Ether (IX) from Methyl 3-Oxo-2-decarboxyceanothate (IVb).—A solution of IVb (250 mg.), m.p. 123°, in dry ether was added to a slurry of lithium aluminum hydride (250 mg.) in ether (30 cc.). The reaction mixture was refluxed for 5 hr. A saturated solution of sodium sulfate was added dropwise until a clear ether solution was obtained. Evaporation to dryness yielded 206 mg. of an oil which was used without further purification. The oil (VII) showed $\nu_{\max}$ 1640 and 886 cm.$^{-1}$ (terminal methylene group).

A solution of 150 mg. of oil VII in ethanol (45 cc.) and hydrochloric acid (7.5 cc.) was boiled under reflux for 5 hr. The solution was cooled with ice and sodium hydroxide (7 gr.) in water (25 cc.) was added. The organic material was extracted with ether. Evaporation of the ether gave 140 mg. of an amorphous compound (VIII), which was used directly for the next stage. Compound VIII showed no absorption bands for terminal methylene or ketone in the infrared spectrum.

Compound VIII (140 mg.) was dissolved in 20 cc. of acetone and oxidized with 0.4 cc. of a 8 *N* solution of chromic acid in sulfuric acid. After 2 min. methanol (5 cc.) was added and the mixture poured over ice. The organic material was extracted with ether. The ether solution was washed with water, dried over sodium sulfate, and evaporated to dryness. The oil obtained was chromatographed on 16 g. of F-20 (basic Alcoa) alumina. The material eluted with petroleum ether: benzene (2:1) was crystallized with methanol giving 57 mg. of compound IX, m.p. 220–224°. The analytical sample showed m.p. 224–226°, $[\alpha]_D$ +155°, $\nu_{\max}$ 1740 cm.$^{-1}$ (ketone on a five-membered ring).

Anal. Calcd. for $C_{29}H_{46}O_2$: C, 81.63; H, 10.87. Found: C, 81.76; H, 10.70.

Pyrolysis of Ceanothic Acid.—Compound X was obtained on pyrolysis of ceanothic acid as described by Julian.[6] Complex X showed m.p. 230–232° (rep. 234°), $\nu_{\max}$ 758 cm.$^{-1}$, 886 cm.$^{-1}$, and 1700 cm.$^{-1}$.

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Syntheses of 9-Keto- and 10-Hydroxy-*trans*-2-decenoic Acids and Related Compounds

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The syntheses of 9-keto- and 10-hydroxy-*trans*-2-decenoic acids noted for Queen Substance[1] and Royal Jelly acid,[2] respectively, of the honey bee have been described. A new synthesis of the keto acid as outlined below was found to be satisfactory:

$$\underset{\text{I}}{\mathrm{I(CH_2)_6C{\equiv}CH}} \xrightarrow{\mathrm{(CH_3)_3NO}} \underset{\text{II}}{\mathrm{OCH(CH_2)_5C{\equiv}CH}} \xrightarrow{\mathrm{CH_2(CO_2H)_2}}$$

$$\underset{\text{III}}{\mathrm{HO_2CCH{=}CH(CH_2)_5C{\equiv}CH}} \xrightarrow[\mathrm{HgSO_4}]{\mathrm{HCO_2H,\ H_2O}} \underset{\text{IV}}{\mathrm{HO_2CCH{=}CH(CH_2)_5COCH_3}}$$

The oxidation of 8-iodo-1-octyne (I) with trimethylamine oxide was effected as described for octanal by Franzen and Otto[3] with a yield of 69%, and the 7-octynal (II) obtained was condensed with malonic acid under Doebner's conditions[4] to afford 9-decyne-*trans*-2-enoic acid (III) in 65% yield. When the latter was hydrated by means of formic acid in the presence of mercuric sulfate,[5] 9-keto-*trans*-2-decenoic acid (IV) was obtained in almost quantitative yield. Observed physical constants including infrared spectra as well as analyses supported the constitution.

10-Hydroxy-*trans*-2-decenoic acid was prepared according to the following scheme:

$$\underset{\text{V}}{\mathrm{CH_2{=}CH(CH_2)_6CO_2H}} \longrightarrow \underset{\text{VI}}{\mathrm{CH_2{=}CH(CH_2)_7OH}} \xrightarrow{\mathrm{HCO_3H}}$$

$$\underset{\text{VII}}{\mathrm{CH_2OHCHOH(CH_2)_7OH}} \longrightarrow \underset{\text{VIII}}{\mathrm{OCH(CH_2)_7OH}} \xrightarrow{\mathrm{CH_2(CO_2H)_2}} \underset{\text{IX}}{\mathrm{HO_2CCH{=}CH(CH_2)_7OH}}$$

Since the condensation of 8-hydroxyoctanal (VIII) with malonic acid has been reported by Fujii and his collaborators,[2c] the description will be confined to the preparation of VIII.

8-Nonenoic acid (V) was prepared by double Barbier-Wieland degradations of 10-undecenoic acid in 25% yield based on the ethyl ester. The preparation of V starting from tetrahydrofurfuryl alcohol[6] required several steps and proved impractical. An alternative method described by Stetter and Dierichs[7] was unsuitable because positive evidence for the migration of the terminal double bond was obtained.

Reduction of the ethyl ester of V with lithium aluminum hydride gave 8-nonenol (VI), which was successively dihydroxylated by means of performic acid[8] to give *dl*-1,2,9-trihydroxynonane (VII) in 80% yield.

Treatment of the triol with periodate[9] gave VIII.[10]

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Preparations of other triols which gave VIII upon glycol fission have been explored as follows:

Ethyl 9-undecynoate[11,12] prepared by treating 10,11-dibromoundecanoic acid with concentrated alkali[13] followed by esterification was degradated by the Barbier-Wieland method to 8-decynoic acid, whose ethyl ester was converted to *cis*-8-decenol by hydrogenation over the Lindlar's catalyst[14] followed by reduction with lithium aluminum hydride. This unsaturated carbinol was dihydroxylated to afford *threo*-1,8,9-trihydroxydecane in 75% yield. This triol gave VIII when treated with periodate.

9-Decenoic acid[13,15] was isomerized by heating over 200° with potassium hydroxide in diethylene glycol to afford 8-decenoic acid, presumably in a form of an equilibrium mixture of *cis*- and *trans*-isomers.[16] Oxidation with chromic acid gave suberic acid in 70% yield. Ethyl 8-decenoate was converted similarly to 8-decenol and to the nonvolatile 1,8,9-triol.

The preparation of other homologous hydroxyaldehydes and of ω-hydroxy-α,β-unsaturated acids therefrom will be described below.

Trihydroxyoctadecane[17] prepared from commercial oleyl alcohol was cleaved by periodate to afford 9-hydroxynonanal.[18]

Aleuritic acid, 9,10,16-trihydroxyhexadecanoic acid, obtained from shellac resin[19] was subjected to the glycol fission and 7-hydroxyheptanol[20] was secured as a sole neutral product.

Performic acid oxidation of 10-undecenol[21] gave 1,2,11-trihydroxyundecane in 91.8% yield, and the successive glycol fission resulted in the formation of 10-hydroxydecanal.[10]

All these ω-hydroxyaldehydes were exceedingly unstable and polymerized to rubberlike or gelatinous materials on standing in the air. Crude hydroxyaldehydes, however, afforded ω-hydroxy-α,β-unsaturated acids in no less than 40% yields when used immediately after isolation in the subsequent condensation with malonic acid. Thus 9-hydroxy-*trans*-2-nonenoic acid, 11-hydroxy-*trans*-2-undecenoic acid and 12-hydroxy-*trans*-2-dodecenoic acid[2a] were obtained from 7-hydroxyheptanal, 9-hydroxynonanal, and 10-hydroxydecanal, respectively.

Experimental[22]

8-Iodo-1-octyne (I).—A solution of 22 g. of 8-chloro-1-octyne[23] and 34 g. of sodium iodide in 300 ml. of acetone was heated under reflux for 24 hr. and precipitates were removed by filtration. Evaporation of the filtrate followed by distillation *in vacuo* afforded 18.6 g. (60%) of 8-iodo-1-octyne as a colorless liquid b.p. 115–117° (19 mm.), n^{16}_D 1.5078.

Anal. Calcd. for $C_8H_{13}I$: C, 40.69; H, 5.55. Found: C, 40.07; H, 5.68.

7-Octynal (II).—To a solution of 15 g. (0.2 mole) of trimethylamine oxide[3] in 200 ml. of chloroform was added 16.1 g. (0.068 mole) of I under ice-cooling over a period of 45 min. After refluxing for 1 hr. the reaction mixture was decomposed with 60 ml. of 2 *N* hydrochloric acid. The organic layer was separated, washed with water, and dried ($MgSO_4$). Evaporation of chloroform followed by distillation *in vacuo* gave 5.8 g. (69%) of II, b.p. 82–85° (16 mm.) n^{14}_D 1.4658, ν_{max} (liquid film) at 3300, 2760, 2160, 1758, cm.$^{-1}$. Since II was quite unstable, its 2,4-dinitrophenylhydrazone, m.p. 93.5–95.5° (from ethanol) was analyzed.

Anal. Calcd. for $C_{14}H_{16}O_4N_4$: C, 55.25; H, 5.30. Found: C, 55.58; H, 5.43.

9-Decyne-*trans*-2-enoic Acid (III).—To an ice-cooled solution of 4 g. (0.04 mole) of malonic acid in 16 ml. of pyridine was added 3.2 g. (0.025 mole) of II in a course of 10 min. After adding 1 ml. of piperidine to the solution the mixture was kept in the dark at 50° for 33 hr. and at room temperature for an additional 28 hr. The reaction mixture was poured into 60 ml. of water and the product was extracted with ether. The ethereal solution was washed with dilute hydrochloric acid and water and dried ($MgSO_4$). Recrystallizations of the evaporation residue from petroleum ether (b.p. 40–60°) gave 2.8 g. (65%) of III as colorless prisms, m.p. 47.5–48.5°, ν_{max} (Nujol) at 3260, 2099, 1691, 1635, 990 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.97; H, 8.45.

9-Keto-*trans*-2-decenoic Acid (IV).—To a solution of 0.2 g. of mercuric sulfate in 15 ml. of 80% formic acid was added 0.49 g. of III with stirring and the mixture was heated on a boiling water bath for 50 min. After cooling, the black precipitate was removed by filtration and the filtrate was dilute with 10 ml. of water and extracted with ether. The ethereal solution was washed with water and dried ($MgSO_4$). Evaporation of the solvent afforded a waxy material, m.p. 49.5–52.0°. Two recrystallizations from a mixture of petroleum ether (b.p. 40–60°) and ethyl ether afforded 0.5 g. (99%) of the keto acid, m.p. 54–55° (reported[1c] m.p. 54–55°) as colorless prisms, which gave correct analyses for carbon and hydrogen, ν_{max} (Nujol) at 1710, 1690, 1640, 993 cm.$^{-1}$ [reported[1c] λ_{max} (Nujol) at 5.83, 5.90, 6.07 μ].

8-Nonen-1-ol (VI) from 9-Decenoic Acid.—Esterification of 57 g. of 9-decenoic acid[13] in the conventional manner gave 65.6 g. (95%) of ethyl 9-decenoate, b.p. 135° (27.5 mm.), n^{22}_D 1.4366.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.72; H, 11.14.

To a Grignard reagent prepared from 54.9 g. (0.35 mole) of bromobenzene and 9.3 g. of magnesium in 110 ml. of ether was added 30 g. (0.302 mole) of ethyl 9-decenoate. Dehydration of the resulting crude carbinol followed by distillation *in vacuo* gave 71.9 g. (81.7%) of 1,1-diphenyl-1,9-decadiene, b.p. 174° (5 mm.), n^{22}_D 1.5540.

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Anal. Calcd. for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 90.58; H, 9.29.

Oxidation of 50 g. of the aforementioned diene dissolved in 500 ml. of glacial acetic acid with 36.2 g. of chromic acid in 40 ml. of water gave 15.7 g. (58%) of 8-nonenoic acid (V), b.p. 113–114° (3 mm.), n^{20}_D 1.4492 [reported[5] b.p. 116–118° (1 mm.), n^{15}_D 1.4492; b.p. 145° (15 mm.)[24]]. The *p*-phenylphenacyl ester prepared by the usual manner[25] melted at 54.5–55.3° after single recrystallization from ethanol.

Anal. Calcd. for $C_{23}H_{26}O_3$: C, 78.82; H, 7.48. Found: C, 78.86; H, 7.40.

Reduction of 20.2 g. (0.11 mole) of ethyl 8-nonenoate, b.p. 117–118° (20 mm.), n^{22}_D 1.4352 [reported[6] b.p. 114–116° (15 mm.)], prepared from V with 2.6 g. of lithium aluminum hydride in 100 ml. of ether gave 15.2 g. (97%) of 8-nonen-1-ol (VI), b.p. 133–134° (20 mm.), n^{22}_D 1.4452 [reported[6] b.p. 135° (20 mm.), n^{23}_D 1.4450], ν_{max} (liquid film) at 990, 910 cm.$^{-1}$. The sample gave correct analyses.

***dl*-1,2,9-Trihydroxynonane (VII).**—To a solution of 14.2 g. (0.1 mole) of VI in 80 ml. of 99% formic acid was added 11.4 g. of 30% hydrogen peroxide under vigorous stirring at 40°. After 3 hr. at the same temperature, the solvent was removed under diminished pressure. To the residue 107 ml. of 2 *N* alcoholic potassium hydroxide was added and heated under reflux for 1 hr. Ethanol was removed under diminished pressure and the residue was poured into 100 ml. of hot water with vigorous agitation. The oily layer was separated, dissolved into 200 ml. of ethyl acetate, and dried ($MgSO_4$). Evaporation of the solvent furnished 15.0 g. (80%) of crude triol as a colorless liquid. This was refluxed with 66 g. of acetic anhydride in the presence of 7 g. sodium acetate for 2 hr. and triacetate thus obtained was purified by distillation. A fraction (21.6 g.), b.p. 176° (8 mm.), n^{22}_D 1.4419, weighed 216 g. (71.5% yield based on VI).

Anal. Calcd. for $C_{15}H_{26}O_6$: C, 59.58; H, 8.67. Found: C, 59.73; H, 8.63.

8-Decen-1-ol from 9-Decenoic Acid.—A mixture of 42.5 g. (0.25 mole) of 9-decenoic acid[13] and 74 g. of potassium hydroxide dissolved in 400 ml. of diethylene glycol was heated under reflux at 200–210° for 15 hr. The hot reaction mixture was poured into 2 l. of water and strongly acidified with concentrated hydrochloric acid. The acid organic layer was extracted with ether and the ethereal solution was washed with water and dried ($MgSO_4$). Evaporation of the ether followed by distillation afforded impure 8-decenoic acid, b.p. 126–127° (6.5 mm.), n^{28}_D 1.4490, iodine value (Wijs) 136.8. Esterification in a conventional way followed by distillation gave 45.6 g. (92.3%) of ethyl 8-decenoate, b.p. 135–136° (33 mm.), n^{27}_D 1.4379, iodine value (Wijs) 127.9: calcd. 128.5; ν_{max}(liquid film) at 965 cm.$^{-1}$, not at 990 and 910 cm.$^{-1}$. Saponification followed by vacuum distillation afforded pure 8-decenoic acid, b.p. 122–123° (4 mm.), n^{29}_D 1.4475 [reported[26] b.p. 155–157° (14 mm.)], iodine value (Wijs) 149.7; calcd. 149.1, yield 36.7 g. or 86.1% as calculated on the basis of the starting acid; ν_{max} (liquid film) at 965 cm.$^{-1}$, not at 990 and 910 cm.$^{-1}$.

The *p*-phenylphenacyl ester of 8-decenoic acid, m.p. 59.0–58.9° (from ethanol) showed a distinct depression of m.p. when admixed with the ester derived from 9-decenoic acid, m.p. 59.0–60.1°.

Anal. Calcd. for $C_{24}H_{28}O_3$: C, 79.09; H, 7.74. Found for 8-isomer: C, 79.23; H, 7.88, for 9-isomer: C, 79.12; H, 7.81.

As given for the preparation of VI, 39.6 g. (0.2 mole) of ethyl 8-decenoate was reduced with 4.8 g. of lithium aluminum hydride in 120 ml. of ether to afford 27.3 g. (87.2%) of 8-decen-1-ol, b.p. 96–97° (7 mm.), n^{25}_D 1.4500.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.51; H, 13.04.

***cis*-8-Decen-1-ol from 9-Undecynoic Acid.**—Ethyl 9-undecynoate, b.p. 150° (18 mm.), n^{18}_D 1.4508, was prepared according to the published procedure[11] [reported[11] b.p. 197° (49 mm.)] and its infrared spectrum has no absorption maximum in the 3300 and 2140–2100 cm.$^{-1}$ regions. Treatment of 80 g. of ethyl 9-undecynoate with phenylmagnesium bromide prepared from 130 g. of bromobenzene and 20.5 g. of magnesium in 300 ml. of ether followed by usual work-up[13] gave 83 g. (79%) of 1,1-diphenyl-1,9-undeceyne, b.p. 215° (6 mm.) as a viscous oil.

Anal. Calcd. for $C_{23}H_{26}$: C, 91.33; H, 8.67. Found: C, 90.99; H, 8.70.

Oxidation of 82 g. of the 1,1-diphenyl-1,9-undecenyne with chromium oxide in acetic acid in the same manner as described before gave 27 g. (53%) of 8-decynoic acid, b.p. 122° (0.2 mm.), m.p. 38.5–39°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.19; H, 9.51.

Esterification of 27 g. of 8-decynoic acid in the usual way gave 25.3 g. (80.5%) of ethyl 8-decynoate, b.p. 102–104° (3 mm.).

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.31; H, 10.13.

Partial hydrogenation of 25 g. (0.128 mole) of ethyl 8-decynoate in 130 ml. of ethanol at atmospheric pressure in the presence of 5 g. of the Lindlar's catalyst[14] gave 21.0 g. (80%) of ethyl *cis*-8-decenoate, b.p. 128–130° (23 mm.).

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.60; H, 11.02.

Reduction of 21.0 g. of ethyl *cis*-8-decenoate with 3 g. of lithium aluminum hydride afforded 14.3 g. (86%) of *cis*-8-decen-1-ol, b.p. 130° (29 mm.).

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.93; H, 13.02.

1,8,9-Trihydroxydecane.—Hydroxylation of 23.5 g. of 8-decen-1-ol (isomeric mixture) was effected by the same procedure for the preparation of VII and 29.1 g. of crude triol was obtained. Acetylation of the triol gave 33.6 g. (70.9%) of triacetate, b.p. 161.5–162.5° (3.5 mm.), n^{22}_D 1.4429.

Anal. Calcd. for $C_{16}H_{28}O_6$: C, 60.74; H, 8.92. Found: C, 60.39; H, 8.97.

1,2,11-Trihydroxyundecane.—As given above 10-undecen-1-ol[21] was dihydroxylated to give 1,2,11-trihydroxyundecane, m.p. 74–75° (from ethyl acetate), in 91.8% yield.

Anal. Calcd. for $C_{11}H_{24}O_3$: C, 64.66; H, 11.84. Found: C, 64.46; H, 11.74.

11-Hydroxy-*trans*-2-undecenoic Acid.—To a solution of 10 g. of *threo*-1,9,10-trihydroxyhexadecane[17] in 400 ml. of ethanol was added a solution of 7.5 g. of potassium periodate in 400 ml. of 1 *N* sulfuric acid under vigorous stirring at 40° in a course of 20 min. After 10 min. the turbid solution was cooled to 15° and diluted with 2 l. of water. The organic layer was extracted with ether and the ethereal solution was washed with water. Evaporation of ether gave an oily residue which was successively steam-distilled in the presence of 0.5 g. of hydroquinone. The nonvolatile portion was extracted with ether and dried ($MgSO_4$). Evaporation of the solvent afforded 4.0 g. (77%) of an oily substance which gradually polymerized to a gelatinous material. The 2,4-dinitrophenylhydrazone from the freshly prepared crude hydroxyaldehyde melted at 66–67° (reported[18] m.p. 69°). A mixture of 14.4 g. of the crude hydroxyaldehyde, 10 g. of malonic acid, and 25 ml. of pyridine was kept at room temperature for 1 week with occasional shaking and then heated

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(24) A. Seher, *Fette, Seifen, Anstrichmittel*, **58**, 1077 (1956).

(25) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p. 200.

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on a boiling water bath for 2 hr. After cooling, 50 ml. of water was added and extracted with ether. The ethereal solution was washed with dilute hydrochloric acid and successively extracted three times with 50-ml. portions of 5% aqueous sodium hydroxide. Acidification of the aqueous alkaline solution with dilute hydrochloric acid followed by extraction with ether furnished an oily material which solidified on cooling in Dry Ice–methanol bath. Recrystallizations from a mixture of *n*-hexane and ethyl ether gave 7.2 g. (40%) of colorless crystals, m.p. 66–67.5°.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.88; H, 10.04.

The infrared spectrum (Nujol) showed absorption maxima at 3390, 1690, 1685, and 975 cm.$^{-1}$. Reported absorption maxima for natural Royal Jelly acid[27] (Nujol) are at 3390, 1710, 1658, and 976 cm.$^{-1}$ and for the synthetic one[1a] (Nujol), at 2.92, 5.89, and 6.05 μ.

In an analogous way 8-hydroxyoctanal [2,4-dinitrophenylhydrazone, m.p. 64 and 87–96° (double melting points) reported[10] m.p. 91–93°], and 10-hydroxy-*trans*-2-decenoic acid were obtained from *dl*-1,2,9-trihydroxynonane as well as 1,8,9-trihydroxydecane, and 10-hydroxydecanal (2,4-dinitrophenylhydrazone, m.p. 100°; reported[10] m.p. 101–103°) and 12-hydroxy-*trans*-2-dodecenoic acid[1a] were obtained from 1,2,11-trihydroxyundecane.

Migration of the Double Bond in Nonenoic Acid During the Preparation from 2-Allylcyclohexane-1,3-dione.—2-Allylcyclohexane-1,3-dione was treated exactly according to the published procedure[7] and the acid obtained was purified by esterification followed by saponification, b.p. 110–114° (2.5 mm.), iodine value (Wijs) found, 156; calcd. for nonenoic acid, 162.

Oxidation of 5 g. (0.032 mole) of this acid with a solution of 23.5 g. of potassium permanganate in 500 ml. of water under slightly alkaline conditions gave 3.5 g. of a mixture of dibasic acids, m.p. 83–93°. Neutralization value found, 696; calcd. for pimeric acid, 701; for suberic acid, 644. This mixture was fractionally recrystallized from water into suberic acid, m.p. 139–141°, and pimelic acid, m.p. 95–97°; both were identified by mixed melting points with authentic specimens as well as by analyses for carbon and hydrogen.

9-Hydroxy-*trans*-2-nonenoic Acid from Alueritic Acid.—Aleuritic acid, m.p. 99.8–100.1° (reported[28] m.p. 100–101°), was obtained from commercial wax-free shellac resin according to the published procedure.[19] To a solution of 4 g. of potassium periodate in 200 ml. of 1 *N* sulfuric acid was added a solution of 5 g. of aleuritic acid in 400 ml. of ethanol and the mixture was kept at 35–40° for 20 min. with vigorous agitation. The reaction mixture was diluted with 500 ml. of water and extracted repeatedly with ether. The ethereal solution was washed with aqueous sodium bicarbonate and water and dried ($MgSO_4$). Evaporation of ether afforded crude hydroxy aldehyde, the 2,4-dinitrophenylhydrazone of which melted at 82.5–85° and gave correct analyses for carbon and hydrogen (reported[20] m.p. 99.5°). A mixture of the crude hydroxyaldehyde thus obtained, 4 g. of malonic acid, 8 ml. of pyridine, and 1 ml. of piperidine was treated in the same manner as described for 11-hydroxy-*trans*-2-undecenoic acid, and 1 g. of crude hydroxy acid, m.p. 58–60° was obtained. Recrystallizations from a mixture of petroleum ether (b.p. 40–60°) and ethyl ether gave 9-hydroxy-*trans*-2-nonenoic acid, m.p. 64.5–65.5°, ν_{max} (Nujol) at 3365, 1686, 1658, 984 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.88; H, 9.45.

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Electrolysis of Quaternary Phosphonium Salts

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Horner and co-workers[1,2] have recently reported the formation of tertiary phosphines from the electrolysis of various quaternary phosphonium halides. The present note describes the electrolysis of some other quaternary phosphonium salts under different conditions.

We have found that the electrolysis of several substituted triphenylphosphonium nitrates and trifluoroacetates at an aluminum cathode and a gold or platinum anode in a single-compartment cell yields triphenylphosphine oxide. This is in contrast to the results of Horner who found that, in a divided cell, phosphines were formed at a mercury or lead cathode.

The original purpose of this work was to investigate the use of quaternary phosphonium salts in the dimerization reaction previously described for ammonium salts.[3,4] Although bibenzyl was obtained in 31% yield (along with 35% of triphenylphosphine oxide) from the electrolysis of benzyltriphenylphosphonium nitrate in dimethylformamide, no dimer was obtained from the electrolysis of allyltriphenylphosphonium nitrate or 9-fluorenyltriphenylphosphonium nitrate. Each of these electrolyses afforded substantial amounts of triphenylphosphine oxide. The reaction mixtures were in general much less convenient to work with than those resulting from the electrolysis of quaternary ammonium salts.

It is possible that the quaternary phosphonium salt is first cleaved to a hydrocarbon radical and triphenylphosphine which is then oxidized to triphenylphosphine oxide. In actual fact, the electrolysis of benzyltriphenylphosphonium nitrate in methanol gave 5% of triphenylphosphine in addition to 44% of triphenylphosphine oxide.

Further evidence in support of such a reaction path is obtained from the electrolysis of triphenylphosphine in methanol in the presence of ammonium nitrate. In an undivided cell with an aluminum cathode and a platinum anode a yield of 54% of triphenylphosphine oxide is obtained.

Another possible mechanism for the formation of triphenylphosphine oxide is the oxidation of triphenylphosphine by nitrate ion. That such a reac-

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