extracted by means of two 25-mL portions of CH_2Cl_2. The combined extracts were washed with 0.1 M KOH and dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure and the NMR of the residue taken without further purification.

This general procedure was used throughout and as determined from a controlled experiment had no effect on product ratios.

Isomer ratios and percent reactions were obtained by integrating peaks due to absorption by 5-methyl hydrogens. The hydrogens for each of the three components have different chemical shifts. Reactions were interrupted at different times and followed to at least 80% completion. From plots of several points, the times to reach 50% reaction were taken as $t_{1/2}$.

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Registry No. *trans*-1 (R = *p*-$NO_2C_6H_4O$), 36912-38-6; *trans*-1 (R = *o*-$NO_2C_6H_4O$), 78609-79-7; *trans*-1 (R = *m*-$NO_2C_6H_4O$), 78609-80-0; *cis*-1 (R = *p*-$NO_2C_6H_4O$), 36912-37-5; *trans*-1 (R = 8-quinolinyloxy), 78609-81-1; *trans*-1 (R = *p*-$CHOC_6H_4O$), 78609-82-2; *trans*-1 (R = *o*-$CHOC_6H_4O$), 78609-83-3; *trans*-1 (R = *p*-C_6H_5N = CHC_6H_4O), 78609-84-4; *trans*-1 (R = *p*-CNC_6H_4O), 68666-60-4; $ZnCl_2$, 7646-85-7.

Kolbe Electrosynthesis of Alkanes with Multiple Quaternary Carbon Atoms

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Quaternary carbons in alkanes have been shown to affect their physical properites, particularly melting point, viscosity, and density. Tetraalkylmethanes such as 13-decyl-13-heptyltritriacontane are liquids,[1] while the corresponding *n*-$C_{50}H_{102}$ melts at 92 °C.[2] Levina and coworkers have noted that highly branched alkanes of a C_9H_{20}–$C_{17}H_{36}$ structure with two or three quaternary carbon atoms, separated by a methylene group, generally have higher viscosities and densities and become vitrified at low temperatures, ca. −45 to −95 °C.[3]

In conjunction with another study, it appeared of interest to examine the properties of alkanes with two–four quaternary carbons, each substituted with two ethyl groups. The syntheses of 3,3,6,6-tetraethyloctane (**2**), 3,3,6,6,9,9-hexaethylundecane (**11**), and 3,3,6,6,9,9,12,12-octaethyltetradecane (**12**) were carried out as indicated in Scheme I. The Kolbe electrolyses were accomplished readily by means of a cell with a platinum gauze anode and a mercury cathode.[4] The electrolysis of 3,3-diethylpentanoic acid (**1**) afforded 81% of the normal Kolbe coupling product (**2**) plus a mixture of compounds of which **3**–**5** undoubtedly arose from carbonium ions formed by anodic oxidation of the free radicals which were intermediates of the electrolysis of the carboxylic acid.[4] They were separated by gas chromatography and their proposed identities are based on elemental and spectral analyses.

The formation of byproducts **3** and **4** may be ascribed to the oxidation of the 2,2-diethylbutyl radical to the corresponding carbonium ion which rearranged to the more stable tertiary 1,1-diethylbutylcarbonium ion. Coupling of the latter, or deprotonation, could have produced the compounds. Abstraction of a hydrogen atom on the 4-position of the 2,2-diethylbutanecarboxylate ion, followed by oxidation of the new radical to a carbonium ion and coupling of the ions, might have led to **5**. It is conceivable that the intermediate 2,2-diethylbutyl carboxylate radical coupled with the 2,2-diethylbutyl radical, and the resulting ester was transesterified with methanol to give **6**.[4a]

The crossed-coupling of **1** and **7**, which was prepared in situ by attack of methoxide ion on 3,3-diethyl-1,5-pentanedioic anhydride, gave four major products: **2**, **3**, **8**, and **9**, representing 77% of the reaction mixture. A number of non-Kolbe minor components were isolated and their identities are suggested from spectral data (see Experimental Section).

The ester **9** was saponified to the acid **10**, which was electrolyzed with **1**, and the desired hydrocarbons **11** and **12** as well as **2** resulted. No attempt was made to separate other components of the mixture.

The melting points of **2**, **11**, and **12** are 7–8, 39.5–41.5, and 77–79 °C, respectively, while the corresponding *n*-isomers melt at 18, 47.6, and 65.8 °C.[5] It is interesting that the C_{30} hydrocarbon (**12**) has a higher melting point than triacontane. 2,2,5,5,8,8,11,11-Octamethyldodecane has been reported to melt at 37–38 °C, while *n*-$C_{20}H_{42}$ has a melting point of 36.8 °C.[6] These four highly branched alkanes have the quaternary carbons separated by two methylenes, which apparently permit the substituent groups to pack readily into not severely hindered but compact arrangments. Molecular models seem to support this view.

Experimental Section

Materials. 3,3-Diethylpentanoic acid (**1**) was prepared by a previously described procedure.[7] The sodium salt of hydrogen methyl 3,3-diethyl-1,5-pentanedioate (**7**) was made in situ by causing sodium methoxide to react with 3,3-diethyl-1,5-pentanedioic acid anhydride which had been obtained by treating the corresponding diacid with acetic anhydride.[8] 3,3-Diethyl-1,5-pentanedioic acid was synthesized by the acid hydrolysis of 2,4-dicyano-3,3-diethylglutarimide;[9] the latter was prepared from ethyl 2-cyano-3-ethyl-2-pentenoate and cyanoacetamide by the method of McElvain and Clemens.[10]

Electrolysis of 1. In a 1-L resin pot, fitted with a mechanical stirrer, internal cooling coil, reflux condenser, stopcook, and a platinum gauze anode (6 × 7 cm), 2 cm from the mercury cathode, were placed 47.5 g (0.3 mol) of **1**, 65 mL (0.3 mol) of 25% sodium methoxide in methanol, and 300 mL of anhydrous methanol. A direct current of 120 V and 13.7 amp was applied until the voltage and amperage reached a steady state and the evolution of gas had ceased. The reaction was stopped after 90 min by draining the mercury cathode while the potential was still applied. The methanol was removed by distillation, and the residue was dissolved in Et_2O, washed with 10% NaOH, and dried (Na_2SO_4). After removal of the Et_2O, the residue was distilled through a spinning band column to give three fractions: bp –50 °C (4.4 mm), 6.7 g; –114 °C (4 mm), 13.3 g; 114 °C (1.4 mm), 13.5 g; and residue, 2.1 g. The components of the fractions were isolated by prepa-

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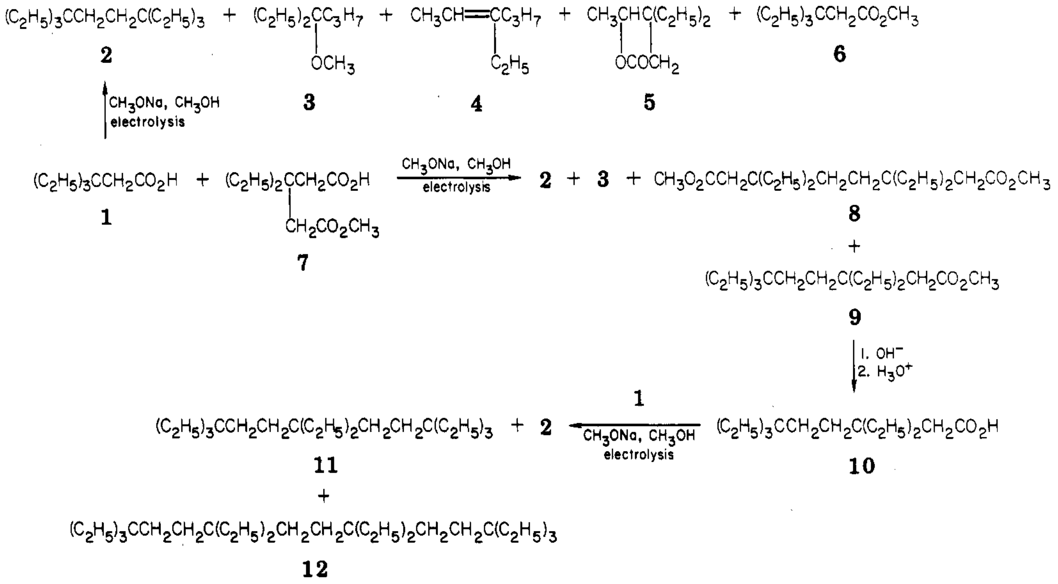
Scheme I



rative GC and identified as follows. 2: bp 140–142 °C (20 mm); mp 7–8 °C; n^{25}_{D} 1.4524; ^{1}H NMR (CCl_4) δ 0.5–1.5, (m, 34, CH_2, CH_3); IR (neat) 2970 (s), 2935 (s), 2835 (s), 1460 cm^{-1} (m); viscosity in centistokes vs. temperature (°C), 5.24/37.8, 2.78/66.7, 1.67/98.9; D^{20}_4 0.8324; yield 81%.

Anal. Calcd for $C_{16}H_{34}$: C, 84.86; H, 15.14. Found: C, 84.95; H, 14.84. 3: bp 72–76 °C (30 mm); n^{25}_{D} 1.4164; ^{1}H NMR (CCl_4) δ 0.5–1.0 (m, 9, CH_3), 1.1–1.7 (m, 8, CH_2), 3.03 (s, 3 H, OCH_3); IR (neat) 1090 (s), 1075 cm^{-1} (w); yield 11%.

Anal. Calcd for $C_9H_{20}O$: C, 74.93; H, 13.98. Found: C, 74.74; H, 13.72.

Trace quantities of three compounds were isolated by GC, and spectral analyses suggested the following structures. 4:[11] ^{1}H NMR (CCl_4) δ 0.7–1.1 (m, 6, CH_3), 1.2–1.5 (m, 2,CH_2), 1.60 (d, 3, $CH_3CH{=}$), 1.8–2.3 (m, 4, $={}C(CH_2)_2$), 5.0–5.4 (m, 1, $CH{=}$; IR (neat) 3190 (m), 2765–3060 (s), 1940 (m), 1840 (m), 1740 (m), 1670 cm^{-1} (m). 5: ^{1}H NMR (CCl_4) δ 0.6–1.0 (m, 6, CH_3), 1.1–1.7 (m, 7, CH_2, CH_3), 2.20 (s, 2, CH_2CO_2), 4,27 (q, 1, CHOCO); IR 1775 cm^{-1} (s). 6: ^{1}H NMR (CCl_4) δ 0.6–0.95 (m, 9, CH_3), 1.1–1.6 (m, 6, CH_2), 2.10 (s, 2, CH_2CO_2), 3.60 (s, 3, CO_2CH_3).

Electrolysis of a Mixture of 1 and 7. A solution of 36.4 g (0.23 mol) of 1 in 350 mL of dry methanol was added to a solution of the sodium salt of 7, prepared by adding 25.0 g (0.15 mol) of 3,3-diethyl-1,5-pentanedioic anhydride to a solution of sodium methoxide, made from 6.9 g (0.3 mol) of sodium in 165 mL of methanol. The mixture was electrolyzed as described previously at 120 V and 20 amp for 4.5 h, when the amperage was 3. The solvent was removed by distillation, and the residue was dissolved in Et_2O, washed with 100 mL of H_2O and 100 mL of 1 N HCl, and dried. The Et_2O was distilled and the 43.1 g of residue was distilled through a spinning band column to give four major components: 2 (46%), 3 (11%), 8 (9.5%) [bp 135–136 °C (0.5 mm); n^{25}_{D} 1.4596; ^{1}H NMR (CCl_4) δ 0.6–1.0 (m, 12, CH_3), 1.0–1.6 (m, 12, CH_2), 2.14 (s, 4, CH_2CO_2), 3.60 (s, 6, CO_2CH_3); IR 1737 cm^{-1} (s)].

Anal. Calcd for $C_{18}H_{34}O_4$: 68.75; H, 10.90. Found: C, 69.02; H, 11.10. 9 (32%): bp 140–144 °C (2 mm); n^{25}_{D} 1.4550; ^{1}H NMR (CCl_4) δ 0.5–0.95 (m, 15, CH_3), 0.95–1.6 (m, 14, CH_2), 2.12 (s, 2, CH_2CO_2), 3.60 (s, 3, CO_2CH_3); IR 1740 cm^{-1} (s).

Anal. Calcd for $C_{17}H_{34}O_2$: C, 75.50; H, 12.67. Found: C, 75.45; H, 12.40.

Preparation of 10 and 3,3,6,6-Tetraethyl-1,8-octanedioic Acid. A mixture of 30.2 g (0.11 mol) of 9, 52.8 g (0.8 mol) of 85% KOH, 135 mL of H_2O, and 55 mL of ethanol was heated at reflux for 18.5 h and worked up in the usual way. The acid (22.4 g, 78%) was recrystallized from CH_3CN; mp 48–50 °C.

Anal. Calcd for $C_{16}H_{32}O_2$: C, 74.94; H, 12.58. Found: C, 74.73; H, 12.53.

A similar saponification of 5 g of 8, afforded 4.3 g (94%) of the dibasic acid.

Anal. Calcd for $C_{16}H_{30}O_4$: C, 67.09; H, 10.56. Found: C, 67.23; H, 10.55.

Electrolysis of a Mixture of 1 and 10. A mixture of 31.6 g (0.2 mol) of 1, 25.6 g (0.1 mol) of 10, 64.8 g (0.3 mol) of 25% sodium methoxide in methanol, and 400 mL of anhydrous methanol was electrolyzed for 3 h with an initial 110 V and 16 amp. The solvent was removed by distillation and the residue was diluted with petroleum ether, bp 60–65 °C. The solution was washed with H_2O and 10% HCl and dried over molecular sieves. The solvent was removed by distillation and the residue (43.5 g) was distilled through a spinning band column to give 10 fractions and a residue. The latter was recrystallized from acetone and afforded 5.4 g (27%) of 12: mp 77–79 °C; ^{1}H NMR (CCl_4) δ 0.50–0.94 (m, 30, CH_3), 0.94–1.54 (m, 32, CH_2); IR 2950 (s), 2910 (s), 2850 (s), 1450 (s), 1370 cm^{-1} (m).

Anal. Calcd for $C_{30}H_{62}$: C, 85.22; H, 14.78. Found: C, 85.02; H, 14.69.

Redistillation of fractions 8–10 gave 10.4 g (32%) of 11: bp 145–146 °C (0.8 mm); mp 39.5–41.5 °C (acetone); IR 2960 (s), 2935 (s), 2880 (s), 1460 (s), 1375 cm^{-1} (s).

Anal. Calcd for $C_{23}H_{48}$: C, 85.09; H, 14.91. Found: C, 84.90; H, 14.81.

Acknowledgment. We are grateful to P. R. Stapp who had prepared previously a sample of 3,3,6,6-tetraethyloctane and determined some of its physical properties.

Registry No. 1, 6637-50-9; 2, 78715-64-7; 3, 62813-72-3; 4, 620-00-8; 5, 78715-65-8; 6, 78715-66-9; 7·Na, 78739-30-7; 8, 78715-67-0; 9, 78715-68-1; 10, 78715-69-2; 11, 78715-70-5; 12, 78715-71-6; 3,3,6,6-tetraethyl-1,8-octanedioic acid, 78715-72-7; 3,3-diethyl-1,5-pentanedioic anhydride, 4160-89-8.

Molecular Rearrangements and Fragmentations during the Aromatization of Diels–Alder Adducts Derived from 1-Benzylisobenzofuran

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We have eariler reported[1] that 1-benzylisobenzofuran can be readily generated and captured as a Diels–Alder

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