ture of the exocyclic and endocyclic acids. The nmr spectrum indicated that the endocyclic isomer predominated over the exocyclic by about 7:1. Esterification of the acid mixture with diazomethane gave **14**: bp 170–185° (0.5 mm); ν_{CO} 1760, 1730 cm^{-1}; nmr peaks ($CDCl_3$) at δ 2.2 (2 H, m), 3.04 (2 H, s), 3.65 (5 H, s superimposed on m), 4.0 (2 H, m), 5.15 (2 H, s), 5.5 (1 H, m), 7.30 (5 H, s).

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.60; H, 6.72; N, 4.67.

Hydroboration of 14. 1-Benzyloxycarbonyl-3-hydroxy-4-piperidineethanol (15).—A solution of **14** (1.8 g, 6.3 mmol) in glyme (10 ml) at 0° was treated with 1.0 *M* diborane solution in tetrahydrofuran (3 ml, 3 mmol). After 0.5 hr, water (4 ml), 30% hydrogen peroxide (10 ml) and potassium carbonate (10 g) were carefully added, and the solution was stirred at room temperature for 3 days. The reaction mixture was poured into water and extracted with ether. Chromatography of the crude product (1.6 g) on silicic acid using 30% ether–benzene gave recovered **14** (0.8 g, 44%) and **15** (0.45 g, 16 mmol, 45%): nmr peaks ($CDCl_3$) at δ 1.0–2.0 (5 H, m), 2.0–5.0 (7 H, m), 5.1 (2 H, s), and 7.35 (5 H, s).

Anal. Calcd for $C_{15}H_{21}NO_4$: C, 64.49; H, 7.58. Found: C, 64.77; H, 7.80.

***N*-(2-Oxo-4-carbethoxybutyl)-2-ethylaziridine (18).**—2-Ethylaziridine (1.77 g, 0.025 mol) was dissolved in triethylamine (10 ml) and added dropwise during 10 min to a solution of ethyl 5-bromolevulinate[24] (5.56 g, 0.025 mol) in benzene (50 ml) at 0°. After stirring 2 hr at 0° triethylamine hydrobromide was removed by filtration and the solvent was removed using a rotary evaporator at room temperature. The product, obtained as a clear pale yellow oil (5.0 g, 94%), was used in subsequent experiments within 0.5 hr.

Ethyl *N*-Benzoyl-*N*-(2-chlorobutyl)-5-aminolevulinate (19).—A solution of **18** (5.56 g, 0.025 mol) in benzene (50 ml) was added dropwise to benzoyl chloride (3.5 g, 0.025 mol) in benzene (50 ml) at 0°. After stirring for 20 min the solvent was removed using a rotary evaporation, and the residue was dissolved in chloroform and washed with dilute potassium carbonate, dilute hydrochloric acid, and water. Evaporation of the chloroform gave the crude haloamide: ν_{CO} 1735, 1640 cm^{-1}; nmr peaks ($CDCl_3$) at δ 1.23 (3 H, s), 0.6–2.0 (5 H, unresolved m), 2.9–2.3 (4 H, d), 4.1 (2 H, q), 4.38 (2 H, s), 7.39 (5 H, broad s). Attempts to effect complete purification by distillation or silicic acid chromatography failed.

***N*-Benzoyl-6-(2-carbethoxyethyl)-2-ethyl-3,4-dihydro-2*H*-1,4-oxazine (20).**—A solution of **19** (1.0 g, 2.8 mmol) in dry tetrahydrofuran (10 ml) was treated with potassium *tert*-butoxide (0.317 g, 2.8 mmol) and stirred at room temperature for 3 hr. Gaseous hydrochloric acid was passed through the solution. The solvent was removed and the residue was dissolved in a small amount of chloroform and eluted through Florisil with chloroform giving **20** (0.4 g, 1.2 mmol, 44%). Rechromatography gave the analytical sample: ν_{CO} 1740, 1640 cm^{-1}; $\nu_{C=C}$ 1690 cm^{-1}; nmr signals ($CDCl_3$) at 1.21 (3 H, t), 0.7–2.0 (5 H, complex m), 2.2–2.7 (2 H, m), 4.1 (2 H, q), 2.9–4.5 (3 H, unresolved m), 6.6, 5.8, (1 H, singlets in 1:2 ratio), 7.47 (5 H, s).

Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.13; H, 7.25; N, 4.42. Found: C, 67.86; H, 6.98; N, 4.41.

Reduction of this material by $NaBH_4$ slowly (overnight) gave *N*-benzoyl-2-ethyl-6-(3-hydroxypropyl)-3,4-dihydro-2*H*-1,4-oxazine (**21**) as indicated by mass spectral parent ion 275 and infrared absorption data: ν_{OH} 3440 cm^{-1}; ν_{CO} 1640 cm^{-1}; no ester carbonyl; nmr peaks ($CDCl_3$) at δ 0.7–2.5 (9 H, complex m), 2.32 (1 H, s, exchanged by D_2O), 3.9–4.5 (5 H, complex unresolved signal), 6.65, 5.8 (1 H, singlets in 1:2 ratio), 7.52 (5 H, s).

Registry No.—**2b**, 30338-60-4; **4b**, 30338-61-5; **4d**, 30338-62-6; **5b**, 30338-63-7; **5d**, 30338-64-8; **6a**, 30338-65-9; **8a**, 30338-66-0; **9b**, 30338-67-1; **10a**, 30338-68-2; *t*-**10b**, 30338-69-3; *c*-**10b**, 30338-70-6; *t,t*-**10c**, 30338-71-7; *t,c*-**10c**, 30338-72-8; **10d**, 30338-73-9; **10e**, 30338-74-0; **11b**, 30338-75-1; *t,t*-**12b**, 30338-76-2; *c,c*-**12b**, 30338-77-3; *t,t,t*-**12c**, 30409-18-8; *t,t,c*-**12c**, 30338-78-4; **12f**, 30338-79-5; *t,t*-**13a**, 30338-80-8; *c,c*-**13a**, 30338-81-9; *t,t,t*-**13c**, 30338-82-0; *t,t,c*-**13c**, 30338-83-1; *t,c,c*-**13c**, 30338-84-2; **14**, 30338-85-3; **15**, 30338-86-4; **19**, 30338-87-5; **20**, 30409-19-9; **21**, 30344-94-6.

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The Synthesis of Polyalkyl-1-tetralones and the Corresponding Naphthalenes[1]

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The stepwise synthesis of specifically substituted trialkyl-3,4-dihydro-1(2*H*)-naphthalenones (1-tetralones), the corresponding naphthalenes, and partially hydrogenated derivatives, several having the cadalene-type 1,4,6 substitution, has been reexamined. Individual steps have been improved and new approaches with *fewer* steps and higher overall yields have been devised. Syntheses utilizing lactones in Friedel–Crafts reactions were also carried out. These latter Friedel–Crafts reactions are responsible for rearrangements during tetralone syntheses which were previously attributed to polyphosphoric acid during cyclization.

The synthesis of cadalene (**1**) became important to us as a route to pure polyalkylnaphthalenes and as a model to develop new and improved hydrocarbon syntheses.[3,4]

(1) E. J. Eisenbraun and C. W. Hinman, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **10** [1], 33 (1965).

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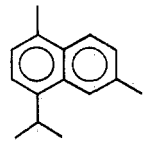
(3) (a) S. Dev and P. C. Guha, *J. Indian Chem. Soc.*, **25**, 13 (1948); (b) B. A. Nagasampagi, S. Dev, and (in part) C. Rai and K. L. Murthy, *Tetrahedron*, **22**, 1949 (1966); (c) L. Ruzicka and L. Ehmann, *Helv. Chim. Acta*, **15**, 140 (1932).

(4) Correspondence regarding samples of hydrocarbons **6**, **7**, **9a**, 1,2,3,4-tetrahydro-1,4,5-trimethylnaphthalene, and 1,4,5-trimethylnaphthalene should be directed to A. J. Streiff, American Petroleum Institute, Carnegie-Mellon University, Pittsburgh, Pa. 15213.

It is of interest that most of the reagents used in an earlier synthesis[3a] which leads to **1** in 18% yield through



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seven steps have been supplanted and the synthesis is now so drastically modified that comment is required, particularly since some of the reagents and steps remain as textbook favorites. To ensure validity in our comparison, we repeated the preparation of **1** and obtained the reported yields.[3a] This synthesis, however, is impractical for large-scale preparations.

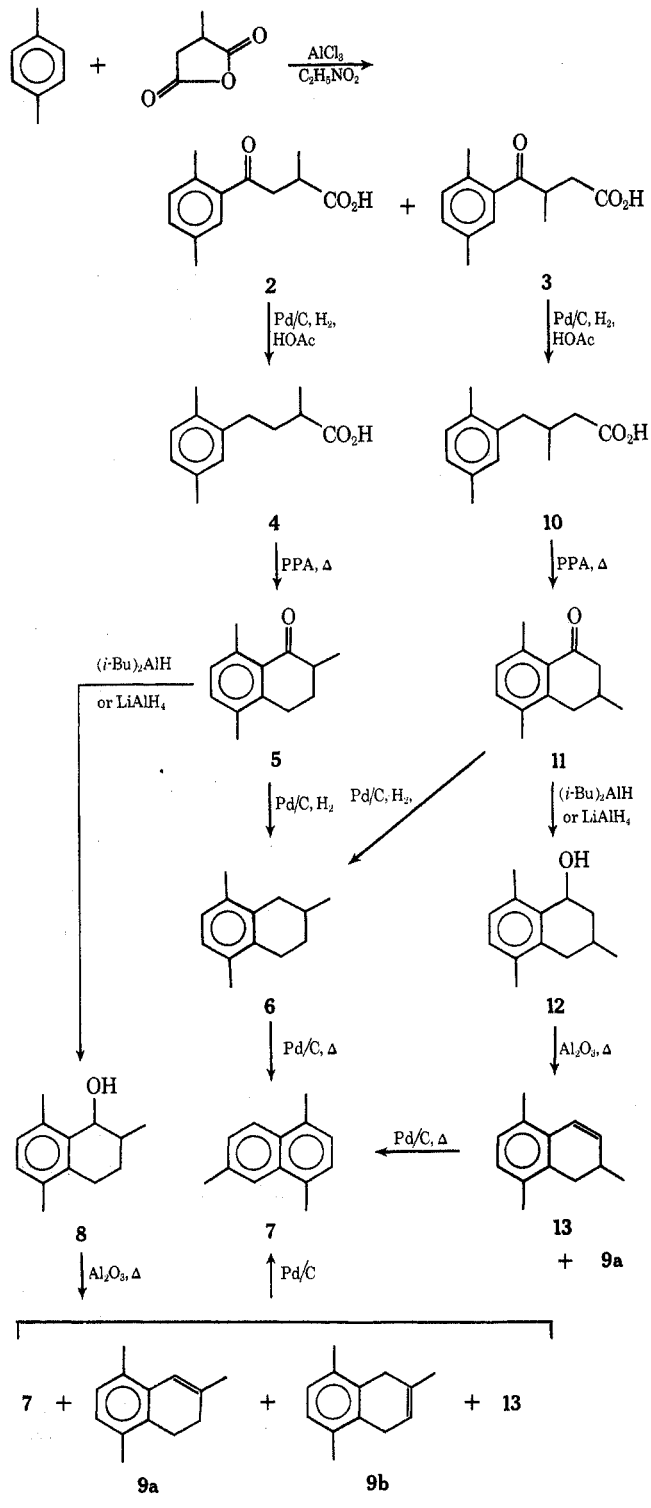
The Friedel–Crafts acylation came under immediate scrutiny because of the difficulty in removing nitrobenzene from the reaction products in large-scale operations. Substitution of the more volatile nitroethane is a major improvement. The reaction of *p*-xylene, methylsuccinic anhydride, and aluminum chloride strongly favors the formation of **2** over **3** when nitroethane is used. This ratio, 61:1 (**2**:**3**), changes to 57:1 with nitromethane and 44:1 with nitrobenzene. The ratio is also altered if excess aromatic hydrocarbon is used as sole solvent since the reaction using methylsuccinic anhydride with excess benzene gave a product ratio of 2.3:1 (α-methyl isomer to β-methyl isomer), whereas in nitroethane this ratio was 7.3:1. We also abandoned the earlier practice[3a] of aging Friedel–Crafts reaction mixtures.[5]

The Clemmensen reaction is a popular method for reducing the ketone carbonyl group of γ-oxo acids[6a] and we have found it to be superior to the Wolff–Kishner procedure. However, low-pressure hydrogenolysis using Pd/C catalyst in acetic acid is even better for the reduction of the benzoyl-type γ-oxo acids of Scheme I to the deoxy acids in 95+% yields.[6b,c] We greatly prefer the use of polyphosphoric acid[6d] (PPA) to the acid chloride–$AlCl_3$ procedure[3a] for cyclization of γ-arylbutyric acids (**4** to **5** or **10** to **11**).

Dehydration of **8** was done with hot alumina.[6e] This procedure is convenient for large-scale reactions but does lead to a mixture of isomeric dihydronaphthalenes, which, however, were readily aromatized with Pd/C to **7**.[6c] Formic acid[3a] dehydration may be preferable since there is less double migration. Dehydration with iodine[3b] gave polymeric products in some cases and hot thoria[6f] also caused formation of isomeric dihydronaphthalenes. Selenium[3a] dehydrogenation was not acceptable because of the expense of the reagent and the inconvenience in disposing of large volumes of H_2Se. Consequently, Pd/C catalyst was used.[6c]

We sought to reduce the number of steps in the synthesis by treating the tetralones **5** and **11** with Pd/C which gave **7** in 43 and 44% yields.[6g] The formation of naphthols which were difficult to remove in some cases dictated other routes.[6g] For 1-tetralone, 2-methyl-1-tetralone, 3-methyl-1-tetralone, and 4-methyl-1-tetralone, the yield of corresponding naphthalenes were 37, 44, 46, and 35%, respectively, and the naphthol impurities were easily removed by extraction with alkali. The best synthesis of **7** was completed in 67% overall yield *via* the sequence [**2**, (82%), **4** (95%), **5** (94%), **6** (93%), **7** (98%)] of Scheme I. The isolation and purification of **3** was accomplished by dis-

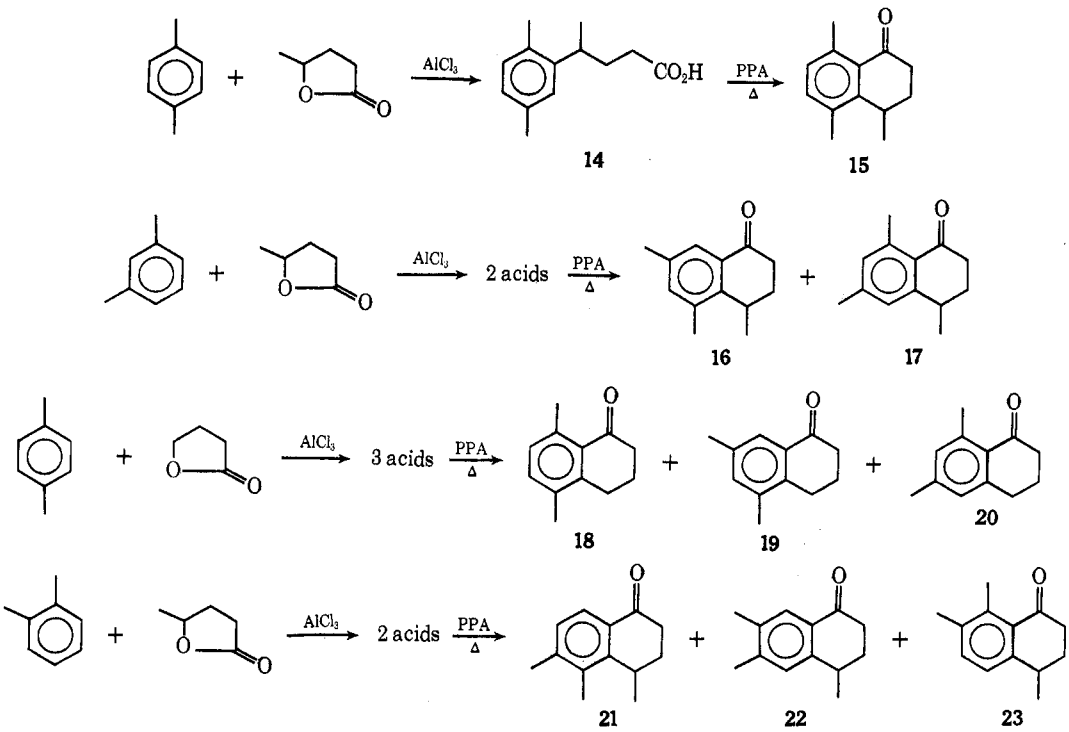
SCHEME I



(5) On standing, gases accumulate in Friedel–Crafts reaction mixtures and once the reaction mixture is disturbed, the release of these gases cause the flask to overflow.

(6) (a) E. L. Martin, *Org. React.*, **1**, 157 (1942); (b) J. W. Burnham and E. J. Eisenbraun, *J. Org. Chem.*, **36**, 737 (1971); (c) R. G. Melton, E. J. Eisenbraun, P. W. K. Flanagan, and M. C. Hamming, *Org. Prep. Proc.*, **2**, 37 (1970); (d) H. R. Snyder and F. X. Werber, "Organic Syntheses," Collect. Vol. III, E. C. Horning, Ed., Wiley, New York, N. Y., 1955, p 798; (e) H. Pines and W. O. Haag, *J. Amer. Chem. Soc.*, **83**, 2847 (1961); (f) A. J. Lundeen and R. Van Hoozer, *ibid.*, **85**, 2180 (1963); (g) J. M. Springer, C. W. Hinman, E. J. Eisenbraun, P. W. Flanagan, M. C. Hamming, and D. E. Linder, *J. Org. Chem.*, **36**, 686 (1971).

SCHEME II



tilling and crystallizing the mother liquors obtained from crude **2**.

We also required several di- and trimethyltetralones as precursors to methylated dihydronaphthalenes, tetralins, and naphthalenes not readily prepared using Scheme I. The tetralone **15** was readily obtained[7a] in pure form as shown in Scheme II. However, this procedure, when applied to *m*- and *o*-xylene using γ-valerolactone[7b] or *p*-xylene and γ-butyrolactone,[7c] gave mixtures of the intermediate acids. Since neither these acids nor their methyl esters were cleanly separable by preparative glc, we cannot be specific about their structures. They were cyclized by hot PPA to the corresponding 1-tetralones (Scheme II) and these were separated by preparative glc and identified by instrumental methods. For the 1-tetralones from *m*-xylene and γ-valerolactone, the ratio 77:23 (**16**:**17**) was determined by analytical glc and found to be the same as the ratio of peak areas for the observed methyl esters, which is evidence that rearrangement did not take place during the PPA cyclization. This is contrary to Mosby's observation[7a] that the PPA cyclization of 4-(2,4-dimethylphenyl)-pentanoic acid leads to **17**, whereas another route (acid chloride and $AlCl_3$) gave **16**. Our observations support the earlier work of Vig and Singh[7d] as well as Rao and Dev,[7e] who also cyclized this acid with PPA and obtained **16**. However, it should be noted that rearrangement as well as loss of isopropyl group has recently been reported[7f] for the PPA cyclization of γ-(5-isopropyl-4-methoxy-2-methylphenyl)butyric acid.

Since our results with the γ-butyrolactone and γ-valerolactone were variable, we studied the $AlCl_3$-catalyzed condensation of γ-valerolactone and *p*-xylene under a variety of conditions to obtain the best yield of the acid **14** as a reference point. This procedure involves dropwise addition of γ-valerolactone (1 mol) to a well-stirred mixture of *p*-xylene (2 mol) and $AlCl_3$ (1 mol) at a maximum temperature of 60°. Altering the reaction conditions by adding $AlCl_3$ last[7a] caused the yield of **14** to drop from 81 to 35%. We noted that the crude **14** regardless of method of preparation was accompanied by two acids which appear as small flanking peaks (2–5% total) on the glc trace of the methyl ester mixture of the crude acids including **14** as the major product. Cyclization of this mixture of acids with hot PPA gave mainly **15**. Glc analysis showed the presence of *ca.* 2% of **16** but **17** did not separate from **15** using SE-31 substrate.[8a,b]

Examination of the recovered *p*-xylene, from the preparation of **14**, by glc on a Bentone column[8a,b] revealed that it had been slightly isomerized to *m*-xylene (98:2). Evidently isomerization is occurring before condensation or the product acid, **14** in this case, is formed and then isomerized.

Application of the reaction conditions which gave 81% yield of **14** to γ-butyrolactone and *p*-xylene failed to give more than 23% or less of a combined yield of three acids (analyzed as methyl esters in the ratio 5:82:13 in order of emergence from an SE-31 column).[8b]

(7) (a) W. L. Mosby, *J. Amer. Chem. Soc.*, **74**, 2564 (1952); (b) W. L. Mosby, *J. Org. Chem.*, **18**, 485 (1953); (c) C. S. Kadyrov and D. Z. Lainapov, *Zh. Org. Khim.*, **2**, 1272 (1966); (d) O. P. Vig and S. Singh, *Science and Cult. (Calcutta)*, **22**, 403 (1957); *Chem. Abstr.*, **51**, 12867*d* (1957); (e) G. S. K. Rao and S. Dev, *J. Indian Chem. Soc.*, **36**, 1 (1959); (f) K. Yamada, S. Takada, Y. Hayakawa, and Y. Hirata, *Bull. Chem. Soc. Jap.*, **42**, 3011 (1969).

(8) (a) M. Van der Stricht and J. Van Rysselberge, *J. Gas Chromatogr.*, **1**, No. 8, 29 (1963). (b) A 10 ft × 0.25 in. Bentone column at 70° was used for analysis of xylene mixtures. Other glc analyses were carried out on a 11 ft × 0.25 in. 10% SE-31 on DMCS-treated acid-washed Chromosorb W column with temperatures ranging from 160 to 240°. Preparative separations were made on Carbowax 20M columns. Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were determined on Varian HR-60 and A-60 spectrometers. Mass spectra were obtained with a Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer. Ir and uv spectra were obtained with Beckman IR-5A and Cary 14 spectrometers, respectively. Melting points are corrected. The petroleum ether used for recrystallization boiled at 60–68°. (c) Filtration through Dicalite filter aid improves the separation of layers during ether extraction.

These, in turn, were cyclized to the 1-tetralones **20**:**18**:**19** (5:84:11) in the order of emergence from the SE-31 column.[8b] In addition, the recovered *p*-xylene from the γ-butyrolactone and *p*-xylene reaction contained 7% *m*-xylene.[8a,b] Hence, isomerization is even more pronounced for the γ-butyrolactone case and merely reflects the difference in reactivity and stability of intermediate species generated from these lactones by $AlCl_3$.

The Friedel–Crafts reaction of *o*-xylene and γ-valerolactone (Scheme II) gave two acids which were cyclized to a mixture of three tetralones in the ratio 3:63:34 (**23**:**22**:**21**) in order of emergence from a Carbowax or silicone rubber column. Thus, although the Friedel–Crafts alkylation of an aromatic hydrocarbon with a γ-lactone is a shorter route than the conventional anhydride acylation, the latter, in certain cases, is the preferred procedure.

In addition to hydrocarbons **6**, **7**, **9a**, **9b**, and **13**, the described syntheses provided 1,2,3,4-tetrahydro-1,5,7-trimethylnaphthalene, 1,2,3,4-tetrahydro-1,5,8-trimethylnaphthalene, 1,2,3,4-tetrahydro-1,6,8-trimethylnaphthalene, 1,3,5-trimethylnaphthalene, 1,3,8-trimethylnaphthalene, and 1,4,5-trimethylnaphthalene. Data are given in the Experimental Section.

Experimental Section[8-10]

3-(2,5-Dimethylbenzoyl)-2-methylpropionic Acid (2).—Methylsuccinic anhydride (2109 g, 18.5 mol), *p*-xylene (2162 g, 20.4 mol), and distilled nitroethane (6 l.) were mixed and cooled to 10°. Anhydrous $AlCl_3$ (5435 g, 40.7 mol) was added slowly to the vigorously stirred reaction mixture over a period of 5 hr, at 15°. Approximately 15 min after the final addition, ice and water were drained from the cooling vessel. The reaction mixture was stirred for an additional 90 min[5] and was then poured onto approximately 50 lb of ice and stirred until the red-brown color had disappeared. Concentrated HCl (3 l.) was then added to complete the decomposition. The reaction product was extracted with ether,[8c] washed, dried ($MgSO_4$), filtered, and concentrated until crystals developed on refrigeration. The decanted liquor was further concentrated under aspirator vacuum to give additional **2**, total weight 3322 g (82%). Recrystallization from ether–petroleum ether (bp 60–68°) gave **2**: mp 118–119°; ir ($CHCl_3$) 1695 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 220 (30), 133 (100), 105 (42), 41 (31), 39 (40); nmr ($CDCl_3$) δ 11.75 (s, 1, CO_2H), 7.42 (s, 1, isolated Ar H), 7.10 (AB q, 2, vicinal Ar H), 3.50–2.78 (m, 3, side chain), 2.40 (s, 3, Ar CH_3 ortho to carbonyl), 2.32 (s, 3, Ar CH_3 meta to carbonyl), 1.18 (d, 3, CH_3); uv max (95% C_2H_5OH) 211 mμ (log ε 4.33), 245 (3.95), and 293 (3.18).[9a]

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.90; H, 7.02.

The methyl ester of **2** was prepared with CH_2N_2: mp 22–23°; ir (neat) 1680 (C=O) and 1730 cm^{-1} (ester C=O); mass spectrum (70 eV) *m/e* (rel intensity) 234 (12), 133 (100), 105 (26), 79 (11), 77 (16), 15 (19).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.80; H, 7.56.

Hydrogenolysis of 2 to 4-(2,5-Dimethylphenyl)-2-methylbutyric Acid (4).—The hydrogenolysis of 20 g of **2** at 50 psi in the presence of 0.5 g of 10% Pd/C in 55 ml of acetic acid gave 17.8 g (95%) of **4**: ir ($CHCl_3$) 1695 cm^{-1} (C=O); mp 54–55°; mass spectrum (70 eV) *m/e* (rel intensity) 206 (33), 133 (76), 132 (58), 119 (100), 74 (39), 41 (32); nmr ($CDCl_3$) δ 11.74 (s, 1, CO_2H), 6.94 (AB q, 2, vicinal Ar H), 6.92 (s, 1, isolated Ar H), 2.70–2.36 (m, 3, Ar CH_2 and >$CHCH_3$), 2.20–1.44 (m, 2, Ar-CH_2CH_2), 1.24 (d, 3, >$CHCH_3$); uv max (95% C_2H_5OH) 215 mμ (log ε 4.03), 268 (2.75), and 276 (2.77).[9a]

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.80; H, 8.59.

A Clemmensen reduction[6a] gave **4** in 89% yield.

The methyl ester of **4** was prepared with CH_2N_2: bp 102° (0.4 mm); ir (neat) 1730 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 220 (16), 133 (19), 132 (21), 119 (41), 88 (100), 15 (21).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.66; H, 9.10.

PPA Cyclization of 4 to 2,5,8-Trimethyl-1-tetralone (5).—To 7248 g of well-stirred PPA[6d] at 90° was added 2126 g (10.3 mol) of solid **4**. The reaction mixture became brown colored and the temperature rose to 115–120° after about 20 min. An identical portion of PPA was added and stirring at 90–100° was continued for an additional 30 min. After cooling to 60°, the reaction mixture was poured into ice water (25 lb of ice and 20 l. of H_2O). Ether was added and the mixture was stirred to hasten decomposition of the heavy dark reaction product. The mixture was extracted with 8 l. of ether which was washed successively with 800 ml of 5% NaOH and with water and then dried ($MgSO_4$). Concentration of the ether solution afforded 1820 g (94%) of **5**: bp 95–100° (0.2 mm); mp 20° from isopropyl alcohol; ir (neat) 1675 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 188 (41), 146 (100), 118 (27), 117 (25), 115 (19); nmr (CCl_4) δ 6.95, 6.79 (AB q, 2, Ar H), 2.46 (s, 3, Ar CH_3 peri to carbonyl), 2.10 (s, 3, Ar CH_3), 2.9–1.2 (envelope, 5, Ar CH_2CH_2CH), 1.08 (d, 3, CH_3); uv max (95% C_2H_5OH) 213 mμ (log ε 4.73), 254 (4.18), and 300 (3.62).[9a]

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.89; H, 8.43.

The red 2,4-dinitrophenylhydrazone of **5** was prepared and recrystallized from 95% ethanol, mp 183–184°.

Anal. Calcd for $C_{19}H_{20}N_4O_4$: C, 61.94; H, 5.47; N, 15.21. Found: C, 61.70; H, 5.67; N, 15.40.

Conversion of 5 to 1,2,3,4-Tetrahydro-2,5,8-trimethylnaphthalene (6).—Hydrogenolysis of 10 g of **5** in the presence of 0.25 g of 10% Pd/C in 50 ml of acetic acid at 55 psi and 65° gave 8.6 g (93%) of **6** as a clear colorless liquid: bp 77° (0.6 mm); mp 3–6°; mass spectrum (70 eV) *m/e* (rel intensity) 174 (91), 159 (100), 132 (85), 119 (42), 115 (25); nmr (CCl_4) δ 6.72 (s, 2, Ar H), 2.59 (m, 3), 2.11 (s, 6, CH_3), 2.00–1.10 (m, 4), 1.08 (d, 3, CH_3); uv max (isooctane) 268 mμ (log ε 2.39) and 273 (2.28).[9a]

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.68; H, 10.43.

A Clemmensen reduction[6a] of **5** gave **6** in 86% yield.

Dehydrogenation of 6 to 1,4,6-Trimethylnaphthalene (7).—Dehydrogenation of 1097 g (6.3 mol) of **6** in the presence of 12 g of 10% Pd/C for 13 hr at the reflux temperature afforded 1052 g (6.2 mol) of **7** in 98% yield as a clear colorless liquid: bp 90° (0.9 mm) [lit.[3c] 140–142° (15 mm)]; mass spectrum (70 eV) *m/e* (rel intensity) 170 (100), 169 (18), 155 (69), 153 (14), 152 (12); nmr (CCl_4) δ 7.68 and 7.52 (d, 2, Ar H), 7.10 and 6.88 (m, 3, Ar H), 2.40 (s, 6, CH_3), 2.32 (s, 3, CH_3); picrate mp 134–135° (lit.[3c] 133°).

3-(2,5-Dimethylbenzoyl)butyric Acid (3).—Distillation and crystallization of the mother liquor remaining from the isolation of **2** afforded **3** as colorless crystals from petroleum ether:[8b] mp 81–82°; mass spectrum (70 eV) *m/e* (rel intensity) 220 (33), 157 (89), 133 (100), 105 (47), 41 (40), 39 (61); nmr ($CDCl_3$) δ 11.40 (s, 1, CO_2H), 7.38 (s, 1, isolated Ar H), 7.08 (AB q, 2, vicinal Ar H), 3.68 (m, 1, >$CHCH_3$), 3.05–2.28 (octet, 2, CH_2CO_2H), 2.32 (two s, 6, two Ar CH_3), 1.11 (d, 3, $CHCH_3$); uv max (95% C_2H_5OH) 211 mμ (log ε 4.34), 245 (3.92), and 290 (3.16).[9a]

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.60; H, 7.56.

The methyl ester of **3** was prepared using CH_2N_2: mp 62–63°; ir (neat) 1680 (C=O) and 1725 cm^{-1} (ester C=O); mass spectrum (70 eV) *m/e* (rel intensity) 234 (8), 133 (100), 105 (24), 79 (10), 77 (13), 39 (8).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.90; H, 7.70.

Hydrogenolysis of 3 to 4-(2,5-Dimethylphenyl)-3-methylbutyric Acid (10).—The γ-oxo acid **3** was hydrogenolyzed as described for **2** and then recrystallized from petroleum ether[8b] to give **10**: mp 68–68.5°; mass spectrum (70 eV) *m/e* (rel intensity) 206 (17), 146 (32), 119 (100), 69 (35), 41 (19); nmr ($CDCl_3$) δ 11.69 (s, 1, CO_2H), 6.98, 6.88 (AB q, 2, vicinal Ar H), 6.90 (s, 1, isolated Ar H), 2.76–2.04 [m, 5, $ArCH_2CH(CH_3)CH_2$], 3.26 and

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3.24 (two s, 6, two Ar CH_3), 0.97 (d, 3, $CHCH_3$); uv max (95% C_2H_5OH) 215 mμ (log ε 4.05), 268 (2.78), and 277 (2.82).[9a]

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.77; H, 8.70.

The methyl ester of **10** was prepared with CH_2N_2: bp 110° (0.3 mm); ir (neat) 1725 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 220 (25), 146 (88), 133 (14), 119 (100), 91 (15), 15 (28).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.46; H, 9.09.

Cyclization of 10 with hot PPA[6d] gave a 91% yield of 3,5,8-trimethyl-1-tetralone (11): mp 71–72° from petroleum ether;[8b] mass spectrum (70 eV) *m/e* (rel intensity) 188 (65), 173 (25), 146 (100), 118 (31), 117 (27); nmr (CCl_4) δ 7.01, 6.81 (AB q, 2, Ar H), 2.49 (s, 3, Ar CH_3 peri to carbonyl), 2.17 (s, 3, Ar CH_3), 3.1–1.7 (envelope, 5, $ArCH_2CHCH_3$), 1.07 (d, 3, CH_3); uv max (95% C_2H_5OH) 213 mμ (log ε 4.67), 254 (4.08), and 306 (3.42).[9a]

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.90; H, 8.65.

The red 2,4-DNP of **11** was prepared and recrystallized from 95% ethanol, mp 249–250°.

Anal. Calcd for $C_{19}H_{20}N_4O_4$: C, 61.94; H, 5.47. Found: C, 62.13; H, 5.37.

Hydrogenolysis of **11** in the presence of Pd/C catalyst at 50 psi in acetic acid gave **6**.

Reduction of 5 and 11 to the 2,5,8- and 3,5,8-Trimethyl-1-tetralols (8 and 12).—The reduction of 376 g (2 mol) of **5** in dry ether with 30 g (0.8 mol) of $LiAlH_4$ afforded 361 g (1.9 mol) of **8** as a clear, colorless liquid [bp 95° (0.35 mm)] which crystallized as a mixture of cis and trans isomers, mp 79–81°, from petroleum ether in 95% yield: mass spectrum (70 eV) *m/e* (rel intensity) 172 (91), 157 (100), 143 (22), 142 (37), 141 (25); the nmr spectrum in CCl_4 confirmed the structures.

A similar reduction of 1 mol of **11** using 15 g of $LiAlH_4$ in dry ether afforded 182 g of **12** in 96% yield: mp 76–77°, from petroleum ether;[8b] mass spectrum (70 eV) *m/e* (rel intensity) 172 (45), 157 (100), 143 (14), 142 (38), 141 (23); nmr (CCl_4) δ 6.72 (AB q, 2, vicinal Ar H), 4.51 (t, 1, ArCHOH), 2.90 (s, 1, >CHOH), 2.24 (s, 3, Ar CH_3), 2.09 (s, 3, Ar CH_3 peri to hydroxyl) 2.8–1.1 [envelope, 5, $ArCH_2C(CH_3)HCH_2$], 1.02 (d, 3, $>CHCH_3$); uv max (95% C_2H_5OH) 217 mμ (log ε 4.03), 2.70 (2.77), and 279 (2.75).[9a]

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.38; H, 9.61.

Our recent experience in the reduction of 1-tetralones has shown that diisobutylaluminum hydride (dibal H)[11] is superior to $LiAlH_4$ for this series. The latter gave incomplete reduction of **5** and **11**, presumably due to enolization.

Dehydration of 8 and 12 to 1,2-Dihydro-3,5,8-trimethyl- and 1,4-Dihydro-2,5,8-trimethylnaphthalene and 1,2-Dihydro-2,5,8-trimethylnaphthalene (9a, 9b, and 13).—1,2,3,4-Tetrahydro-2,5,8-trimethyl-1-naphthol (**8**) (20 g, 0.105 mol) was dissolved in 100 ml of cyclohexane and passed through a preheated column (30 mm × 38 cm) containing 33 cm of Harshaw alumina (Al-0104, 1/8 in., B901). The temperature of the column was maintained between 250 and 270°.[6e] The alcohol **8**, which vaporized on contact with the alumina, was swept through the column with a gentle flow of N_2 gas. The solution of **8** was metered onto the column by means of a bellows pump over a period of 2 hr. A second 100-ml portion of cyclohexane was passed through the system as a rinse. The collected solution was washed with water and saturated sodium chloride solution, dried ($MgSO_4$), filtered, concentrated, and distilled to give 14.8 g (75%) of a hydrocarbon mixture, bp 81–93° (0.7 mm). A sample of the product was analyzed by glc on a Carbowax column (0.25 in. × 10 ft, acid-washed Chromosorb W, 80–100 mesh) at 200° and found to contain four components, **9a**, **13**, **9b**, and **7**, in the ratio 81:5:5:8 and in the order of emergence from the glc column. Preparative glc[9b] on a 10 ft × 4 in. diameter column of 20% Carbowax on 60–80 mesh Chromosorb W was used to purify **9a**: bp 66° (0.2 mm); mass spectrum (70 eV) *m/e* (rel intensity) 172 (84), 157 (100), 143 (21), 142 (38), 141 (26); nmr (CCl_4) δ 6.68 (s, 2, Ar H), 6.30 (m, 1, Ar CH=C<), 2.80–2.50 (m, 2, Ar CH_2), 2.40–2.00 (m, 2, allylic CH_2), 1.92 (s, 3, allylic CH_3), 2.16, 2.20 (two s, 6, two Ar CH_3).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: 90.71; H, 9.29.

(11) L. F. Fieser and Mary Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 260.

A similar dehydration of **12** gave **9a** and **13** in about equal amounts. A pure sample of **13** was obtained by fractional distillation and showed bp 75° (0.7 mm); mass spectrum (70 eV) *m/e* (rel intensity) 172 (43), 157 (100), 155 (23), 142 (41), 141 (27); nmr (CCl_4) δ 6.75 (s, 2, Ar H), 6.55 (m, 1, Ar CH=), 5.79 (m, 1, ArCH=CH), 3.4–2.2 [envelope, 3, $ArCH(CH_3)CH_2$], 2.21 (s, 6, Ar CH_3), 1.04 (d, 3, $ArCHCH_3$).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.38; H, 9.47.

1,4-Dihydro-2,5,8-trimethylnaphthalene (**9b**) was obtained as a minor component and was purified by crystallization from methanol: bp 96–100° (1.8 mm); mp 38–40°; mass spectrum (70 eV) *m/e* (rel intensity) 172 (54), 157 (100), 155 (22), 144 (25), 142 (40); nmr (CCl_4) δ 6.74 (s, 2, Ar H), 5.49 (m, 1, vinylic), 3.3–2.9 (envelope, 4, Ar CH_2), 2.12 (s, 6, Ar CH_3), 1.76 (m, 3, allylic CH_3).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.71; H, 9.29.

Friedel–Crafts Reaction of γ-Butyrolactone or γ-Valerolactone with *p*-Xylene.—γ-Valerolactone (1 mol, 100 g) was added dropwise to a well-stirred mixture of 2 mol (212 g) of *p*-xylene and 1 mol (140 g) of $AlCl_3$ cooled initially to 10° in an ice bath. The temperature of the reaction mixture was allowed to rise to 60° during addition of the lactone. After addition (10–15 min) was complete, the reaction mixture was stirred 30 min and then poured onto ice. Concentrated hydrochloric acid (100 ml) was added and the mixture was extracted with ether (two 500-ml portions), washed with water, and then extracted with two 500-ml portions of 10% NaOH solution. The ether layer was dried ($MgSO_4$) and distilled at 1 atm to yield 100 g of mainly *p*-xylene. Glc analysis using the Bentone column[8a,b] showed about 2% *m*-xylene to be present.

The alkaline extract was acidified with 200 ml of concentrated hydrochloric acid and then extracted with ether (two 250-ml portions). From this extract was obtained 190 g (92%) of crude **14**. Glc analysis of crude **14**, using the SE-31 column,[8b] of the methyl esters prepared with diazomethane showed 2–5% of two ester impurities as flanking peaks. These impurities were no longer present after recrystallization of **14** from petroleum ether[8b] which gave 166 g (81%) of pure **14**: mp 111–112° (lit.[7a] mp 109–111°). The methyl ester was prepared with CH_2N_2: bp 95° (0.2 mm); ir (neat) 1740 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 220 (20), 146 (24), 145 (10), 133 (100), 91 (11), 15 (22).[10]

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.62; H, 8.89.

A purified sample of **14**, mp 111–112°, was cyclized with hot PPA[6d] to the 1-tetralone **15**: bp 90° (0.5 mm) [lit.[3c] 138° (12 mm)]; ir (neat) 1681 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 188 (100), 173 (75), 160 (89), 117 (41), 115 (35); nmr (CCl_4) δ 7.01, 6.83 (AB q, 2, Ar H), 2.49 (s, 3, Ar CH_3 peri to carbonyl), 2.23 (s, 3, Ar CH_3), 3.5–1.7 [envelope, 5, $ArCH(CH_3)CH_2CH_2$], 1.17 (d, 3, CH_3).

An equivalent run using γ-butyrolactone gave 160 g of recovered *p*-xylene shown to contain 7% *m*-xylene. The acidic fraction, shown by glc of methyl esters to be a mixture of three acids (5:82:13 in order of emergence from the SE-31 column),[8b] weighed 44 g (23%).

A procedure similar to that of Mosby[7a] was used in the preparation of arylbutyric acids obtained from the reactions of *o*-xylene and *m*-xylene with γ-valerolactone. The acids or acid mixtures were then cyclized in high yield with PPA[6d] to the 1-tetralones **16**, **17**, **18**, **19**, **20**, **21**, **22**, and **23**. These 1-tetralones were isolated by preparative glc on a Carbowax column.[9c,d]

16:[12a] bp 180° (1 mm) [lit.[12a] bp 174–176° (20 mm)]; ir (neat) 1678 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 188 (49), 173 (100), 145 (28), 117 (17), 115 (21); nmr (CCl_4) δ 7.56 (s, 1, Ar H peri to carbonyl), 7.02 (s, 1, Ar H), 3.11 [m, 1, $ArCH(CH_3)$], 2.8–1.5 (m, 4, $ArCOCH_2CH_2$), 2.24, 2.19 (two s, 6, Ar CH_3), 1.21 (d, 3, CH_3).

17: bp 120° (1 mm); ir (neat) 1672 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 188 (93), 173 (29), 160 (100), 117 (33), 115 (32); nmr (CCl_4) δ 6.81 (d, 2, Ar H), 2.50 (s, 3, Ar CH_3 peri to carbonyl), 2.26 (s, 3, Ar CH_3), 2.9–1.4 [m, 5, $ArCOCH_2CH_2CH(CH_3)$], 1.29 (d, 3, CH_3).

(12) (a) I. M. Heilbron and D. G. Wilkinson, *J. Chem. Soc.*, 2537 (1930); (b) E. de Barry Barnett and F. G. Sanders, *ibid.*, 434 (1933); (c) W. P. Campbell and M. D. Soffer, *J. Amer. Chem. Soc.*, **64**, 417 (1942); (d) K. M. Baker, K. H. Bell, and B. R. Davis, *Aust. J. Chem.*, **21**, 2945 (1968).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.84; H, 8.59.

18:[12b] bp 98° (0.2 mm); mp 31.5–33.5°, from petroleum ether[8b] (lit.[12b] mp 33°); ir (neat) 1678 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 174 (66), 146 (100), 118 (31), 117 (28), 115 (23); nmr (CCl_4) δ 7.03, 6.84, (AB, q, 2, Ar H), 2.59 (t, 2, Ar CH_2), 2.38 (s, 3, Ar CH_3 peri to carbonyl), 2.08 (s, 3, Ar CH_3), 2.4–1.6 (m, 4, $ArCOCH_2CH_2$).

19:[3c,12b] bp 86–90° (0.2 mm); mp 49–51°, from petroleum ether[8b] (lit.[12b] mp 50°); mass spectrum (70 eV) *m/e* (rel intensity) 174 (85), 146 (100), 118 (71), 117 (30), 115 (28); nmr (CCl_4) δ 7.56 (s, 1, Ar H peri to carbonyl), 7.04 (s, 1, Ar H), 2.73 (t, 2, Ar CH_2), 2.27–2.22 (two s, 6, Ar CH_3), 2.6–1.9 (m, 4, $ArCOCH_2CH_2$). The red 2,4-dinitrophenylhydrazone was recrystallized from 95% ethanol: mp 272° with darkening at 230° (lit.[7b] mp 268.8–269.4° or at 272–273° with preheated bath).

20: bp 105° (0.6 mm); mass spectrum (70 eV) *m/e* (rel intensity) 174 (46), 146 (100), 100 (19), 117 (18), 115 (15); nmr (CCl_4) δ 6.77 (s, 2, Ar H), 2.82 (t, 2, Ar CH_2), 2.52 (s, 3, Ar CH_3 peri to carbonyl), 2.25 (s, 3, Ar CH_3), 2.6–1.8 (m, 4, $ArCOCH_2CH_2$).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.60; H, 7.83.

21: bp 122 (0.4 mm); mass spectrum (70 eV) *m/e* (rel intensity) 188 (62), 173 (100), 160 (37), 145 (32), 117 (28), 115 (27); nmr (CCl_4) δ 7.70, 7.00 (AB q, 2, Ar H), 3.28 [m, 1, $ArCH(CH_3)$], 2.30, 2.24 (two s, 6, Ar CH_3), 2.9–1.8 (m, 4, $ArCOCH_2CH_2$), 1.29 (d, 3, CH_3).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.93; H, 8.70.

22:[12c] bp 112° (0.5 mm) [lit.[12c] bp 111.5° (0.4 mm)]; mass spectrum (70 eV) *m/e* (rel intensity) 188 (84), 173 (100), 160 (57), 146 (51), 132 (45), 117 (38); nmr (CCl_4) δ 7.66 (s, 1, Ar H peri to carbonyl), 6.96 (s, 1, Ar H), 2.96 [m, 1, $ArCH(CH_3)$], 2.28 (s, 6, Ar CH_3), 2.8–1.6 (m, 4, $ArCOCH_2CH_2$), 1.36 (d, 3, CH_3).

23: bp 115° (0.5 mm); mass spectrum (70 eV) *m/e* (rel intensity) 188 (93), 173 (57), 160 (100), 132 (47), 117 (44), 115 (38); nmr (CCl_4) δ 7.11–6.88 (AB q, 2, Ar H), 2.45 (s, 3, Ar CH_3 peri to carbonyl), 2.27 (s, 3, Ar CH_3), 3.1–1.5 [m, 5, $ArCOCH_2CH_2CH(CH_3)$], 1.32 (d, 3, CH_3).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.83; H, 8.73.

Glc analyses of reaction mixtures showed the following ratios of products in the order of emergence from a Carbowax 20M[8b] column: 23:77 (**17**:**16**), 14:75:11 (**20**:**18**:**19**), 3:63:34 (**23**:**22**:**21**).

Catalytic hydrogenation of **15**, **16**, and **17** as used in the preparation of **6** gave:

1,2,3,4-Tetrahydro-1,5,7-trimethylnaphthalene from 17: bp 57–59° (0.1 mm) [lit.[12d] 87° (0.5 mm)]; mass spectrum (70 eV) *m/e* (rel intensity) 174 (34), 160 (13), 159 (100), 146 (13), 132 (13); nmr (CCl_4) δ 6.67 (d, 2, Ar H), 2.98–2.27 (m, 3, Ar CH_2 and Ar CH<), 2.18 (s, 3, CH_3), 2.07 (s, 3, CH_3), 1.97–1.30 (m, 4, CH_2), 1.22 (d, 3, CH_3).

1,2,3,4-Tetrahydro-1,5,8-trimethylnaphthalene from 15: bp 89° (0.5 mm) [lit.[12d] 88° (1.0 mm)]; mass spectrum (70 eV) *m/e* (rel intensity) 174 (22), 160 (13), 159 (100), 129 (10), 128 (10); nmr (CCl_4) δ 6.70 (s, 2, Ar H), 2.98 (m, 1, Ar CH<), 2.53 (m, 2, Ar CH_2), 2.19 (s, 3, CH_3), 2.06 (s, 3, CH_3), 1.73 (m, 4, CH_2), 1.12 (d, 3, CH_3).

1,2,3,4-Tetrahydro-1,6,8-trimethylnaphthalene from 16: bp 65° (0.3 mm) [lit.[12a] 133–136° (18.5 mm)]; mass spectrum (70 eV) *m/e* (rel intensity) 174 (18), 160 (13), 159 (100), 129 (9), 128 (9); nmr (CCl_4) δ 6.60 (s, 2, Ar H), 2.96 (m, 1, tertiary and Ar CH<), 2.67 (m, 2, Ar CH_2), 2.18 (s, 3, CH_3), 2.15 (s, 3, CH_3), 1.71 (m, 4), 1.09 (d, 3, CH_3).

The following trimethylnaphthalenes were prepared by Pd/C dehydrogenation of tetralins in a manner analogous to the preparation of **7**.

1,3,5-Trimethylnaphthalene from 1,2,3,4-Tetrahydro-1,5,7-trimethylnaphthalene.—Recrystallization from methanol gave mp 43–45° (lit.[12a] mp 47°); mass spectrum (70 eV) *m/e* (rel intensity) 171 (14), 170 (100), 169 (17), 155 (64), 153 (15); nmr (CCl_4) δ 7.82–7.42 (m, 2, Ar H), 7.23–6.93 (m, 3, Ar H), 2.57 (s, 6, CH_3), 2.42 (s, 3, CH_3).

1,3,8-Trimethylnaphthalene from 1,2,3,4-Tetrahydro-1,6,8-trimethylnaphthalene.—Recrystallization from methanol gave mp 48–50° (lit.[12a] mp 48°); mass spectrum (70 eV) *m/e* (rel intensity) 170 (84), 155 (57), 153 (14), 32 (22), 28 (100); nmr (CCl_4) δ 7.50–6.93 (m, 5, Ar H), 2.79 (s, 6, CH_3), 2.34 (s, 3, CH_3).

1,4,5-Trimethylnaphthalene from 1,2,3,4-Tetrahydro-1,5,8-trimethylnaphthalene.—Recrystallization from methanol gave mp 62.5° (lit.[3c] 63°, lit.[7a] 59.6–60.6°); mass spectrum (70 eV) *m/e* (rel intensity) 170 (100), 169 (15), 155 (77), 153 (19), 152 (17); nmr (CCl_4) δ 7.69–6.91 (m, 5, Ar H), 2.73 (s, 3, CH_3), 2.70 (s, 3, CH_3), 2.48 (s, 3, CH_3).

Registry No. –2, 16206-40-9; **2** methyl ester, 30316-11-1; **3**, 16206-39-6; **3** methyl ester, 30316-13-3; **4**, 30316-14-4; **4** methyl ester, 30316-15-5; **5**, 10468-59-4; **5** 2,4-DNP, 30316-40-6; **6**, 30316-17-7; **7**, 2131-42-2; *cis*-**8**, 30318-93-5; *trans*-**8**, 30318-94-6; **9a**, 30316-18-8; **9b**, 30316-19-9; **10**, 30275-76-4; **10** methyl ester, 30316-20-2; **11**, 10468-60-7; **11** 2,4-DNP, 30316-08-6; **12**, 30316-22-4; **13**, 30316-23-5; **14**, 28591-11-9; **14** methyl ester, 30316-09-7; **15**, 10468-61-8; **16**, 27410-97-5; **17**, 27410-98-6; **18**, 5037-63-8; **19**, 13621-25-5; **20**, 30316-30-4; **21**, 30316-31-5; **22**, 30316-32-6; **23**, 30316-33-7; 1,2,3,4-tetrahydro-1,5,7-trimethylnaphthalene, 21693-55-0; 1,2,3,4-tetrahydro-1,5,8-trimethylnaphthalene, 21693-51-6; 1,2,3,4-tetrahydro-1,6,8-trimethylnaphthalene, 30316-36-0; 1,3,5-trimethylnaphthalene, 2131-39-7; 1,3,8-tirmethylnaphthalene ,17057-91-9; 1,4,5-trimethylnaphthalene, 2131-41-1.

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