=CCH_3); mass spectrum, *m/e* 180.129 (57) ($C_{10}H_{16}N_2O$ requires *m/e* 180.126), 114 (26), 98 (100), 55 (57).

***N*-(*trans*-1,3-Butadien-1-yl)-1-pyrrolidinecarboxamide (9)** was prepared in a similar fashion in 44% yield. Recrystallization from hexane–ethyl acetate afforded an analytical sample: mp 163–164 °C; IR ν_{max} (Nujol) 3250, 1671, 1630, 1600, 1510 cm^{-1}; ^1H NMR ($CDCl_3$), δ 5.2–7.5 (m, vinylic and NH), 4.5–4.9 (m, $=CH_2$), 3.0–3.5 (m, NCH_2), 1.5–1.9 (m, NCH_2CH_2); mass spectrum, *m/e* 166.109 (30) ($C_9H_{14}N_2O$ requires *m/e* 166.111), 98 (100), 55 (85).

Phenyl *trans,trans*-1,3-pentadiene-1-thiocarbamate (12) was prepared in a similar fashion in 78% yield. This diene was labile and showed considerable decomposition, with the formation of thiophenol, when stored for 1 week at −20 °C. Recrystallization from ether–hexane afforded an analytical sample: mp 116–118 °C; IR ν_{max} (Nujol) 3220, 1660, 1630, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ (5.0–7.8 (m, C_6H_5, vinylic, and NH), 1.64 (d, J = 6 Hz, $=CCH_3$); mass spectrum, *m/e* 219.070 (17) ($C_{12}H_{13}NOS$ required *m/e* 219.072), 110 (100) (C_6H_5SH probably formed from decomposition), 109 (56), 81(20), 80 (19).

Phenyl *trans*-1,3-butadiene-1-thiocarbamate (8) was prepared in a similar fashion in 47% yield. This diene was labile and showed considerable decomposition, with the formation of thiophenol, when stored for 1 week at −20 °C. Recrystallization from ether–hexane afforded an analytical sample: mp 92–93 °C; IR ν_{max} (Nujol) 3240, 1645, 1610, 1535 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.2–8.0 (m, C_6H_5, vinylic, and NH), 4.5–5.1 (m, $=CH_2$); mass spectrum, *m/e* 205.056 (15) ($C_{11}H_{11}NOS$ requires *m/e* 205.056), 110 (100) (C_6H_5SH probably formed from decomposition), 109 (44), 95 (32).

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Registry No.—**2** (R = H), 21651-12-7; **2** (R = Me), 110-44-1; **3** (R = H), 65899-51-6; **3** (R = Me), 65899-52-7; malonic acid, 141-82-2; *trans*-1-isocyanatobuta-1,3-diene, 65899-53-8; *trans,trans*-1-isocyanatopenta-1,3-diene, 65899-54-9.

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Chloromethylation of Ortho-Disubstituted Benzenes. A Simple Preparation of Some Useful α Isomers of Indan, Tetralin, and Benzosuberane

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Functionalization of ortho-disubstituted benzenes by the chloromethylation procedure has been shown to yield more of the so-called "α isomer" than previously anticipated. The chloromethyl functionality is readily modified to the corresponding alcohol or aldehyde. The aldehyde can be oxidized to the carboxylic acid or reacted with malonic acid (Doebner) to give acrylic acid derivatives. These high-yield manipulations, combined with key purification techniques, have permitted the synthesis of some novel "α-substituted" derivatives of indan, tetralin, and benzosuberane.

We required preparative amounts of indan, tetralin, and benzosuberane derivatives which were substituted on the benzene ring next to the carbocyclic ring, i.e., **1**, **3**, or **5**, the so-called α isomers, and which were capable of being elaborated to derivatives containing functionalized alkyl chains of varying length. However, in contrast to reasonably facile preparations of **2**,[2] **4**,[3] or **6**,[4] i.e., the β isomers, no direct or general methods have been reported for obtaining preparatively useful quantities of isomerically pure α isomers.[5] In general most aromatic substitution reactions of ortho-disubstituted benzenes give a preponderance of the β isomer although some specific conditions of nitration or halogenation have been reported to give mixtures rich in the α isomer.[6]

Thus, the tetralin derivative **3e** has been prepared by a long sequence beginning with the corresponding nitro derivative obtained by fractional distillation[7] or from partially hydro-

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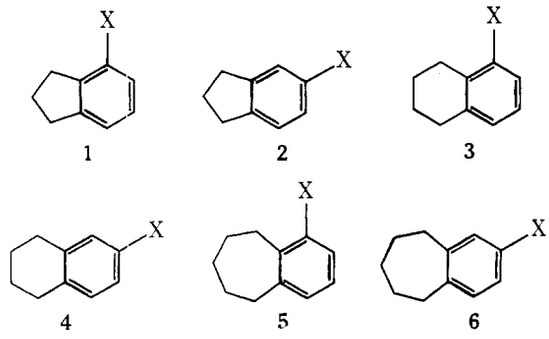

a, X = CH_2Cl d, X = CHO
b, X = CH_2OAc e, X = COOH
c, X = CH_2OH f, X = CH=CHCOOH

genated mixtures of naphthalene derivatives.[8] The indan and benzosuberane acids **1e** and **5e** have been obtained by grignard reactions on the halo derivatives themselves formed by ring closure sequences of the appropriate halo-substituted benzenes.[7,9] Partial separation of the mixed carboxylic acids obtained from chloromethylation of the hydrocarbon has also been reported.[9,10]

The chloromethylation of ortho-disubstituted benzenes[11] was eventually recognized to produce two isomers and estimations of isomer ratios have either been unsubstantiated[5] or ingenious but indirect.[9,12] However, they have been uniformly discouraging for preparative purposes in ascribing low percentages (5–25%) to the α isomer. In this paper we wish to describe methods which permit: (i) direct analysis of the ratio of mixtures of the monochloromethylation isomers of indan, tetralin, and benzosuberane that indicate larger amounts of the α isomer than previously reported, and (ii) short, high-yield modifications and enrichment procedures which permit isolation of preparatively useful quantities of some new α-substituted derivatives of these hydrocarbons.

The Synthetic Sequence. Chloromethylation of the hydrocarbons under standard conditions[5,9] produced a mixture of the monochloromethylated isomers **1a–6a**. Displacement by acetate yielded **1b–6b**, subsequent hydrolysis to the alcohols produced **1c–6c**, and oxidation produced the aldehydes **1d–6d**. All were high-yield steps necessitating no intermediate purification. Substantial amounts of **2c** and **6c** could be directly crystallized leaving mixtures predominating in the corresponding α isomer.

The aldehyde functionality permitted separation of all isomer mixtures by thin layer, gas liquid, or column chromatography. The aldehydes could be oxidized to the carboxylic acids **1e–6e** or transformed into mixtures of the acrylic acids **1f–6f** from which further separations were possible.[16]

Isomer Ratios and Structure Proof. In the ^1H NMR spectra of the α aldehydes, **1d, 3d,** and **5d**, the benzylic hydrogens "peri" to the formyl group experienced a downfield shift that allows them to be easily distinguished from the other benzylic hydrogens. This is presumably due to an anisotropic effect of the carbonyl group since it does not occur in the β isomers, **2d, 4d,** and **6d**. The phenomenon occurs also to some extent with the carboxylic acids **1e–6e**. This constitutes the first unambiguous structure proof reported for any of these compounds and underlines the general lack of characterization even for those compounds previously reported. Chemical shift differences in the ^1H NMR spectra also seem more useful for rapid differentiation of α and β isomers in the aldehydes (C**H**O) and acrylic acids (C**H**=CH—COOH) than minor differences in the IR or UV spectra.[17]

The ratio of isomers could most accurately and generally be measured on mixtures functionalized to the aldehydes.[18] Thus we have determined that the chloromethylation reaction yields the following isomer ratios (α:β), indan (30:70), tetralin (42:58), benzosuberane (22:78), and *o*-xylene (32:68), which are substantially more favorable for the α isomers than previously estimated, e.g., ref 9 and 10 report indan (19:81), tetralin (24:76), benzosuberane (5:95), and *o*-xylene (19:82). The simple enrichment procedures permit the following mixtures of alcohols to be obtained: indan (72α:28β) and benzosuberane (55α:45β). Consequently, as demonstrated, the sequences here described become preparatively useful for obtaining a variety of α-substituted derivatives of ortho-disubstituted benzenes.

The formation of the carcinogen bis(chloromethyl) ether makes the chloromethylation reaction potentially hazardous.[19] Therefore we are investigating some recent aromatic functionalization methods to ascertain their degree of α substitution.[20a–c]

Experimental Section

Melting points were obtained on a Buchi SMP-20 melting range apparatus. IR spectra (ν_{max} in cm^{-1}) were recorded on a Perkin-Elmer 237B spectrophotometer. UV spectra [λ_{max} in nm (ϵ)] were obtained in 95% EtOH on a Perkin-Elmer Coleman-124 spectrophotometer. Proton magnetic resonance (^1H NMR) spectra were recorded on Varian T-60 (60 MHz) or Varian HA-100 (100 MHz) instruments; all values are recorded in ppm (δ) with reference to Me_4Si. All ^1H NMR were taken in $CDCl_3$ with 1% Me_4Si. Band shape is indicated by s (singlet), d (doublet), t (triplet), m (multiplet), and b (broad). TLC was performed using silica gel G (0.25-mm layers) on glass plates (Merck). Refractive indices were taken on an Officine Galileo Di Milano (Jo. 50532) refractometer. Analytical GLC data were obtained on: (i) a Hewlett Packard F&M 402 instrument using 0.25 in. × 6 ft column packed with 3% OV-210 on Chromosorb W, an oven temperature of 130 °C, and flow rate of nitrogen at 70 mL/min or (ii) a Perkin-Elmer 990 using a $\frac{1}{8}$ in. × 12 ft column packed with 3% OV-17, on Chromosorb W, temperature 150 °C, and nitrogen flow rate 25 mL/min. Petroleum ether with boiling range 30–60 °C was used exclusively. Microanalyses were obtained from Spang Microanalytical Laboratory, Ann Arbor, Mich.

Chloromethylation. Preparation of 1a–6a. Chloromethylation was accomplished by heating at 60 °C a mixture of hydrocarbon, aqueous formaldehyde, hydrochloric acid, and sulfuric acid according to Arnold and Barnes.[5] The mixture of monochloromethyl isomers was purified by distillation to obtain: **1a/2a**, 61% from indan; bp 80–90 °C (0.3 mm), n^{25}_D 1.5615 (lit.[21] bp 111 °C (4 mm), n^{21}_D 1.5625); ^1H NMR 7.28–7.05 (3 H, m, aromatic H), 4.56 (1 H, s, C**H**$_2$Cl), 3.10–2.68 (4 H, m, benzylic H), 2.40–1.70 (2 H, m). **3a/4a**: 59% from tetralin; bp 90–100 °C (0.3 mm); n^{19}_D 1.5705 (lit.[5] bp 110–114 °C (0.3 mm)); ^1H NMR, 7.28–6.95 (3 H, m, aromatic H), 4.59 and 4.51 (total 2 H, 2 s, ratio 54:46, C**H**$_2$Cl of α and β isomer, respectively), 3.00–2.61 (4 H, m, benzylic H), 2.08–1.65 (4 H, m). **5a/6a**: 40% from benzosuberane (45% recovered benzosuberane); bp 105–115 °C (0.5 mm); n^{26}_D 1.5610 (lit.[22] bp 140 °C (9 mm), n^{23}_D 1.5672); ^1H NMR 7.13–6.85 (3 H, m, aromatic H), 4.53, 4.44 (total 2 H, 2 s, ratio 22:78, C**H**$_2$Cl of α and β isomer, respectively), 2.98–2.64 (4 H, m, benzylic H), 2.03–1.48 (6 H, m). Similarly *o*-xylene yielded a mixture of monochloromethylated isomers[10] in 60% yield: bp 110–120 °C (14 mm); n^{19}_D 1.1542; ^1H NMR 7.26–7.00 (3 H, m, aromatic H), 4.60, 4.52 (total 2 H, 2 s, ratio 32.68, C**H**$_2$Cl of α and β isomer, respectively), 1.50–1.20 (6 H, m).

Preparation of Alcohols 1c–6c via Acetates 1b–6b. (i) As similarly described[13] the monochloromethylated hydrocarbons **1a–6a** (*X* g) were converted to the corresponding acetates, **1b–6b**, by anhydrous sodium acetate (*X* g) in glacial acetic acid (2–3*X* mL) after refluxing for 10 h. Yields of crude products were ≥95% and essentially pure by spectroscopy. Thus were obtained **1b/2b**: IR 1735 (OAc); ^1H NMR 7.38–7.12 (3 H, m, aromatic H), 5.08, 5.05 (2 H, d, C**H**$_2$OAc of both isomers), 3.18–2.68 (4 H, m, benzylic H), 2.08 (3 H, s, OCOC**H**$_3$), 2.44–1.75 (2 H, m). **3b/4b**: IR 1735 (OAc); ^1H NMR 7.23–6.84 (3 H, m, aromatic H), 5.08, 5.00 (total 2 H, 2 s, ratio 42:58, C**H**$_2$OAc of α and β isomer, respectively), 2.96–2.51 (4 H, m, benzylic H), 2.08 (3 H, s, OCOC**H**$_3$), 2.00–1.57 (4 H, m). **5b/6b**: IR 1735 (OAc); ^1H NMR 7.08 (3 H, s, aromatic H), 5.13, 5.03 (total 2 H, 2 s, ratio 27:73, CH_2OAc of α and β isomers, respectively), 2.05–2.65 (4 H, m, benzylic H), 2.09 (3 H, s, OCOC**H**$_3$), 2.00–1.45 (6 H, m).

(ii) The acetate mixtures were hydrolyzed in methanol and aqueous sodium hydroxide after heating and stirring for 30 min at 50 °C.[14] Yields of crude alcohol were ≥90% and quite pure as judged by ^1H NMR. Dissolution of **1c/2c** in petroleum ether and cooling yielded two crops of pure **2c** (~65%) so that the mother liquors contained a

mixture enriched in **1c**. Similar treatment yielded pure **6c** (57%) plus an enriched (in **5c**) mixture of **5c/6c**. The remaining alcohols **1c**, **3c**, **4c**, and **5c** were obtained in pure form by reduction of the corresponding aldehydes (vide infra).

Preparation of Aldehydes 1d–6d.[29] The benzylic alcohols, **1c–6c**, were readily oxidized by Corey's pyridinium chlorochromate reagent[15] after stirring for 2 h at room temperature in CH_2Cl_2. The crude product was filtered through a short column of silica gel (or Florisil) with benzene to produce the corresponding aldehyde **1d–6d**, as a yellowish oil in 90% yield. Purity of this material was excellent as judged by ^1H NMR and TLC (benzene–petroleum ether, 1:1). A mixture of α and β isomers could be resolved by GLC or separated on a preparative scale (10–20 g) by the short, wide column technique[23] using silica gel H (Merck, particle size 10–40 × 10^{-6} m) and benzene–petroleum ether (1:1) as eluent. The aldehydes were susceptible to air oxidation but nicely characterized by spectroscopy (as well as conversion to the corresponding alcohols, carboxylic acids, or acrylic acids) as follows (bp are from bulb-to-bulb distillations and approximate only). **1d:** bp 80 °C (0.2 mm), 2,4-DNP, mp 231–232 °C; n^{22}_D 1.5707; IR 1683 (ArCHO); UV 252 (10 970); ^1H NMR 10.18 (1 H, s, C**H**O), 7.72–7.08 (3 H, m, aromatic H), 3.53–3.12 (2 H, t, benzylic H "peri" to CHO), 3.10–2.71 (2 H, t, other benzylic H), 2.40–1.91 (2 H, m).

2d: bp 79 °C (0.2 mm) (lit.[21] bp 136 °C (23 mm)); 2,4-DNP, mp 242–244 °C; n^{22}_D 1.5719; IR 1683 (ArCHO); UV 248 (12 540); ^1H NMR 9.95 (1 H, s, C**H**O), 7.75–7.10 (3 H, m, aromatic H), 3.13–2.60 (4 H, m, benzylic H), 2.34–1.82 (2 H, m).

3d: bp 85 °C (0.3 mm); 2,4-DNP, mp 230 °C; n^{22}_D 1.5769; IR 1685 (ArCHO); UV 254 (10 810); ^1H NMR 10.43 (1 H, s, C**H**O), 7.86–7.18 (3 H, m, aromatic H), 3.38–3.05 (2 H, m, benzylic H "peri" to CHO), 3.03–2.60 (2 H, m, other benzylic H), 2.04–1.58 (4 H, m).

4d: bp 79 °C (0.3 mm) (lit.[24] bp 116–119 °C (3 mm)); 2,4-DNP, mp 216–218 °C; n^{20}_D 1.5740; IR 1688 (ArCHO); UV 266 (13 710); ^1H NMR 10.29 (1 H, s, C**H**O), 7.94–7.25 (3 H, m, aromatic H), 3.11–2.60 (4 H, m, benzylic H), 2.14–1.60 (4 H, m).

5d: bp 78 °C (0.2 mm); 2,4-DNP, mp 176–177 °C; n^{20}_D 1.5671; IR 1681 (ArCHO); UV 254 (8620); ^1H NMR 10.38 (1 H, s, C**H**O), 7.78–7.04 (3 H, m, aromatic H), 3.46–3.18 (2 H, m, benzylic H "peri" to CHO), 3.04–2.70 (2 H, m, other benzylic H), 2.00–1.43 (6 H, m).

6d: bp 79 °C (0.20 mm); 2,4-DNP, mp 222–223 °C; n^{20}_D 1.5716; IR 1681 (ArCHO); UV 260 (15 350); ^1H NMR 9.93 (1 H, s, C**H**O), 7.75–7.05 (3 H, m, aromatic H), 3.01–2.65 (4 H, m, benzylic H), 2.05–1.38 (6 H, m).

In the ^1H NMR spectra the distinctive chemical shifts of aldehydic protons for each isomer allowed easy analysis of isomer ratios. The following data were obtained by oxidizing mixtures of the corresponding alcohols (values from integration of GLC separations in brackets): from "normal" mixture of **1c/2c**, ratio of **1d/2d** = 30:70 (31:69), from "enriched" mixture of **1c/2c**, ratio of **1d/2d** = 72:28 (70:30); normal mixture of **3c/4c** gave **3d/4d** = 42:58 (41:59); a "normal" mixture of **5c/6c** gave **5d/6d** = 22:78 (24:76); the "enriched" mixture of **5c/6c** gave **5d/6d** = 55:45 (53:47).

Preparation of the Alcohols 1c–6c: Chromatographically pure samples of the various aldehydes, **1c**, **3c**, **4c**, **5c** (0.5 g), were reduced by $NaBH_4$ (100 mg) in ethanol (30 mL) at room temperature. Workup after 30 min produced the corresponding alcohols in >85% yield. Analytical samples were obtained by bulb-to-bulb distillation. Alcohols **2c** and **6c** were crystalline (vide supra) and sublimed for analysis.

1c: bp 101 °C (0.5 mm); IR 3610 (OH), 790; ^1H NMR 7.11 (3 H, s, aromatic H), 4.52 (1 H, 6 s, C**H**$_2$OH), 3.10–2.50 (4 H, m, benzylic H), 2.75 (1 H, s, disappears with D_2O, CH_2O**H**), 2.32–1.78 (2 H, m). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.19; H, 8.10.

2c: mp 73–75 °C (lit.[12] mp 74 °C); IR 3600 (OH), 826; ^1H NMR 7.18 (3 H, s, aromatic H), 4.58 (2 H, s, C**H**$_2$OH), 2.90 (4 H, t, benzylic H), 2.14 (1 H, 6 s, disappears with D_2O, CH_2O**H**), 2.32–1.78 (2 H, m). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.69; H, 8.18.

3c: bp 104 °C (0.5 mm) (lit.[8] bp 106 °C (0.5 mm)); IR, 3590 (OH), 780; ^1H NMR 7.15 (3 H, s, aromatic H), 4.60 (2 H, s, C**H**$_2$OH), 2.80 (1 H, 6 s, disappears with D_2O, CH_2O**H**), 2.97–2.58 (4 H, m, benzylic H), 2.05–1.81 (4 H, m). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.30; H, 8.70.

4c: bp 103 °C (0.5 mm) (lit.[24] bp 133 °C (4 mm)); IR 3590 (OH), 830, 815; ^1H NMR 7.00 (3 H, s, aromatic H), 4.53 (2 H, s, C**H**$_2$OH), 2.64 (1 H, bs, disappears with D_2O, CH_2O**H**), 2.92–2.54 (4 H, m, benzylic H), 1.98–1.60 (4 H, m). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found C, 81.47; H, 8.83.

5c: bp 109 °C (0.5 mm); IR 3600 (OH), 800, 790; ^1H NMR 7.02 (3 H, s, aromatic H), 4.62 (2 H, s, C**H**$_2$OH), 2.75 (1 H, bs, disappears with D_2O, CH_2O**H**), 3.00–2.60 (4 H, m, benzylic H), 1.98–1.40 (6 H, m). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.58; H, 9.20.

6c: mp 64–65 °C (lit.[25] mp 65 °C); IR 3600 (OH), 828; ^1H NMR 7.02 (3 H, s, aromatic H), 4.53 (2 H, s, C**H**$_2$OH), 2.70 (1 H, bs, disappears with D_2O, CH_2O**H**), 2.94–2.58 (4 H, m, benzylic H), 1.98–1.38 (6 H, m). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.79; H, 9.13.

Preparation of the Carboxylic Acids 1e–6e.[29] The acids could be obtained after oxidation of the corresponding aldehydes **1d–6d** by prolonged exposure to air, $CoCl_2$/NaOCl,[26] Ag_2O,[9] or Jones conditions. Only the indan mixture, **1e/2e**, could be resolved by TLC (ether–benzene, 1:9). Partial separation of isomers can evidently be achieved by fractional crystallization of the barium salts.[9,10] The free acids were nicely crystallized from ether–petroleum ether and sublimed for analysis.

1e: mp 151–154 °C (lit.[27] mp 153 °C); ^1H NMR 10.88 (1 H, bs, disappears with D_2O, COO**H**), 8.04–7.01 (3 H, m, aromatic H), 3.45 (2 H, t, benzylic H "peri" to COOH), 2.97 (2 H, t, other benzylic H), 2.07 (2 H, m).

2e: mp 182–184 °C (lit.[21] mp 177, 183 °C[12]); ^1H NMR 11.83 (1 H, bs, disappears with D_2O, COO**H**), 8.05–7.16 (3 H, m, aromatic H), 2.98 (4 H, t, benzylic H), 2.09 (2 H, m). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.83; H, 6.19.

3e: mp 148–150 °C (lit.[7] mp 151 °C); ^1H NMR, 11.20 (1 H, bs, disappears with D_2O, COO**H**), 8.15–7.10 (3 H, m, aromatic H), 3.22 (2 H, m, benzylic H "peri" to COOH), 2.90 (2 H, m, other benzylic H), 1.81 (4 H, m). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.94; H, 6.79.

4e: mp 156–158 °C (lit.[24] mp 154–155 °C); ^1H NMR 11.93 (1 H, bs, disappears with D_2O, COO**H**), 8.20–7.14 (3 H, m, aromatic H), 2.90 (4 H, m, benzylic H), 1.85 (4 H, m). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.65; H, 6.86.

5e: mp 105–107 °C (lit.[9] mp 107 °C); ^1H NMR 11.05 (1 H, bs, disappears with D_2O, COO**H**), 8.18–7.11 (3 H, m, aromatic H), 3.25 (2 H, m, benzylic H "peri" to COOH), 2.91 (2 H, m, other benzylic H), 1.82 (6 H, m). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.32; H, 7.40.

6e: mp 178–179 °C (lit.[9] mp 178 °C); ^1H NMR 11.87 (1 H, bs, disappears with D_2O, COO**H**), 8.21–7.14 (3 H, m, aromatic H), 2.91 (4 H, m, benzylic H), 1.87 (6 H, m). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.58; H, 7.27.

Preparation of Acrylic Acids 1f–6f.[29] As described by Standridge et al.[28] the aldehyde(s) **1d–6d**, malonic acid, and a catalytic amount of piperidine were heated in dry pyridine for 2.5 h and worked up to give the acrylic acid(s), **1f–6f**, in >90% yields and essentially pure by ^1H NMR. The "enriched" mixture of **1f/2f** when crystallized from CH_2Cl_2 yielded directly pure **1f** in 50–60% yield. When the resulting mother liquors were dissolved in acetone and the solvent was allowed to evaporate slowly **1f** and **2f** were deposited as distinct crystal forms which could be mechanically separated. The mixture of **3f/4f** also yielded some pure **3f** (~20%) on fractional crystallization from chloroform or benzene.[16] These derivatives could be crystallized from acetone, ether, or dichloromethane and sublimed for analysis.

1f: mp 174–176 °C; ^1H NMR 9.82 (1 H, bs, disappears with D_2O, COO**H**), 8.10, 7.85 (1 H, d, C**H**=CHCOOH, J = 16 Hz), 7.58–7.15 (3 H, m aromatic H), 6.58, 6.30 (1 H, d, CH=C**H**COOH, J = 16 Hz), 3.29–2.78 (4 H, m, benzylic H), 2.43–1.81 (2 H, m). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.24; H, 6.27.

2f: mp 164–166 °C (lit.[21] mp 161 °C); ^1H NMR 10.17 (1 H, bs, disappears with D_2O, COO**H**), 8.00, 7.75 (1 H, d, C**H**=CHCOOH, J = 16 Hz), 7.56–7.15 (3 H, m, aromatic H), 6.60, 6.35 (1 H, d, CH=C**H**COOH, J = 16 Hz), 3.25–2.58 (4 H, m, benzylic H), 2.40–1.81 (2 H, m).

3f: mp 211–213 °C; ^1H NMR 9.25 (1 H, bs, disappears with D_2O, COO**H**), 8.28, 8.01 (1 H, d, C**H**=CHCOOH, J = 16 Hz), 7.58–7.02 (3 H, m, aromatic H), 6.50, 6.22 (1 H, d, CH=C**H**COOH, J = 16 Hz), 3.04–2.57 (4 H, m, benzylic H), 2.18–1.65 (4 H, m). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.84; H, 6.96.

4f: mp 173–175 °C (lit.[24] 171–172 °C); ^1H NMR 9.22 (1 H, bs, disappears with D_2O, COO**H**), 7.91, 7.66 (1 H, d, C**H**=CHCOOH, J = 16 Hz), 7.48–6.97 (3 H, m, aromatic H), 6.57, 6.31 (1 H, d, CH=CHCOOH, J = 16 Hz), 3.04–2.55 (4 H, m, benzylic H), 2.09–1.58 (4 H, m). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.44; H, 6,87.

5f: mp 163–165 °C; ^1H NMR 10.63 (1 H, bs, disappears with D_2O-COO**H**), 8.41, 8.16 (1 H, d, C**H**=CHCOOH, J = 15 Hz), 7.58–7.08 (3 H, m, aromatic H), 6.46, 6.21 (1 H, d, CH=C**H**COOH, J = 15 Hz), 3.20–2.64 (4 H, m, benzylic H), 2.68–1.40 (6 H, m). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.37; H, 7.60.

6f: mp 161–163 °C; ^1H NMR 9.40 (1 H, bs, disappears with D_2O,

COOH), 7.97, 7.71 (1 H, d, CH=CHCOOH, J = 16 Hz), 7.51–7.10 (3 H, m, aromatic H), 6.59, 6.34 (1 H, d, CH=CHCOOH, J = 16 Hz), 3.08–2.64 (4 H, m, benzylic H), 2.15–1.45 (6 H, m). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.48; H, 7.49.

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Registry No.—**1a,** 65898-31-9; **1b,** 65898-32-0; **1c,** 65898-33-1; **1d,** 51932-70-8; **1d** DNP, 65898-34-2; **1e,** 4044-54-6; **1f,** 65898-35-3; **2a,** 18775-42-3; **2b,** 65898-36-4; **2c,** 51632-06-5; **2d,** 30084-91-4; **2d** DNP, 65898-37-5; **2e,** 65898-38-6; **2f,** 56635-88-2; **3a,** 17450-62-3; **3b,** 65898-39-7; **3c,** 41790-30-1; **3d,** 41828-13-1; **3d** DNP, 65898-40-0; **3e,** 4242-18-6; **3f,** 65898-41-1; **4a,** 17450-63-4; **4b,** 65898-42-2; **4c,** 6883-81-4; **4d,** 51529-97-6; **4d** DNP, 65898-43-3; **4e,** 1131-63-1; **4f,** 7498-69-3; **5a,** 65898-44-4; **5b,** 65898-45-5; **5c,** 65898-46-6; **5d,** 65898-47-7; **5d** DNP, 65898-48-8; **5e,** 4087-43-8; **5f,** 65898-49-9; **6a,** 41635-37-4; **6b,** 55037-99-5; **6c,** 65898-50-2; **6d,** 65898-51-3; **6d** DNP, 65898-27-3; **6e,** 41068-24-0; **6f,** 65898-28-4; indan, 496-11-7; tetralin, 119-64-2; benzosuberane, 1075-16-7; *o*-xylene, 95-47-6; 3-(chloromethyl)-*o*-xylene, 13651-55-3; 4-(chloromethyl)-*o*-xylene, 102-46-5.

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(29) The following examples represent typical systematic names for the types of compounds described in this paper: **1f,** 3-(4-indanyl)propenoic acid; **4d,** 5,6,7,8-tetrahydronaphthalene-2-carboxaldehyde; **5e,** benzcycloheptene-2-carboxylic acid.

Metalation of Ethylbenzene with *n*-Pentylsodium in the Presence of *N,N,N′,N′*-Tetramethylethylenediamine

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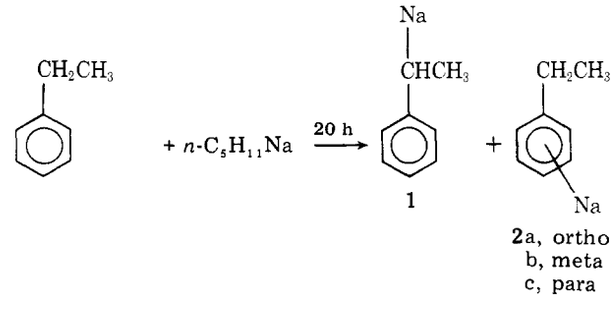
Ethylbenzene was metalated with *n*-pentylsodium activated by *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) to give exclusively α-methylbenzylsodium (**1**) after 1 h in yields in excess of 95%. An examination of the reaction at shorter reaction times (5, 15, and 30 min) revealed that metalation occurred initially in a kinetically controlled process giving, in addition to **1**, *o*-, *m*-, and *p*-ethylphenylsodium (**2a, 2b,** and **2c**) and a disodio compound identified as α,α-disodioethylbenzene (**3**). With time, the ring and disodio compounds isomerized to the α isomer **1** in a thermodynamically controlled sequence.

Relatively few reports appear in the literature regarding the activation of organosodium reagents such as *n*-pentylsodium with *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) even though this effect is well documented for the corresponding organolithium reagents.[2] Trimitsis and coworkers[3] found that *n*-pentylsodium in the presence of TMEDA promoted the quantitative dimetalation of 1,3-dimethylnaphthalene and *m*-xylene on the benzylic carbons. In the absence of TMEDA, monometalation occurred in low yield. Recently, this laboratory[4] reported that cumene was metalated with *n*-pentylsodium activated with TMEDA to give α-cumylsodium in good yields and high isomeric purity. When TMEDA was omitted from the reaction, metalation occurred on the ring giving *m*- and *p*-isopropylphenylsodium.

In view of the rather profound effect which TMEDA had on the above reactions, we were prompted to investigate the metalation of ethylbenzene by *n*-pentylsodium in the presence of TMEDA. Previously, Benkeser and co-workers[5] reported that ethylbenzene was metalated by *n*-pentylsodium (no TMEDA) giving 68% α-methylbenzylsodium (**1**) along with 19% *m*- and 13% *p*-ethylphenylsodium (**2b** and **2c**) in an



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