Small amounts of dialkylphosphines are formed. Data summarizing the product distribution from phosphine addition to a primary, a tertiary, and two cyclic olefins are shown in Table III. The amounts of dialkylphosphine formed are small and reflect the tendency of the more basic monoalkylphosphine to exist as RPH_3^+. Because monoalkylphosphines are more basic than phosphine and capture most of the protons present, the concentration of both olefin cation and free monoalkylphosphine is low. Hence, formation of dialkylphosphine is slow. Olefin type appears to have little effect on the product distribution.

The increased basicity of monoalkylphosphines over that of phosphine decreases carbonium ion formation in acid-catalyzed systems so that addition of RPH_2 to olefins is a slow reaction. Therefore, high yields of monoalkylphosphines can be obtained. Acid-catalyzed addition of phosphine to tertiary olefins provides a synthesis of alkylphosphines having phosphorus bonded to a tertiary carbon atom.

TABLE III

COMPOSITION OF PRODUCTS

Time = 16 hours Catalyst = CH_3SO_3H

	Olefin Reacted, Mole %	°C.	PH_3, Atm.	Product Composition, Mole %	
				RPH_2	R_2PH
Dodecene-1	28	90	41	98	2
4-Methylcyclohexene-1[a]	34	60	32	97	3
1-Methylcyclopentene-1	41	60	30	90	10
C_{12}-Polypropene	91	90	50	96	4

[a] Rapid isomerization to 1-methylcyclohexene-1 is caused by the acid catalyst.

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WHITING, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

Unsymmetrical Tetraalkylmethanes. III.[1] Syntheses from 3-Ethyl-3-methylglutaric Acid

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Two unsymmetrical tetraalkylmethanes, 11-ethyl-11-methyltricosane (X) and 11-ethyl-11-methylpentacosane (XIV), have been synthesized from 3-ethyl-3-methylglutaric acid by the reactions summarized in Chart I.

In the course of an investigation of methods for the synthesis of unsymmetrical tetraalkylmethanes, a number of procedures have been considered for building up the desired quaternary carbon atom structure. The possibility of an approach of some generality appeared to be through β,β-disubstituted glutaric acids. These compounds may be obtained from the condensation of simple or cyclic ketones with alkyl cyanoacetates according to the method of Guareschi,[4] which has been extended by Vogel.[5]

The present report describes the methods by which two relatively high molecular weight unsymmetrical tetraalkylmethanes were synthesized from 3-ethyl-3-methylglutaric acid. The reactions employed are summarized by the equations shown in Chart I.

The direct conversion of 3-ethyl-3-methylglutaric anhydride to a 3-ethyl-3-methyl-5-keto acid, such as compound XII, was suggested by the work of Newman and Smith[6] who have studied the addition of Grignard reagents to anhydrides at low temperatures. However, negative results were obtained when an ether-pyridine solution of 3-ethyl-3-methylglutaric anhydride was treated with ethylmagnesium bromide.

It was decided then to synthesize the keto acid, XII, through the ester–acid chloride, II. This compound was obtained readily from 3-ethyl-3-methylglutaric anhydride via the intermediate ester acid, I.

Percival, Wagner, and Cook[7] have prepared highly-branched ketones in quite satisfactory yields by the reaction of acid chlorides with Grignard reagents at −65° in the presence of ferric chloride. It was felt, however, that this method would have no special advantages, for the present purposes,

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[1] Paper II. N. Rabjohn and H. H. Farmer, *J. Org. Chem.*, **23**, 522 (1958).

[2] Abstracted in part from the Ph.D. thesis of H. H. Farmer, 1955.

[3] Supported in part by the Petroleum Research Fund of the American Chemical Society.

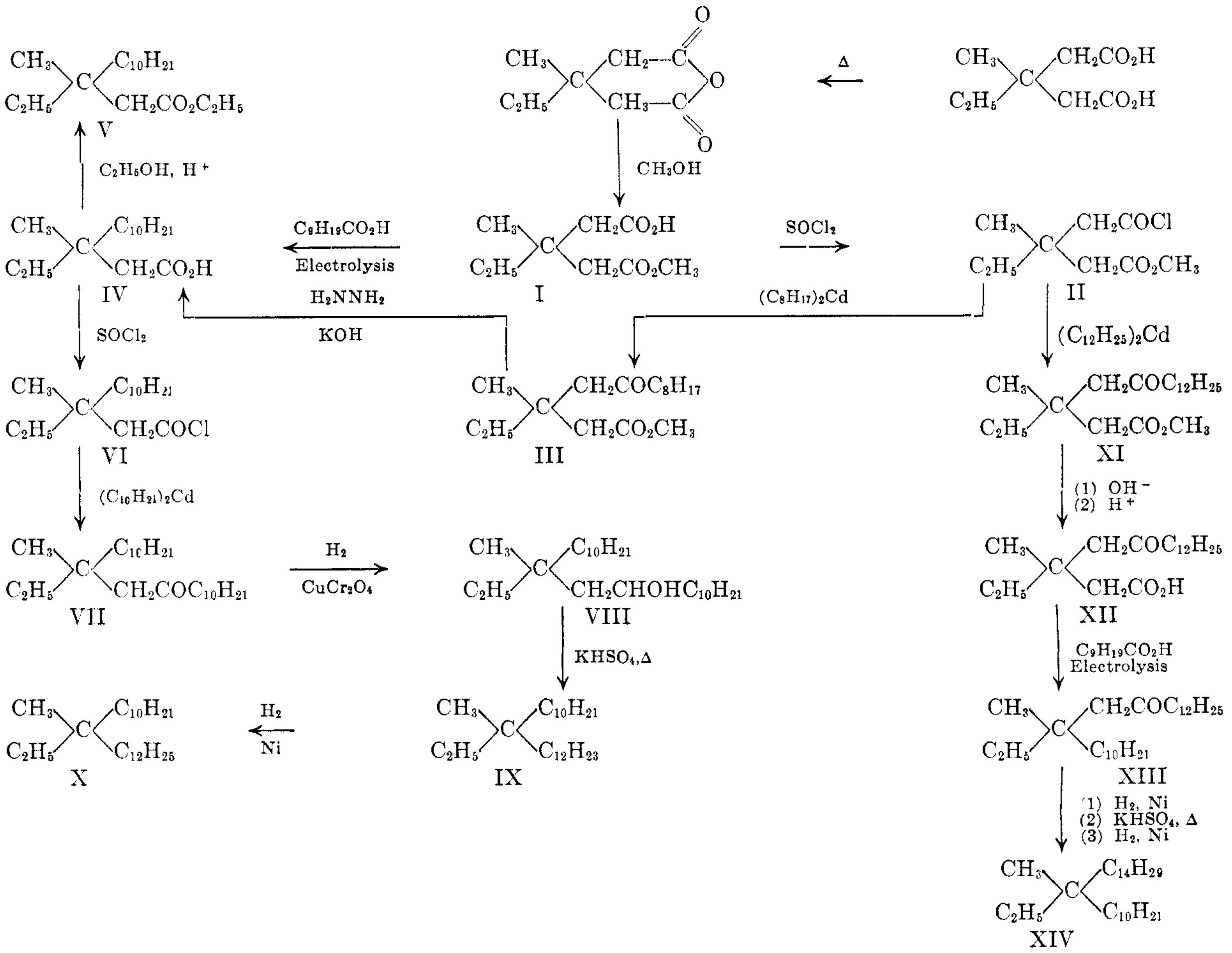
[4] I. Guareschi, *Atti. accad. sci. Torino*, **36**, 443 (1900).

[5] A. I. Vogel, *J. Chem. Soc.*, 1758 (1934).

[6] M. S. Newman and A. S. Smith, *J. Org. Chem.*, **13**, 592 (1948).

[7] W. C. Percival, R. B. Wagner, and N. C. Cook, *J. Am. Chem. Soc.*, **75**, 3731 (1953).

CHART I



over the well known use of alkylcadmium reagents since it was contemplated that only cadmium reagents from primary halides would be employed.[8]

Accordingly, the ester–acid chloride II was caused to react with dioctyl- and didodecylcadmium to give the keto esters III and XI, respectively, in good yields. An organocadmium reagent, didodecylcadmium, was used also to transform the dialkyl substituted tridecanoic acid (IV) to the branched ketone VII. The acid IV was obtained without difficulty from the keto ester III by the conventional Huang-Minlon modification of the Wolff-Kishner reaction.[9]

The Kolbe electrolysis reaction,[10] which provides one of the nicest means of extending a carbon chain, was employed to convert the acid-ester I to the acid IV, and the dialkyl substituted ketoheptadecanoic acid XII to the highly substituted ketone XIII. An electrolytic cell was employed with smooth platinum electrodes of about 150 cm.^{2} area. With this apparatus, the reactions could be carried out at a current of approximately 10 amp. at about 100 volts. The successful reactions were accomplished in yields of 30–50% in methanol with a concentration of sodium ion of about 0.05 molar. Water and isopropyl alcohol were tried as solvents, but none of the expected acid could be isolated from these runs.

The ketones VII and XIII were taken to the tetraalkylmethanes X and XIV by way of intermediate alcohols and olefins, such as VIII and IX. In the case of the transformation XIII→XIV, the intermediates were not isolated. The ketones were reduced catalytically over copper–chromium oxide and Raney nickel catalysts, with the latter appearing to be the more effective. The results of the high pressure reductions of the ketones were disappointing in that the yields were nowhere near quantitative.

The secondary alcohols were dehydrated easily at reduced pressure over potassium acid sulfate to give mixtures of olefins. The latter were reduced in the presence of Raney nickel catalyst at 150°. This relatively higher temperature appeared to be necessary to complete the reductions. The products were washed repeatedly with cold, concentrated sulfuric acid to remove any traces of olefins.

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[8] J. Cason, *Chem. Revs.*, **40**, 15 (1947).

[9] Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

[10] For leading references see B. W. Baker, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 2218 (1955) and S. Stallberg-Stenhagen, *Arkiv Kemi*, **6**, 537 (1954).

Infrared absorption spectra of the quaternary hydrocarbons X and XIV indicated that they were free of olefins and oxygen containing compounds which had been employed as intermediates in the syntheses.

The twenty-six carbon hydrocarbon, 11-ethyl-11-methyltricosane (X), was found to melt at −6 to −7° while the twenty-eight carbon compound, 11-ethyl-11-methylpentacosane (XIV), had a melting point of 6 to 8°. Their straight chain analogs are reported[11] to melt at 56–57° and 61–72°, respectively.

EXPERIMENTAL[12]

Methyl hydrogen 3-ethyl-3-methylglutarate (I). 3-Ethyl-3-methylglutaric acid[13] (334 g.) was converted to its anhydride by heating at 125–130°/25 mm. The material (275 g.) which distilled at 160–170°/25 mm. was collected and a small sample was converted to 3-ethyl-3-methylglutaric acid mono-α-naphthamide for identification purposes, m.p., 126–127°; lit.[14] anhydride, b.p. 185°/20 mm., mono-α-naphthamide, m.p. 126°. This anhydride (274 g.) was heated under reflux for 2 hr. with 100 ml. of methanol and the reaction mixture was distilled. There was obtained 250 g. (75%) of the acid ester (I); b.p. 128–130°/2 mm., n_{D}^{25} 1.4470.

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.43; H, 8.57; neut. equiv. 188. Found: C, 57.62; H, 8.51; neut. equiv. 189.

Reaction of ethylmagnesium bromide with 3-ethyl-3-methylglutaric anhydride. A solution of 23.5 g. (0.16 mole) of 3-ethyl-3-methylglutaric anhydride in 100 ml. of dry ether and 100 ml. of dry pyridine was cooled in a Dry Ice–acetone bath. It was stirred vigorously while 0.16 mole of ethylmagnesium bromide in 100 ml. of ether was added dropwise over a period of 1 hr. An insoluble, yellow complex formed as the Grignard reagent was added. The reaction mixture was stirred for an additional hour and was decomposed by pouring onto an ice and saturated ammonium chloride solution. A vigorous evolution of gas took place. The ether layer was separated and the water solution was extracted several times with ether. The combined ether solutions were extracted with 4 portions of 5% sodium bicarbonate solution and these extracts were acidified then with hydrochloric acid. Extraction of this mixture with ether afforded 2 g. of an oil which boiled at 165–170°/18 mm. It gave a positive test with 2,4-dinitrophenylhydrazine reagent, but failed to form an hydantoin derivative. It was caused to react with thionyl chloride, and the reaction product was treated with aniline; no anilide could be isolated.

4-Carbomethoxy-3-ethyl-3-methylbutanoyl chloride (II). A mixture of 23 g. (0.12 mole) of methyl hydrogen 3-ethyl-3-methylglutarate (I) and 44 g. (0.37 mole) of thionyl chloride was allowed to stand at room temperature for 36 hr. Distillation afforded 23.9 g. (95%) of the acid chloride; b.p. 120–122°/20 mm. A sample of this material was converted to an α-naphthamide derivative for identification purposes; m.p., 71–73°.

Anal. Calcd. for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40. Found: C, 72.86; H, 7.56.

Methyl 3-ethyl-3-methyl-5-ketotridecanoate (III). A Grignard reagent was prepared from 3.15 g. (0.13 g.-atom) of magnesium, 25 g. (0.13 mole) of *n*-octyl bromide, and 150 ml. of dry ether. It was treated with 14 g. (0.07 mole) of cadmium chloride, and the ether was replaced with benzene in the usual manner. A solution of 23.9 g. (0.12 mole) of 4-carbomethoxy-3-ethyl-3-methylbutanoyl chloride (II) in 50 ml. of dry benzene was added then dropwise so that the heat of the reaction just kept the solvent refluxing. After all of the acid chloride had been added, the reaction mixture was heated under reflux for 1.5 hr., allowed to cool, and poured onto a mixture of ice and water. The benzene layer was separated and the aqueous portion was extracted with benzene. The combined benzene extracts were washed with water, 5% sodium bicarbonate solution, again with water, and dried over anhydrous calcium sulfate. After removing the drying agent and solvent, the residue was distilled to give 23 g. (70%) of product; b.p., 144–146°/1 mm., n_{D}^{25} 1.4460.

Anal. Calcd. for $C_{17}H_{32}O_3$: C, 71.78; H, 11.34. Found: C, 71.74; H, 11.29.

3-Ethyl-3-methyltridecanoic acid (IV). *A.* A mixture of 20 g. (0.07 mole) of methyl 3-ethyl-3-methyl-5-ketotridecanoate (III), 14 g. of potassium hydroxide (85%), 13 ml. of 85% hydrazine hydrate, and 100 ml. of diethylene glycol was heated under reflux for 2 hr. The condenser was removed and the heating was continued until the temperature in the flask had risen to 215°. The condenser was replaced and the reaction mixture was heated at reflux temperature for 5 hr. The solution was allowed to cool, was diluted with 500 ml. of water, and was made acidic to Congo Red with hydrochloric acid. The oil which separated was taken up in ether and separated from the aqueous portion. The ether extract was dried over anhydrous calcium sulfate, the ether was removed, and the residue distilled. There was obtained 9.3 g. (51%) of product which boiled at 165–170°/1 mm., n_{D}^{25} 1.4521.

B. The Kolbe electrolysis reactions were carried out in a 2-l. resin pot with four openings on the top flange. These were fitted with a condenser, a single-blade mechanical stirrer, a two-hole rubber through which passed a copper cooling coil, and an electrode assembly. The latter consisted of an outer smooth platinum cylinder 10 cm. long and 3 cm. in diameter, an inner smooth platinum cylinder 6 cm. long and 2.5 cm. in diameter, and a coil of 20-gage platinum wire 5 cm. long and 1 cm. in diameter placed inside the inner cylinder. The outer cylinder and the central coil were attached to a common lead, and served as the anode. The metal parts were supported on a glass frame which was inserted in a rubber stopper.

The resin pot was placed in a metal bath and water at about 20° was circulated through the cooling coil and bath.

In the resin pot were placed 188 g. (1 mole) of 4-carbomethoxy-3-ethyl-3-methylbutyric acid (I), 515 g. (3 moles) of capric acid, 4 g. of sodium dissolved in methanol, and enough additional methanol to bring the total volume to about 2 l. The stirrer was located near the bottom of the outer electrode, and the solution was stirred rapidly while a current of 7 amp. was passed through the mixture for 14 hr.

The reaction mixture was transferred to a 5-l. flask and diluted with 500 ml. of water to which had been added 80 g. of potassium hydroxide. Most of the methanol was removed by distillation, and the aqueous and organic layers were separated. The aqueous layer was washed well with ether, heated, and acidified with concentrated hydrochloric acid. The material which separated was taken up in ether, and the solution was washed with water and dried over anhydrous calcium sulfate. After evaporating the ether, the residue was distilled to give 91 g. (48%) of material which boiled at 168–171°/1 mm.; n_{D}^{25} 1.4515.

Anal. Calcd. for $C_{16}H_{32}O_2$: C, 74.94; H, 12.58. Found: C, 74.83; H, 12.79.

Ethyl 3-ethyl-3-methyltridecanoate (V). A solution of 100 g. (0.4 mole) of 3-ethyl-3-methyltridecanoic acid (IV) in 500 ml. of absolute ethanol and 5 ml. of concentrated sulfuric

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(11) G. Egloff, *Physical Constants of Hydrocarbons*, Vol. V, Reinhold Publishing Co., N. Y., 1953, pp. 248, 258.

(12) All melting points are uncorrected. The authors are indebted to R. L. Elliott and R. E. Bolin for the semimicro carbon and hydrogen analyses. They would like also to thank Dr. E. E. Pickett for the infrared data.

(13) H. H. Farmer and N. Rabjohn, *Org. Syntheses*, **36**, 28 (1956).

(14) F. B. Thole and J. F. Thorpe, *J. Chem. Soc.*, **99**, 422 (1911).

acid was refluxed for 20 hr. under a Soxhlet extractor which contained calcium carbide to remove the water formed during the course of the reaction. The reaction mixture was poured slowly into about 1 l. of 5% sodium bicarbonate solution and the organic layer was taken up in ether. The ether solution was washed well with water, dried over anhydrous calcium sulfate, filtered, and concentrated. The residue was distilled to give 93 g. (84%) of ester; b.p., 132–133°/1 mm., n_D^{25} 1.4411.

Anal. Calcd. for $C_{18}H_{36}O_2$: C, 75.99; H, 12.76. Found: C, 75.67; H, 12.69.

3-Ethyl-3-methyltridecanoyl chloride (VI). From 103 g. (0.4 mole) of 3-ethyl-3-methyltridecanoic acid (IV) and 142 g. (1.2 moles) of thionyl chloride there was obtained 99 g. (90%) of acid chloride; b.p., 138–142°/1 mm.

Anal. Calcd. for $C_{16}H_{31}OCl$: C, 69.91; H, 11.37. Found: C, 69.86; H, 11.66.

11-Ethyl-11-methyl-13-ketotricosane (VII). A Grignard reagent was prepared from 9.4 g. (0.4 g.-atom) of magnesium, 88 g. (0.4 mole) of *n*-decyl bromide, and 250 ml. of dry ether. To this was added 36.6 g. (0.2 mole) of cadmium chloride, and the ether was replaced with dry benzene in the usual fashion. A solution of 99 g. (0.36 mole) of 3-ethyl-3-methyltridecanoyl chloride (VI) in 100 ml. of dry benzene then was added over a period of about 30 min. and the reaction mixture was heated under reflux for 2 hr. It was allowed to cool and was decomposed by pouring onto a mixture of ice and dilute sulfuric acid. The organic layer was separated, washed with water, and concentrated by distillation. The residue was distilled to give 45 g. (33%) of product; b.p., 178–183°/1 mm., n_D^{25} 1.4529.

Anal. Calcd. for $C_{26}H_{52}O$: C, 82.03; H, 13.77. Found: C, 82.20; H, 13.90.

11-Ethyl-11-methyl-13-tricosanol (VIII). A mixture of 38 g. (0.1 mole) of 11-ethyl-11-methyl-13-tricosanone (VII), 15 g. of copper–chromium oxide catalyst, and 50 ml. of methylcyclohexane was hydrogenated at 200° and 2500 p.s.i. for 9 hr. After removal of the catalyst and solvent, the residue was distilled to give 21.1 g. (55%) of material which boiled at 195–197°/0.5 mm.; n_D^{25} 1.4570.

Anal. Calcd. for $C_{26}H_{54}O$: C, 81.60; H, 14.22. Found: C, 81.91; H, 14.47.

11-Ethyl-11-methyl-12(13)tricosene (IX). A mixture of 20 g. (0.05 mole) of 11-ethyl-11-methyl-13-tricosanol (VIII) and 10 g. of potassium acid sulfate was heated at 150–170°/1 mm. for 10 hr. It was filtered and the filtrate was distilled to give 13.5 g. (71%) of a mixture of olefins which boiled at 176–179°/1 mm., n_D^{25} 1.4541.

Anal. Calcd. for $C_{26}H_{52}$: C, 85.63; H, 14.37. Found: C, 85.77; H, 14.52.

11-Ethyl-11-methyltricosane (X). A mixture of 14 g. (0.04 mole) of 11-ethyl-11-methyl-12(13)-tricosene (IX), 6 g. of Raney nickel catalyst, and 50 ml. of methylcyclohexane was hydrogenated at 150° and 2500 p.s.i. for 6 hr. After removal of the catalyst and solvent, the residue was distilled to afford 9.6 g. (69%) of a fraction which boiled at 180–188°/1 mm. This was washed 3 times with concentrated sulfuric acid, then with water, 5% sodium bicarbonate solution, and again with water. Upon redistillation the hydrocarbon boiled at 185–188°/1 mm., n_D^{25} 1.4496.

Anal. Calcd. for $C_{26}H_{54}$: C, 85.15; H, 14.84. Found: C, 85.20; H, 15.13.

Methyl 3-ethyl-3-methyl-5-ketoheptadecanoate (XI). A Grignard reagent was prepared from 150 g. (0.6 mole) of dodecyl bromide and 15.7 g. (0.65 g.-atom) of magnesium in 200 ml. of anhydrous ether. It was treated with 64 g. (0.35 mole) of anhydrous cadmium chloride, and the ether was replaced with 150 ml. of dry benzene in the usual fashion. A solution of (103 g. 0.5 mole) of 4-carbomethoxy-3-ethyl-3-methylbutanoyl chloride (II) in 200 ml. of benzene was added dropwise then to the organocadmium reagent. After all had been added, the mixture was heated to reflux for 2 hr., allowed to cool and poured onto ice and sulfuric acid. The benzene layer was separated, washed with water, 5% sodium bicarbonate solution, water, saturated sodium chloride solution, and finally dried over anhydrous calcium sulfate. The solvent was removed by distillation and the residue was distilled. The material which boiled at 165–195°/1 mm. was collected, and it solidified partially upon standing. It was dissolved in methanol, and on cooling there was obtained 7 g. of a white solid; m.p., 47–50°. It was presumed to be tetracosane; lit.,[15] m.p. 50–52°. The methanol was removed by distillation and the residual keto ester was distilled. There was obtained 96.5 g. (57%) of material which boiled at 178–180°/1 mm., n_D^{25} 1.4520.

Anal. Calcd. for $C_{21}H_{40}O_3$: C, 74.06; H, 11.84. Found: C, 74.04; H, 11.98.

3-Ethyl-3-methyl-5-ketoheptadecanoic acid (XII). A mixture of 94 g. (0.28 mole) of methyl 3-ethyl-3-methyl-5-ketoheptadecanoate (XI), 40 g. (1 mole) of sodium hydroxide and 1.25 l. of water was heated under reflux for 4 hr., allowed to cool, acidified with concentrated hydrochloric acid, and extracted with ether. The ether solution was concentrated and distilled to give 90 g. (99%) of acid; b.p., 201–202°/1 mm., n_D^{25} 1.4600.

Anal. Calcd. for $C_{20}H_{38}O_3$: C, 73.57; H, 11.73. Found: C, 73.46; H, 11.63.

11-Ethyl-11-methyl-13-pentacosanone (XIII). The previously described apparatus for the Kolbe electrolysis was employed. In the resin flask were placed 90 g. (0.28 mole) of 3-ethyl-3-methyl-5-ketoheptadecanoic acid (XII), 258 g. (1.5 moles) of capric acid, 2 g. of sodium dissolved in methanol, and enough methanol to bring the volume of the solution to approximately 2 l. A current of 7–8 amp. was passed through the reaction mixture for 8 hr. It was transferred to a 3-l. flask, 56 g. (0.85 mole) of 85% potassium hydroxide was added, and the mixture was distilled slowly until 500 ml. of methanol had been collected. To the residue was added 1 l. of water and the distillation was continued until the temperature of the distillate reached 100°. The mixture was allowed to cool, the layers were separated, and the aqueous layer was extracted twice with petroleum ether (b.p. 60–68°). The aqueous solution was acidified, extracted with ether, and worked up to give 21 g. of crude 3-ethyl-3-methyl-5-ketoheptadecanoic acid; b.p. 130–185°/1 mm.

The combined organic layers were washed with water, the petroleum ether removed by distillation, and the residue was distilled to afford 27.4 g. (25%) of ketone which boiled at 215–217°/0.5 mm., n_D^{25} 1.4521.

Anal. Calcd. for $C_{28}H_{56}O$: C, 82.27; H, 13.81. Found: C, 82.04; H, 13.97.

11-Ethyl-11-methylpentacosane (XIV). A mixture of 27.4 g. (0.07 mole) of 11-ethyl-1-methyl-13-pentacosanone (XIII), 10 g. of Raney nickel catalyst, and 50 ml. of methylcyclohexane was hydrogenated at 150° and 2700 p.s.i. for 10 hr. The catalyst was removed by filtration, and the filtrate was concentrated to remove the solvent. The residue was heated then with 10 g. of potassium acid sulfate at 150–160°/1 mm. for 8 hr. The reaction mixture was filtered to remove the dehydrating agent. The filtrate was distilled to give 16.1 g. of a mixture of olefins which boiled at 190–197°/0.5 mm.; n_D^{25} 1.4531. This material was dissolved in 50 ml. of methylcyclohexane, 6 g. of Raney nickel catalyst was added, and the mixture was hydrogenated at 150° and 2000 p.s.i. for 7 hr. The catalyst was removed by filtration and the solvent was evaporated. The residue was treated with three 25-ml. portions of concentrated sulfuric acid. The hydrocarbon was dissolved in petroleum ether (b.p. 60–68°) and the solution was washed with water, 5% sodium bicarbonate solution, again with water, and dried. After removing the solvent, there was obtained 10.1 g. (43% based on original ketone) of hydrocarbon which boiled at 181–183°/1 mm., n_D^{25} 1.4496.

Anal. Calcd. for $C_{28}H_{58}$: C, 85.19; H, 14.81. Found: C, 85.40; H, 14.98.

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(15) Ref. (11), p. 244.