furnished the enynolone **18** (670 mg, 38% from **6**), which was crystallized from CH_2Cl_2–hexane: mp 77–79 °C; UV λ 232 nm (ε 12 200); IR ($CHCl_3$) ν 3450, 2215, 1738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.72 (1 H, s), 4.39 (2 H, s), 3.52 (1 H, m), 3.02 (1 H, quintet with st, J = 8 Hz), 2.86 (1 H, t of d of d, J = 17, 8, 3 Hz), 2.52 (1 H, d of d, J = 19, 10 Hz), 2.47 (1 H, d of d of d, J = 19, 10, 2.5 Hz), 2.32 (1 H, d of d, J = 17, 2 Hz), 2.26 (1 H, d, J = 19 Hz), 2.06 (1 H, d of d, J = 19, 8 Hz), 1.7 (1 H, br s). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.98; H, 7.13. Further elution of the column with 10% ethyl acetate in methylene chloride gave a mixture of bis-enynols **11** and **12** (160 mg, 7.5% from **6**).

Tricyclo[6.3.0.0^{2,6}]undec-1(8)-ene-4,9-dione (19). The enynolone **18** (200 mg) was added in small batches to 7 mL of magnetically stirred methanesulfonic acid over a period of 30 min. The dark mixture was stirred at room temperature for 3 h and then poured in water (20 mL). The solution was extracted with methylene chloride (3 × 15 mL). The extract was washed with water, followed by brine, and dried over Na_2SO_4. Evaporation of the solvent followed by passage of the residue through a silica gel (10 g) column using 20% ethyl acetate in methylene chloride as eluent furnished triquinane **19** (140 mg, 70%) as an oil, which was distilled bulb-to-bulb: bp 120 °C (bath) (0.1 torr); UV λ 241 (ε 11 350), 298 (980) nm; IR ($CHCl_3$) ν 1730, 1692, 1638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.57 (1 H, m), 3.46 (1 H, quintet with st, J = 8 Hz), 2.78 (2 H, t, J = 5 Hz), 2.75 (1 H, m), 2.65 (1 H, d of d, J = 18, 9 Hz), 2.55 (1 H, d of d, J = 18, 10 Hz), 2.51 (2 H, m), 2.36 (1 H, d with st, J = 16 Hz), 2.26 (1 H, d, J = 16 Hz), 2.09 (1 H, d of d, J = 18, 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 217.4 (s), 203.9 (s), 186.0 (s), 147.6 (s), 44.8 (d), 44.7 (t), 42.9 (d), 40.8 (t), 39.3 (t), 32.0 (t), 24.2 (t); mp 60–61 °C (ether). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98% H, 6.86. Found: C, 74.78; H, 6.75.

Acknowledgment. The research efforts of the Principal Investigator are supported by the National Institutes of Health (GM 29258-11) and the National Science Foundation (CHE 8118391). We are also grateful to the NSF and NIH (CA-14599) for funds allowing the purchase of the NMR equipment used in this research.

Registry No. **2**, 89487-21-8; **2** (tetrahydro derivative), 36269-15-5; **2** (tetrahydro bisketal), 63127-34-4; **2** (tetrahydro dibromo bisketal), 63127-35-5; **3**, 36269-16-6; **4**, 36269-18-8; **6**, 51716-63-3; **6** (adduct with **9**), 89487-28-5; **9** (alkyne), 18669-04-0; **10**, 89487-16-1; **11**, 89487-18-3; **11** (α-ethoxyethoxy ether), 89487-17-2; **12**, 89487-19-4; **12** (α-ethoxyethoxy ether), 89487-32-1; **13**, 89487-20-7; **13** (tetrahydro derivative), 89487-22-9; **13** (tetrahydro bisketal), 89487-23-0; **13** (tetrahydro dibromo bisketal), 89487-24-1; **14**, 89487-25-2; **15**, 89487-26-3; **16**, 89487-27-4; **18**, 89487-30-9; **18** (α-ethoxyethoxy ether), 89487-29-6; **19**, 89487-31-0.

Synthesis of Trialkylacetic Acids by the Anodic Oxidation of 3,3-Disubstituted-2-oxo Carboxylic Acids

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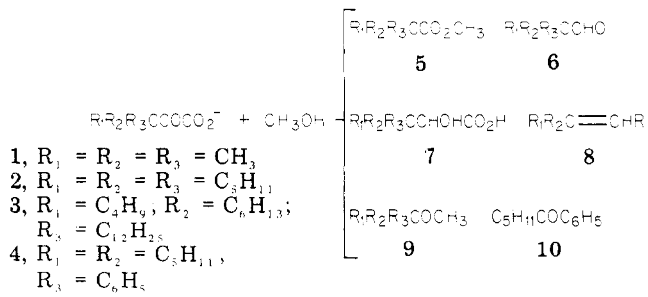
The "non-Kolbe" electrolysis of 3,3-disubstituted-2-oxo carboxylates **1–3** in methanol produced mixtures of methyl trialkylacetates **5**, trialkylacetaldehydes **6**, in some cases 2-hydroxy-3,3,3-trialkylpropionic acids **7**, trialkylethylenes **8**, and methyl trialkylmethyl ethers **9**. When one of the substituents on the 3-carbon of the 2-oxo carboxylate was phenyl **4**, molecular rearrangement was not observed. In addition to products **5–9**, with the exception of **7**, there was obtained with **4** an alkyl phenyl ketone **10**. The methyl trisubstituted acetates were saponified to the desired trialkylacetic acids.

Although the oxidative decarboxylation of 3,3-dialkyl-2-oxo carboxylic acids ($R_1R_2R_3CCOCO_2H$) offers a possible way for preparing trialkylacetic acids with variations in the substituents,[1] it was thought that the Kolbe electrolysis method might afford an alternative way of obtaining these materials. This was based on the demonstrated fact that carbocations may be present in anodic oxidations and produce "non-Kolbe" materials, the nature of which varies with solvent and other conditions.[2]

Substitution in the 2-position of an acid by a carbocation stabilizing group, e.g., alkyl, alkoxyl, aryl, etc., decreases the yield of Kolbe dimers, and alcohols, olefins, ethers, etc. are formed by carbonium ion mechanisms. Previous studies of the anodic oxidation of pyruvic, α-oxobutyric, and α-oxovaleric acids in methanol showed that good yields of methyl esters were realized in addition to other products.[3]

Scheme I. Products of Electrolysis of $R_1R_2R_3COCO_2^-$ in CH_3OH



1, $R_1 = R_2 = R_3 = CH_3$
2, $R_1 = R_2 = R_3 = C_5H_{11}$
3, $R_1 = C_4H_9$; $R_2 = C_6H_{13}$; $R_3 = C_{12}H_{25}$
4, $R_1 = R_2 = C_5H_{11}$, $R_3 = C_6H_5$

In the present investigation four 2-keto acids **1–4** (Scheme I) were studied. They contained 6–25 carbon atoms, and the substituents were varied, including phenyl in the last case. It was thought that the aryl system might

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(1) Rabjohn, N.; Schwarz, R. M. *J. Org. Chem.* **1983**, *48*, 1931.

(2) For leading references, see: (a) Eberson, L. In "Organic Electrochemistry"; Baizer, M. M., Ed.; Dekker: New York, 1973; p 470. (b) Ross, S. D.; Finkelstein, M.; Rudd, E. J. "Anodic Oxidation"; Academic Press: New York, 1975; p 187. (c) Rifi, M. R.; Covitz, F. H. "Introduction to Organic Electrochemistry, Dekker: New York, 1974; p 267. (d) Eberson, L.; Nyberg, K. In "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Lund, H., Eds.; Dekker: New York, 1978; Vol. 12, Chapter 2.

(3) Wladislaw, B.; Zimmerman, J. P. *J. Chem. Soc. B* **1970**, 290. De la Fuente, J.; Rozas, R.; Lissi, E. *Bol. Soc. Chil. Quim.* **1982**, 198; *Chem. Abstr.* **1982**, *97*, 38342d.

Table I. Products of Electrolysis of 3,3-Dipentyl-2-oxooctanoic Acid (2)

neutralization, %	yields, % (by GC)			
	5	6	7	8
10	70	8.5	11	9
100	66	6.5	8	15
200	59	5	6	29

Table II. Electrolysis Products of 2-Oxo-3-pentyl-3-phenyloctanoic Acid (4)

anode	neutralization, %	yields, % (by GC)				
		5	6	8	9	10
Pt	100	31.6	3.1	0.9	62.0	2.5
Pt	10	38.2	trace	2.7	50.5	8.5
Pt	200	23.2	3.4	8.8	62.0	2.6
C	100	47.3	7.6	1.1	39.2	4.9
C	10	52.6	8.0	1.2	36.3	1.9
C	1	42.7	12.6	trace	40.5	4.1

offer the possibility of rearrangement and also affect the nature and relative amounts of products arising from the anodic oxidation.

The 2-keto acids were synthesized by the autoxidation of the anions of ethyl 2-cyano-3,3-dialkyl carboxylates, followed by saponification, according to previously described methods.[4] They were converted to anions by sodium methoxide, and the electrolyses were conducted in methanol. Some variations in experimental conditions were examined.

Results

The reaction mixtures from the electrolyses of the anions of **1**–**4** were separated by distillation and gas chromatography. The products, shown in Scheme I, were identified by spectral methods. The electrolysis of **1** with an equivalent amount of sodium methoxide afforded only the "non-Kolbe" compounds **5** (60%), **6** (15%), and **7** (12%). No coupling products were observed under the experimental conditions employed and apparently the olefin **8** was lost due to its volatility.

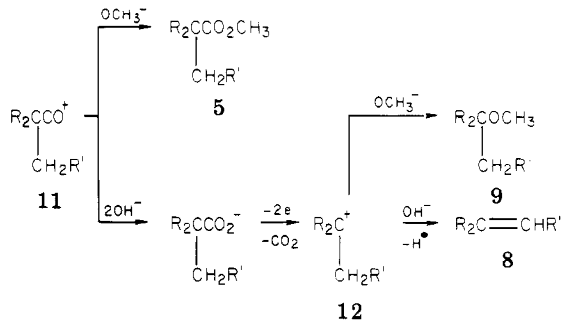
Since problems were experienced in separating the previous reaction mixture, it was decided that a larger 2-keto acid, such as **2**, might offer experimental advantages. Three runs were made with different proportions of the acid and sodium methoxide, and the results are given in Table I.

Samples were removed from an electrolysis mixture of **2** at several intervals, and the products appeared to arise continuously in roughly the expected relative amounts.

The higher molecular weight acid **3** gave the corresponding methyl ester **5** in 50% yield and a mixture of other compounds that was not separated completely.

The products from cationic intermediates of the electrolysis of carboxylate ions may have rearranged structures.[5] The possibility of this occurring with the acylium ion from 2-oxo-3-pentyl-3-phenyloctanoic acid (**4**) was examined. The main products isolated were **5** and **9**. Small amounts of three other compounds were identified, i.e., **6**, **8**, and 1-phenyl-1-hexanone (**10**), but no direct evidence of rearrangement or coupling was observed. The results of a number of experiments, with some variations in conditions, are recorded in Table II. The best yields of methyl ester **5** were realized when the reaction was carried out with a graphite anode and 10% neutralization of the 2-oxo acid. Methyl ether formation was greatest with a Pt anode and high methoxide ion concentration. The same ether resulted in 91% yield as the only product when equal molar amounts of dipentylphenylacetic acid and sodium methoxide were electrolyzed in CH_3OH.

Scheme II



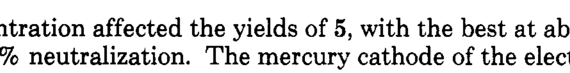
The methyl esters **5** were saponified fairly readily to the desired trisubstituted acetic acids.

Discussion

A number of methods for the preparation of trialkylacetic acids are available, but most apparently are not satisfactory if acids are desired with different and higher alkyl substituents. Since 3,3-dialkyl-2-oxo carboxylic acids may be synthesized with wide variation in the 3,3-substituents,[4] the anodic oxidation of such molecules appeared to offer an approach to the preparation of trialkylacetic acids or derivatives. In a previous study of the electrolysis of pyruvic acid and two other unsubstituted 2-oxo carboxylic acids in methanol, it was found that methyl esters were formed with apparent suppression of the Kolbe coupling reaction.[3]

The electrolyses of the 3,3-dialkyl-2-oxo acids **1**–**4** produced the desired methyl esters **5** in satisfactory yields of 23–70%, depending upon the structure of the 2-oxo acids and experimental conditions. Eberson has summarized the effects of experimental variables on the electrosynthesis reaction.[7] Only substituents in the 2-position of carboxylic acids appear to be critical in determining the amounts of dimers from free-radical intermediates. When the substituents, e.g., alkyl, alkoxyl, aryl, etc., are capable of stabilizing carbonium ions, the yields are frequently 0–10%. In the present study, Kolbe coupling was not observed.

The acylium ions **11**, which obviously resulted from the 2-oxo acids (**1**–**4**) on electrolysis by loss of two electrons (eq 1), were the precursors of the esters **5**, as well as other products shown in Tables I and II. Methoxide ion concentration affected the yields of **5**, with the best at about 10% neutralization. The mercury cathode of the electrolysis cell should have maintained neutrality below equivalence of the reactants. Alkaline conditions have been indicated as among the factors that favor carbonium ion formation in the Kolbe synthesis.[7]



$$R_2\underset{CH_2R'}{\underset{|}{C}}COCO_2^- \xrightarrow{-e} R_2\underset{CH_2R'}{\underset{|}{C}}COCO_2\cdot \xrightarrow{-CO_2} R_2\underset{CH_2R'}{\underset{|}{C}}\overset{\bullet}{C}{=}O \xrightarrow{-e} R_2\underset{CH_2R'}{\underset{|}{C}}\overset{+}{C}{=}O \qquad (1)$$

Since ions **11** and **12** (Scheme II) would react with methoxide ion, the yields of ester **5** and ethers **9** would be related inversely. This was observed with the 2-keto acid

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[4] Rabjohn, N.; Harbert, C. A. *J. Org. Chem.* **1970**, *35*, 3240.

[5] For an excellent review and references, see ref 2b, Chapter 7.

[6] See: (a) Prout, F. S.; Burachinsky, B.; Brannen, W. T., Jr.; Young, H. L. *J. Org. Chem.* **1960**, *25*, 835. (b) Eberson, L. *Ibid.* **1962**, *27*, 3706. (c) Pfeffer, P. E.; Silbert, L. S.; Chirinko, J. M., Jr. *Ibid.* **1972**, *37*, 451.

[7] Eberson, L. "The Chemistry of Carboxylic Acids and Esters"; Patai, S., Ed.; Interscience: New York, 1969; p 62.

4 and indicates an enhanced stability of the substituted benzyl cation due to aryl participation. Also, the formation of olefin **8** from **12** would be expected to decrease the yield of **5** and the data from several electrolyses of 2-keto acid **2** seem to support this view.

Commercial methanol was employed for all of the electrolyses and some water probably was present, which suggests a pathway through carboxylate ions by which the ethers and olefin might have resulted. Acylium ions are known to lose carbon monoxide,[8] but the conditions used for such a reaction are not comparable with the electrolyses of the present study.

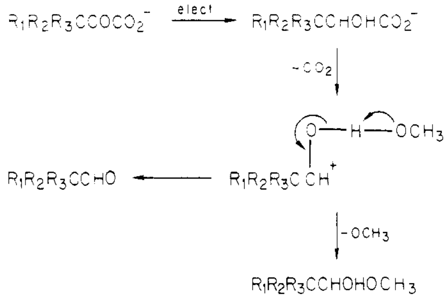
An attempt to determine if products were formed stepwise was made by electrolyzing **2** with 10 mol % of sodium methoxide. Aliquots were removed during 45 min as the amperage changed from 2 to 1.2 A. The data from four samples indicated that the products were produced continuously and there were no very significant variations in the percentages of products (vide infra).

Aldehydes **6** were isolated in low yields from the electrolyses of **2** and **4**. It has been reported that benzaldehyde is formed from benzoyl chloride and cyclohexane in the presence of aluminum chloride,[8a] and such a reaction (eq 2) might be suggested as the source of **6**. However, Olah

$$R_3C\overset{+}{C}{=}O \xrightarrow{\equiv CH} R_3CCHO + \equiv C^{+} \qquad (2)$$

has concluded that there is no simple hydride transfer between acyl cations and alkanes.[8b] Acidic media and complexing of the carbonyl oxygen by either a Lewis or Brønsted acid are required.

It was observed long ago that 2-hydroxy carboxylic acids produce aldehydes on electrolysis.[9] One of the products of the electrolysis of **2** was 3,3-dipentyl-2-hydroxyoctanoic acid, which could have formed an intermediate hydroxycarbonium ion that lost a proton to give the related aldehyde (eq 3). The carbonium ion also might have produced a methoxy hemiacetal.

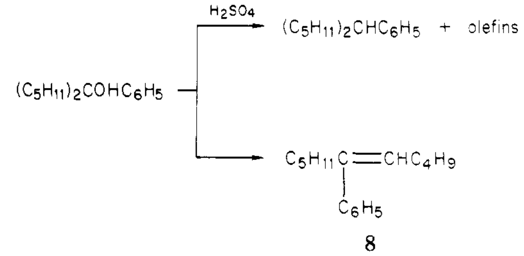


(3)

$R_1 = R_2 = R_3 = C_5H_{11}$

Carbon skeleton rearrangements of acids have been observed in anodic oxidation products, but dimer formation of intermediate radicals is not accompanied by such changes. Typical examples of carbonium ion participation have been shown in the ring expansion of 1-methylcyclohexaneacetic acid,[10] aryl migration in molecules such as 3,3-diphenylpropionic acid,[11] the formation of cyclic ketones on ring expansion of 1-hydroxycycloalkaneacetic acids,[12] and a number of other cases.[5] The possibility that 2-oxo-3-pentyl-3-phenyloctanoic acid (**4**) might rearrange on electrolysis was investigated in some detail. The results of several reactions under different conditions are shown in Table II.

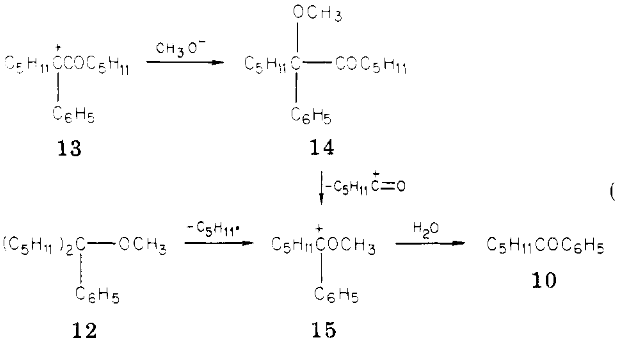
The two major products were the anticipated methyl ester **5** and the methyl ether **9**. In most cases the yields of **9** exceeded those of **5**. The greater stability of the carbonium ion **15** was suggested further by the observation that 6-phenyl-6-undecanol on treatment with concentrated sulfuric acid afforded a single pure product, which was identified as 6-phenylundecane (eq 4). Others have observed a similar carbonium ion hydride transfer of benzyl alcohols in acid media.[13]



(4)

The minor products of electrolysis of **4** were found to be the aldehyde **6**, a mixture of isomeric olefins **8**, and the ketone 1-phenyl-1-hexanone (**10**). The olefins were identical with those obtained by the dehydration of 6-phenyl-6-undecanol (eq 4). Low-pressure hydrogenation of **8** from both sources produced 6-phenylundecane. When the methyl ether from **4**, 1-methoxy-1-phenylundecane, was heated at 110 ± 5 °C for 20 h, the same mixture of olefins resulted.

The structure of the ketone **10** was proven by comparison with the product of the dichromate oxidation of pentylphenylcarbinol. Its origin is not obvious. It was observed previously that the 2-oxo acid **4** undergoes pentyl migration on distillation through a stainless steel spinning-band column to give the rearranged ketone 7-phenyl-6-dodecanone.[14] This suggests the intermediacy of carbocation **13** (eq 5), which might have formed the α-methoxy ketone **14**. α-Cleavage of the latter by anodic oxidation as suggested by the studies of Miller et al.[15] could have given ion **15** (eq 5). It might have arisen also by the anodic cleavage of benzyl ether **12**, based on the work of Weinreb and co-workers.[16] Attack of water on **15** could have led to ketone **10**.



(5)

If the ether **9** were the source of the ketone **10**, it was thought that the ratio of the former to the latter relative to time might be indicative. The keto acid **4** was elec-

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[8] (a) Wenitzescu, C. D.; Ionescu, C. N. *Justus Liebigs Ann. Chem.* **1931**, *491*, 189. (b) Olah, G. A.; Germain, A.; White, A. M. "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1976; Vol. 5, Chapter 35.

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[10] Muhs, M. A. *Diss. Abstr.* **1954**, *14*, 765.

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[13] (a) Barclay, L. R. C.; Sonawane, H. R.; MacDonald, N. M. C. *Can. J. Chem.* **1972**, *50*, 281. (b) Reference 8b, **1970**, Vol. 2, p 715. (c) Deno, N. C.; Boyd, D. B.; Hodge, J. D.; Pittman, C. U., Jr.; Turner, J. O. *J. Am. Chem. Soc.* **1964**, *86*, 1745.

[14] Rabjohn, N.; Harbert, C. A. *J. Org. Chem.* **1970**, *35*, 3726.

[15] Becker, J. Y.; Miller, L. L.; Siegal, T. M. *J. Am. Chem. Soc.* **1975**, *97*, 849.

[16] Weinreb, S. M.; Epling, G. A.; Comi, R.; Reitano, M. *J. Org. Chem.* **1975**, *40*, 1356.

Table III. Product Distribution vs. Time for Electrolysis of 2-Oxo-3-pentyl-3-phenyloctanoic Acid (4)

	yields, % (by GC)				
time, min	ester **5**	aldehyde **6**	olefin **8**	ether **9**	ketone **10**
5	50.8		10.1	36.9	2.1
10	47.5		3.8	45.4	3.3
15	44.6	trace	4.6	49.1	1.6
20	44.0	0.7	7.4	46.5	1.7
30	46.2	1.3	4.8	45.8	1.9

trolyzed in methanol with an equivalent amount of sodium methoxide and a Pt gauze anode. Aliquots were removed periodically and product distributions were determined by GC, and the results are shown in Table III. Although there was a slight decrease in the ratio of ether to ketone after 15 min, the data are not conclusive.

A brief comparison of the influence of Pt vs. C anodes on the yields of the electrolysis products of **4**, recorded in Table II, gave results that agree with established views relative to ester formation, i.e., C anodes favored.[7] The latter are believed to increase carbonium ion generation; however, in the present study the yields of ethers **9** decreased instead of showing an anticipated increase. The aldehyde yields were increased by the C electrode, which is in agreement with an increase in carbonium ion formation. The variations in conditions employed in the electrosyntheses and the number of products isolated make it difficult to infer more about the competing reactions involved other than to recognize the dominance of carbonium ions.

The methyl esters obtained from the 2-keto acids **3** and **4** were converted in good yields to the corresponding trisubstituted acetic acids by saponification with potassium hydroxide in triethylene glycol or ethanol.

Experimental Section

Materials. Trimethylpyruvic acid was made by the permanganate oxidation of pinacolone,[17] and **2** was obtained as described previously.[14] Ethyl 3-butyl-2-cyano-3-hexylpentadecanoate was prepared by the addition of dodecylmagnesium bromide to ethyl 3-butyl-2-cyano-2-nonenoate; yield 47%; bp 216–218 °C (0.5 mm); n^{25}_{D} 1.4570; IR (neat) 2250, 1750 cm^{-1}; ^1H NMR (CCl_4) δ 4.2 (q, 2, OCH_2CH_3), 3.35 (s, 1, CH), 0.7–1.6 (50 H, CH_2CH_3). Anal. Calcd for $C_{28}H_{53}NO_2$: C, 77.18; H, 12.26. Found: C, 77.33; H, 12.43. Oxidation of the product afforded ethyl 3-butyl-3-hexyl-2-oxopentadecanoate; yield 78%; bp 220–225 °C (0.55 mm); n^{25}_{D} 1.4508; IR (neat) 2 C=O at 1700–1750 cm^{-1}; ^1H NMR (CCl_4) δ 4.2 (q, 2, OCH_2CH_3), 0.7–1.6 (50 H, CH_2CH_3). Anal. Calcd for $C_{27}H_{52}O_3$: C, 76.35; H, 12.34. Found: C, 76.48; H, 12.38. Saponification of this keto ester gave **3** (98%); bp 170–174 °C (0.2 mm); n^{25}_{d} 1.4545; IR (neat) 2500–3400 (m) and split C=O at 1700–1750 cm^{-1}; ^1H NMR (CCl_4) δ 10.8 (s, 1, CO_2H), 0.6–1.7 (47 H, CH_2CH_3). Anal. Calcd for $C_{25}H_{48}O_3$: C, 75.70; H, 12.20. Found: C, 75.60; H, 12.31. The saponification of ethyl 3-ethyl-3-phenyl-2-oxooctanoate afforded **4**;[14] bp 155–156 °C (0.3 mm); n^{25}_{D} 1.4998. Anal. Calcd for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 75.13; H, 9.40.

Electrolysis of Keto Acids 1–4. The procedure used for the electrolysis of **4** is representative. A 1-L, four-necked resin flask was fitted with a glass cooling coil, a reflux condenser, a mechanical stirrer, a stopcock, and an electrode assembly. The latter consisted of a mercury cathode separated by 2 cm from a 6 × 7 cm platinum gauze anode.

A solution of 7.6 g (0.25 mol) of **4**, 5.4 g (0.25 mol) of a 25% CH_3ONa solution, and 400 mL of CH_3OH was electrolyzed with cooling at an initial direct current of 118 V and 6.8 A. After 60 min, a steady state of 108 V and 0.9 A had been reached and the electrolysis was discontinued.

The reaction mixture was concentrated by distillation, and the residue was treated with 100 mL of 10% HCl, extracted with four 20-mL portions of ether, and dried (Na_2SO_4), and the ether was evaporated. The reaction product was examined by GC, and the components were separated and identified as described below.

(a) Electrolysis Products of 1. A GC on 6% SE 30 of the reaction product showed the presence of three components, 12%, 15%, and 60%. It was treated with 5% NaOH and extracted with ether. The H_2O layer, after acidification, produced 1.75 g of a solid; mp 84–86 °C (CH_3OH); ^1H NMR ($CDCl_3$) δ 6.0–6.4 (s, 2, OH, CO_2H), 3.9 (s, 1, CH), 1 (s, 9, $(CH_3)_3C$). The δ 6.0–6.4 signal disappeared upon the addition of D_2O. The IR (neat) had 3000–3700 (br) and 1700 cm^{-1}. The data agree with those of 3,3-dimethyl-2-hydroxybutyric acid; mp 86–87 °C.[18] Preparative GC on SE-30 of the residue from the nonaqueous phase produced a low-boiling component (15%), which was shown to be pivalaldehyde by IR, NMR, and the formation of a (2,4-dinitrophenyl)hydrazone; mp 207–208 °C (lit. mp 208–209 °C).[19] The major component (60%) had IR 1050, 1700 cm^{-1} and ^1H NMR (CCl_4) δ 3.9 (s, 3, OCH_3, 1.5 (s, 9, CH_3), which correspond to the properties of methyl pivalate.

(b) Electrolysis Products of 2. The lowest boiling component of the reaction mixture was identified as 6-pentyl-5-undecene by comparison with a known sample.[1] A compound comprising 6.5% of the mixture was shown to be 2,2-dipentylheptanal by IR and GC comparison with the authentic aldehyde.[14] The major peak (66% by area) was distilled to yield 7.2 g (64%) of methyl 2,2-dipentylheptanoate; bp 115–117 °C (0.5 mm); n^{25}_{D} 1.4440; IR (neat) 1050, 1700 cm^{-1}; ^1H NMR δ 3.6 (s, 3, CH_3), 0.8–1.5 (m, 33, CH_2CH_3). Anal. Calcd for $C_{18}H_{36}O_2$: C, 75.99; H, 12.76. Found: C, 75.87; H, 12.78. The highest boiling component (8%) had the following: ^1H NMR δ 4.5 (s, 1, CH), 7.4–7.8 (s, 2, OH, CO_2H), 0.9–1.5 (m, 33, CH_2, CH_3); IR (neat) 3000–3700, 1700 cm^{-1}. The spectral data correspond to those of 3,3-dipentyl-2-hydroxyoctanoic acid.[1]

(c) Electrolysis Products of 3. Analysis by GC showed the presence of the methyl ester (50%) and 20% of unreacted and hydroxy acids. The methyl 2-butyl-2-hexyltetradecanoate distilled at 118–120 °C (0.2 mm); n^{25}_{D} 1.4515; ^1H NMR (CCl_4) δ 3.6 (s, 3, OCH_3), 0.8–1.6 (m, 47, CH_2CH_3); IR (neat) 1050, 1700 cm^{-1}. Anal. Calcd for $C_{25}H_{50}O_2$: C, 78.47; H, 13.17. Found: C, 78.63; H, 13.29. The acid fraction was not examined.

(d) Electrolysis Products of 4. The GC chromatogram of the reaction product indicated the presence of two major constituents (94% by area) and four minor components. The main components were separated by distillation through a spinning-band column and further purified by preparative GC. They were dipentylphenylmethyl methyl ether and methyl 2-pentyl-2-phenyloctanoate. Data for dipentylphenylmethyl methyl ether: bp 72–73 °C (0.18 mm); n^{25}_{D} 1.4852; IR 1080 (s) cm^{-1}; H NMR δ 7.28 (s, 5, aromatic), 3.04 (s, 3, CH_3), 0.5–2.0 (m, 22, CH_2CH_3). Anal. Calcd for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.19; H, 11.40. Data for methyl 2-pentyl-2-phenyloctanoate: bp 107–108 °C (0.20 mm); mp 43–44 °C; IR 1730 (s), 1140 (s), 1200 (s), 1230 (s) cm^{-1}; ^1H NMR δ 7.22 (s, 5 H, aromatic), 3.55 (s, 3, CH_3), 0.5–2.5 (m, 22, CH_2CH_3). Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.60; H, 10.45.

The four minor components were separated from enriched distillation fractions by preparative GC and identified spectroscopically as 2-pentyl-2-phenylheptanal [bp 114–115 °C (0.15 mm); n^{25}_{D} 1.4912; IR 2825 (m), 2700 (w), 1730 (s) cm^{-1}; ^1H NMR δ 9.44 (s, 1, CHO), 7.25 (s, 5, C_6H_5), 0.7–2.4 (m, 22, CH_2CH_3); (2,4-dinitrophenyl)hydrazone, mp 105–107 °C ($EtOH-CH_3CO_2C_2H_5$). Anal. Calcd for $C_{24}H_{32}N_4O_4$: C, 65.43; H, 7.32. Found: C, 65.24; H, 7.34], pentyl phenyl ketone [mp 26–27 °C (lit.[20] mp 27 °C); IR 1690 (s) cm^{-1}; ^1H NMR δ 8.00 (d, 1, aromatic), 7.85 (d, 1, aromatic), 7.45 (d, 2, aromatic), 7.24 (s, 1, aromatic), 2.80 (t, 2, CH_2), 0.7–2.4 (m, 9, CH_2CH_3)], 6-phenyl-5-undecene [bp 72–73 °C (0.15 mm); n^{25}_{D} 1.5034; ^1H NMR δ 7.20 (s, 5, C_6H_5), 5.57 (t, 1, =CH), 0.6–2.7 (m, 20, CH_2CH_3)], and 6-phenyl-5-undecene

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[lower-boiling form; ^{1}H NMR δ 7.20 (s, 5, C_6H_5), 5.40 (t, 1, =CH), 0.6–2.7 (m, 20, CH_2CH_3)].

Preparation of 6-Phenyl-6-undecanol. The alcohol was obtained (51%) from the reaction of phenylmagnesium bromide with 6-undecanone; bp 107–108 °C (0.15 mm); $n^{25}{}_D$ 1.4950; ^{1}H NMR (CCl_4) δ 7.27 (s, 5, C_6H_5), 1.5–2.0 (s, 4, CH_2), 0.6–1.4 (m, 19, CH_2CH_3). Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.10; H, 11.20.

Reaction of 6-Phenyl-6-undecanol with Acid. (a) H_2SO_4. A mixture of 4.00 g (0.015 mol) of 6-phenyl-6-undecanol and 50 mL of concentrated H_2SO_4 was stirred until homogeneous, poured into 500 mL of ice water, and extracted with four 25-mL portions of petroleum ether (bp 60–65 °C). The combined extracts were dried (Na_2SO_4) and distilled through a spinning-band column. There was obtained 1.46 g (42%) of 6-phenylundecane; bp 88–89 °C (0.20 mm); $n^{25}{}_D$ 1.4812; ^{1}H NMR (CCl_4) δ 7.11 (s, 5, C_6H_5), 2.2–2.6 (s, 1, CH), 0.6–1.9 (m, 23, CH_2CH_3). Anal. Calcd for $C_{17}H_{28}$: C, 87.86; H, 12.14. Found: C, 88.00; H, 12.14.

(b) $KHSO_4$. A mixture of 1.0 g (4.0 mmol) of 6-phenyl-6-undecanol and 0.27 g of fused $KHSO_4$ was heated at 160 ± 5 °C for 4 h. The product was distilled to afford 0.87 g (94%) of mixed 6-phenyl-5-undecenes; bp 93–94 °C (0.15 mm); $n^{25}{}_D$ 1.5040. A sample, 0.46 g (2.0 mmol) of the latter was hydrogenated over 4 mg of PtO_2 catalyst to give 0.42 g (100%) of unpurified 6-phenylundecane; $n^{25}{}_D$ 1.4798.

Saponification of Methyl 2-Pentyl-2-phenylheptanoate. A solution of 2.9 g (0.1 mol) of the ester and 2.9 g (0.05 mol) of 85% KOH in 265 mL of 95% C_2H_5OH, containing 1.5 mL of H_2O, was refluxed for 120 h. The reaction mixture was poured into 500 mL of 10% HCl, extracted with four 100-mL of ether, dried (Na_2SO_4), and concentrated. There was obtained 1.18 g (55%) of 2-pentyl-2-phenylheptanoic acid; mp 81–82 °C (petroleum ether, bp 60–65 °C); IR 3350–2300 (m), 1790 (s), 1290 (s), 950 (s) cm^{-1}; ^{1}H NMR (CCl_4) δ 11.91 (s, 1, CO_2H), 7.28 (s, 5, C_6H_5), 1.7–2.2 (s, 4, CH_2), 0.6–1.4 (m, 18, CH_2CH_3). Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.45; H, 10.43.

Electrolysis of 2-Pentyl-2-phenylheptanoic Acid. A solution of 0.25 g (0.91 mmol) of 2-pentyl-2-phenylheptanoic acid and 0.20 g (0.91 mmol) of 25 wt % CH_3ONa in 400 mL of CH_3OH was electrolyzed in the previously described apparatus at an initial 91 V and 1.0 A. The reaction was discontinued after 1 h when a steady state of 93 V and 0.25 A had been reached. The reaction mixture was acidified and worked up to afford a residue that was purified by evaporative distillation (Kugelsrohr) to give 0.215 g (91%) of 6-methoxy-6-phenylundecane; $n^{25}{}_D$ 1.4851. It was identified by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample.

Oxidation of 2-Pentyl-2-phenylheptanal. The aldehyde was obtained by the titanium(III) cleavage of the corresponding (2,4-dinitrophenyl)hydrazone by the method of McMurry and Silvestri.[21] The product resulted in 44% yield and distilled at 114–115 °C (0.15 mm); $n^{25}{}_D$ 1.4912.

To a solution of Ag_2O, prepared from 1.75 mL (0.56 mmol) of 5% $AgNO_3$, and 0.5 g (1.11 mmol) of NaOH in 5.0 mL of H_2O, was added 70 mg (0.27 mmol) of the aldehyde. The mixture was stirred at 0 °C for 30 min, filtered, acidified with 10% HCl, and extracted with petroleum ether (bp 60–65 °C). The solvent was removed to leave 62 mg (83%) of crude 2-pentyl-2-phenylheptanoic acid, which was identified by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample.

Registry No. **1** (acid), 815-17-8; **2** (acid), 26269-42-1; **3** (acid), 89579-45-3; **3** (ethyl ester), 89579-54-4; **4** (acid), 26269-44-3; **4** (ethyl ester), 89579-55-5; **5** ($R_1 = R_2 = R_3 = CH_3$), 598-98-1; **5** ($R_1 = R_2 = R_3 = C_5H_{11}$), 89579-46-4; **5** ($R_1 = C_4H_9$, $R_2 = C_6H_{13}$, $R_3 = C_{12}H_{25}$), 89579-47-5; **5** ($R_1 = C_4H_9$, $R_2 = C_6H_{13}$, $R_3 = C_{12}H_{25}$; acid), 89579-56-6; **5** ($R_1 = R_2 = C_5H_{11}$, $R_3 = C_6H_5$), 89579-48-6; **5** ($R_1 = R_2 = C_5H_{11}$, $R_3 = C_6H_5$; acid), 89579-57-7; **6** ($R_1 = R_2 = R_3 = CH_3$), 630-19-3; **6** ($R_1 = R_2 = R_3 = C_5H_{11}$), 26269-54-5; **6** ($R_1 = R_2 = C_5H_{11}$, $R_3 = C_6H_5$), 89579-49-7; **6** ($R_1 = R_2 = C_5H_{11}$, $R_3 = C_6H_5$; (2,4-dinitrophenyl)hydrazone), 89579-50-0; **7** ($R_1 = R_2 = R_3 = CH_3$), 4026-20-4; **7** ($R_1 = R_2 = R_3 = C_5H_{11}$), 85613-93-0; **8** ($R_1 = R_2 = C_5H_{11}$, $R = C_4H_9$), 51677-36-2; **8** ($R_1 = C_5H_{11}$, $R_2 = C_6H_5$, $R = C_4H_9$), 89579-51-1; **9** ($R_1 = R_2 = C_5H_{11}$, $R_3 = C_6H_5$), 89579-52-2; **10**, 942-92-7; dodecyl bromide, 143-15-7; ethyl 3-butyl-2-cyano-2-nonenoate, 25594-05-2; ethyl 3-butyl-2-cyano-3-hexylpentadecanoate, 89579-53-3; 6-undecanone, 927-49-1; 6-phenyl-6-undecanol, 67267-86-1; 6-phenylundecane, 4537-14-8.

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Transition-Metal-Promoted Alkylations of Unsaturated Alcohols: The Ethylation of 3-Butyn-1-ol and 3-Buten-1-ol via Titanium Tetrachloride–Organoaluminum Ziegler–Natta Catalyst Systems

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Reaction of 3-butyn-1-ol with diethylaluminum chloride followed by treatment with titanium tetrachloride under a variety of conditions gave selectively up to 70% yields of (*E*)-3-hexen-1-ol, the product expected from a syn ethylmetalation of the multiple bond. No complications arising from in situ β-hydride elimination were observed. Similarly, 4-pentyn-2-ol was ethylated to give (*E*)-4-hepten-1-ol; however, 3-pentyn-1-ol did not give an ethylated product. Additionally, the effect of "third components", i.e., Lewis bases, on the ethylation of 3-butyn-1-ol and 3-buten-1-ol was studied.

Several groups have made progress in adapting Ziegler–Natta polymerization catalyst chemistry to effect the monomethylmetalation of alkene and alkyne functionalities with potential usefulness in organic synthesis.[1-5] Notable in this regard is the work of Negishi and coworkers who found that $(\eta^5\text{-}C_5H_5)_2ZrCl_2\text{–}AlMe_3$ smoothly

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