hz, 1, C-1 vinylic H), 6.84–7.16 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 128.4 (C-1), 128.4 (C-2), 23.2 (C-3 or 4), 23.2 (C-3 or 4), 139.4 (C-5), 125.8 (C-6 or 7), 127.9 (C-6 or 7), 124.1 (C-8), 134.1 (C-9), 133.0 (C-10), 14.1 ($CH_2CH_2CH_3$), 23.7 ($CH_2CH_2CH_3$), 35.2 ($CH_2CH_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 172 (M^+, 60), 143 (70), 129 (100), 115 (16); exact mass spectrum calcd for $C_{13}H_{16}$ 172.1251, found 172.1237.

5-*n*-Butyl-3,4-dihydronaphthalene (26d): 98% from **25**; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7 Hz, 3, $CH_2CH_2CH_2CH_3$), 1.32–1.60 (m, 4, $CH_2CH_2CH_2CH_3$), 2.24–2.36 (m, 2), 2.60 (t, J = 8 Hz, 2, $CH_2CH_2CH_2CH_3$), 2.76 (t, J = 8 Hz, 2, benzylic H), 5.96–6.06 (m, 1, C-2 vinylic H), 6.42 (d, J = 10 Hz, 1, C-1 vinylic H), 6.84–7.16 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 128.3 (C-1), 128.3 (C-2), 23.3 (C-3 or 4), 23.2 (C-3 or 4), 139.6 (C-5), 125.8 (C-6 or 7), 127.9 (C-6 or 7), 124.1 (C-8), 134.1 (C-9), 133.0 (C-10), 13.9 ($CH_2CH_2CH_2CH_3$), 22.7 ($CH_2CH_2CH_2CH_3$), 32.8 ($CH_2CH_2CH_2CH_3$), 32.8 ($CH_2CH_2CH_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 186 (M^+, 60), 143 (63), 129 (100), 115 (15); exact mass spectrum calcd for $C_{14}H_{18}$ 186.1408, found 186.1408.

Summary of Yields and Spectral Data for 5-Alkyltetralins 27. 5-Methyltetralin (27a): 99% from **26a**; ^{1}H NMR ($CDCl_3$) ref 52; mass spectrum (70 eV), m/e (relative intensity) 146 (M^+, 56), 131 (100), 118 (53); exact mass spectrum calcd for $C_{11}H_{14}$ 146.1096, found 146.1098.

5-Ethyltetralin (27b): 98% from **27a**; ^{1}H NMR ($CDCl_3$) ref 53; mass spectrum (70 eV), m/e (relative intensity) 160 (M^+, 23), 145 (14), 131 (74), 84 (100); exact mass spectrum calcd for $C_{12}H_{16}$ 160.1252, found 160.1263.

5-*n*-Propyltetralin (27c). 98% from **26c**: ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7 Hz, 3, $CH_2CH_2CH_3$), 1.44–1.88 (m, 6), 2.52 (t, J = 8 Hz, 2, $CH_2CH_2CH_3$), 2.69 (t, J = 6 Hz, 2, benzylic H), 2.77 (t, J = 6 Hz, 2, benzylic H), 6.86–7.08 (m, 3, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 174 (M^+, 54), 145 (100), 131 (93), 104 (31); exact mass spectrum calcd for $C_{13}H_{18}$ 174.1409, found 174.1409.

5-*n*-Butyltetralin (27d): 97% from **26d**; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7 Hz, 3, $CH_2CH_2CH_2CH_3$), 1.32–1.60 (m, 4), 1.68–1.88 (m, 4), 2.53 (t, J = 8 Hz, 2, $CH_2CH_2CH_2CH_3$), 2.69 (t, J = 6 Hz, 2, benzylic H), 2.77 (t, J = 6 Hz, 2, benzylic H), 6.88–7.06 (m, 3, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 188 (M^+, 49), 145 (100), 131 (90); exact mass spectrum calcd for $C_{14}H_{20}$ 188.1565, found 188.1565.

7-Bromo-3,4-dihydronaphthalene (29). The procedure described for the preparation of 7-bromo-1*H*-indene (**10**) was repeated with 7-bromotetralone[24b] (**28**). The reduction was repeated with 9 g (0.04 mol) of **28** and 1 g (0.026 mol) of sodium borohydride in 100 mL of 1:1 ethanol–THF to afford 7.89 g (87%) of 7-bromotetralol. The dehydration procedure was repeated with 7 g (30 mmol) of 7-bromotetralol and 0.62 g (3.2 mmol) of *p*-toluenesulfonic acid monohydrate in 150 mL of benzene to afford 6.1 g (95%) of 7-bromo-3,4-dihydronaphthalene (**29**): ^{1}H NMR ($CDCl_3$) δ 2.24–2.36 (m, 2), 2.72 (t, J = 8 Hz, 2, benzylic H), 6.0–6.12 (m, 1, vinylic H), 6.37 (d, J = 9 Hz, 1, vinylic H), 6.94–7.28 (m, 3, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 210 (M^+ + 2, 23), 208 (M^+, 26); exact mass spectrum calcd for $C_{10}H_9Br$ 207.9887, found 207.9858.

General Procedure for the Preparation of 6-Alkyltetralins 31 from 7-Bromo-3,4-dihydronaphthalene (29). The procedure described for the preparation of 4-alkylindans **12** from 7-bromo-1*H*-indene (**10**) was repeated with 7-bromo-3,4-dihydronaphthalene (**29**).

Summary of Yields and Spectral Data for 6-Alkyl-1,2-dihydronaphthalenes 30. 1,2-Dihydro-6-methylnaphthalene (30a): 98% from **29**; ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3, CH_3), 2.20–2.24 (m, 2), 2.68 (t, J = 8 Hz, 2, benzylic H), 5.92–6.04 (m, 1, vinylic H), 6.36–6.46 (m, 1, vinylic H), 6.80–7.04 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 27.0 (C-1), 23.3 (C-2), 127.8 (C-3 or 4), 128.4 (C-3 or 4), 126.6 (C-5), 135.7 (C-6), 127.3 (C-7), 127.3 (C-8), 132.3 (C-9), 133.9 (C-10), 20.9 (CH_3); mass spectrum (70 eV), m/e (relative intensity) 144 (M^+, 80), 129 (100), 69 (41); exact mass spectrum calcd for $C_{11}H_{12}$ 144.0940, found 144.0959.

6-Ethyl-1,2-dihydronaphthalene (30b): 98% from **29**; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3, CH_2CH_3), 2.24–2.36 (m, 2), 2.57 (q, J = 7 Hz, 2, CH_2CH_3), 2.73 (t, J = 8 Hz, 2, benzylic H),

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5.96–6.08 (m, 1, C-2 vinylic H), 6.42 (d, J = 10 Hz, 1, C-1 vinylic H), 6.84–7.04 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 27.0 (C-1), 23.3 (C-2), 127.8 (C-3 or 4), 128.4 (C-3 or 4), 126.1 (C-5), 142.2 (C-6), 127.3 (C-7 or 8), 127.8 (C-7 or 8), 132.6 (C-9), 133.9 (C-10), 15.7 (CH_2CH_3), 28.5 (CH_2CH_3); mass spectrum (70 eV), m/e (relative intensity) 158 (M^+, 32), 143 (25), 129 (62), 69 (100); exact mass spectrum calcd for $C_{12}H_{14}$ 158.1096, found 158.1103.

1,2-Dihydro-6-*n*-propylnaphthalene (30c): 99% from **29**; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7 Hz, 3, $CH_2CH_2CH_3$), 1.52–1.72 (m, 2, $CH_2CH_2CH_3$), 2.22–2.32 (m, 2), 2.51 (t, J = 8 Hz, 2, $CH_2CH_2CH_3$), 2.73 (t, J = 8 Hz, 2, benzylic H), 5.96–6.08 (m, 1, C-2 vinylic H), 6.42 (d, J = 10 Hz, 1, C-1 vinylic H), 6.84–7.04 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 27.1 (C-1), 23.3 (C-2), 127.9 (C-3 or 4), 128.4 (C-3 or 4), 126.1 (C-5), 140.7 (C-6), 126.8 (C-7 or 8), 127.3 (C-7 or 8), 132.6 (C-9), 133.9 (C-10), 13.8 ($CH_3CH_2CH_3$), 24.6 ($CH_2CH_2CH_3$), 37.7 ($CH_2CH_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 172 (M^+, 57), 143 (100), 129 (70), 115 (14), 69 (94); exact mass spectrum calcd for $C_{13}H_{16}$ 172.1252, found 172.1249.

6-*n*-Butyl-1,2-dihydronaphthalene (30d): 98% from **29**; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7 Hz, 3, $CH_2CH_2CH_2CH_3$), 1.24–1.44 (m, 2, $CH_2CH_2CH_2CH_3$), 1.48–1.64 (m, 2, $CH_2CH_2CH_2CH_3$), 2.22–2.32 (m, 2), 2.53 (t, J = 8 Hz, 2, $CH_2CH_2CH_2CH_3$), 2.73 (t, J = 8 Hz, 2, benzylic H), 5.96–6.08 (m, 1, C-2 vinylic H), 6.42 (d, J = 10 Hz, 1, C-1 vinylic H), 6.84–7.04 (m, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 27.1 (C-1), 23.3 (C-2), 127.9 (C-3 or 4), 128.4 (C-3 or 4), 126.0 (C-5), 140.9 (C-6), 126.7 (C-7 or 8), 127.3 (C-7 or 8), 132.6 (C-9), 133.9 (C-10), 13.9 ($CH_2CH_2CH_2CH_3$), 22.4 ($CH_2CH_2CH_2CH_3$), 33.7 ($CH_2CH_2CH_2CH_3$), 35.3 ($CH_2CH_2CH_2CH_3$); mass spectrum (70 eV), m/e (relative intensity) 186 (M^+, 40), 143 (63), 129 (42), 69 (100); exact mass spectrum calcd for $C_{14}H_{18}$ 186.1318, found 186.1363.

Summary of Yields and Spectral Data for 6-Alkyltetralins 31. 6-Methyltetralin (31a): 99% from **30a**; ^{1}H NMR ref 50a; mass spectrum ref 54; exact mass spectrum calcd for $C_{11}H_{14}$ 146.1096, found 146.1107.

6-Ethyltetralin (31b): 97% from **30b**; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3, CH_2CH_3), 1.68–1.84 (m, 4), 2.55 (q, J = 7 Hz, 2, CH_2CH_3), 2.64–2.80 (m, 4, benzylic H), 6.84–7.0 (m, 3, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 160 (M^+, 25), 145 (19), 131 (100), 115 (10); exact mass spectrum calcd for $C_{12}H_{16}$ 160.1252, found 160.1260.

6-*n*-Propyltetralin (31c). 98% from **30c**; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7 Hz, 3, $CH_2CH_2CH_3$), 1.56–1.70 (m, 2, $CH_2CH_2CH_3$), 1.72–1.92 (m, 4), 2.50 (t, J = 8 Hz, 2, $CH_2CH_2CH_3$), 2.68–2.88 (m, 4, benzylic H), 6.84–7.0 (m, 3, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 174 (M^+, 7), 145 (22), 131 (100); exact mass spectrum calcd for $C_{13}H_{18}$ 174.1408, found 174.1401.

6-*n*-Butyltetralin (31d). 98% from **30d**; ^{1}H NMR ref 55; mass spectrum ref 54.

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Lewis Acid Catalyzed Conversion of Alkenes and Alcohols to Azides[1]

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Hydrazoic acid, though unreactive to alkenes, adds readily to enol ethers. In the presence of Lewis acids, in particular $TiCl_4$, addition takes place readily to phenylethylenes or 1,1-disubstituted ethylenes to produce alkyl azides. Regiochemical, electronic, and steric influences were explored. $TiCl_4$ also served to catalyze conversion of benzyl or tertiary alcohols to azides. Monosubstituted alkenes or primary alcohols are not affected.

Organic azides are versatile substrates for organic synthesis. Such compounds not only interact with nucleophiles or electrophiles but also serve as nitrene precursors on thermal or photochemical excitation.[2] While aromatic azides can be obtained by a variety of methods, aliphatic azides are prepared chiefly by substitution of alkyl halides, diazo transfer to aliphatic amines, or additions to olefins.[3] Halogen azides have been employed extensively in addi-

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