TABLE I

VAPOR PRESSURE AND HEAT OF SUBLIMATION OF GRAPHITE FILAMENTS

Expt.	T, °K.	Wt. loss, g./sq. cm. sec.	αP, atm.	ΔE_0°, kcal./mole (based on $\alpha = 1$)
1	2503	1.111×10^{-7}	3.62×10^{-8}	177.6
2	2509	1.666×10^{-7}	5.45×10^{-8}	175.9
4	2622	7.370×10^{-7}	2.46×10^{-7}	176.1
6	2633	4.028×10^{-7}	1.35×10^{-7}	180.0
8	2614	4.205×10^{-7}	1.40×10^{-7}	178.5
9	2702	1.944×10^{-6}	6.59×10^{-7}	176.2
10	2413	2.778×10^{-8}	8.90×10^{-9}	177.8
11	2407	2.162×10^{-8}	6.92×10^{-9}	178.6
15	2902	1.488×10^{-5}	5.22×10^{-6}	177.4
16	2879	2.211×10^{-5}	7.73×10^{-6}	173.5
19	2872	1.363×10^{-5}	4.76×10^{-6}	176.0
21	2662	9.090×10^{-7}	3.05×10^{-7}	177.6
22	2770	4.522×10^{-6}	1.55×10^{-6}	175.9

applied to our data would give a value of 141 kcal./mole for ΔE_0°. However, conversely a number of experimental investigations on the vapor pressures of metal filaments have shown that the accommodation coefficients are near unity.

Spectroscopically pure carbon filaments, $^1/_{16}''$ in diameter and 6″ long, were obtained from the Union Carbon Company. These were inserted in large carbon blocks and placed in a vacuum bulb. The filaments were baked out for several hours at temperatures above 2000°K. to remove any remaining impurities. The temperature measurements were made with an optical pyrometer which was calibrated against a Bureau of Standards tungsten ribbon. The emissivity of carbon was obtained from the "International Critical Tables." The temperature was measured over the length of the filament and found to be constant to ±5°K. The filaments were heated by direct current to the desired temperature and weighed at the end of a run for the weight loss due to evaporation. For the temperature range from 2400–2900°K. nearly the entire length of the filament was at the maximum temperature.

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Synthesis of Unsaturated Fatty Acids: Vaccenic Acid

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In an earlier paper,[2] a synthesis of vaccenic acid (*trans*-11-octadecenoic acid)[3–5] was reported according to the following sequence: 11-chloroundecene-1, methyl 12-tridecenoate, the allylically brominated ester and, as the product of coupling the bromo ester with pentylmagnesium bromide, vaccenic acid. We have found that more satisfactory results are obtained at the coupling stage by conducting the reaction not with the allylically brominated ester but with allylically brominated 11-chloroundecene-1. The present report describes a vaccenic acid synthesis utilizing the alternate coupling reaction and proceeding by way of the following compounds: 11-chloroundecene-1 (88% yield from undecylenic acid[2]), allylically brominated 11-chloroundecene-1 (30–40%), 16-chlorohexadecene-7 (51%), hexadecenylmalonic ester (75%) and vaccenic acid (40%).

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Experimental[6]

Allylic Bromination of 11-Chloroundecene-1.—A mixture of 144 g. (0.765 mole) of 11-chloroundecene-1,[2] 46 g. (0.255 mole) of N-bromosuccinimide (97% by titration) and 400 ml. of carbon tetrachloride was boiled under a reflux condenser for 16 hours. Solids were removed by filtration from the reaction mixture, and the carbon tetrachloride solvent stripped from the filtrate. The residue was treated with ten volumes of light petroleum ether and allowed to stand in the cold overnight. The dark-brown oil deposited on the bottom of the flask was separated by decantation, and was discarded. The petroleum ether solution, after thorough washing with several portions of water, was dried over anhydrous magnesium sulfate.

Distillation of the dry solution first at atmospheric pressure and then under reduced pressure afforded 86 g. of distillate, b.p. 68–74° (0.5 mm.) with bath temperatures up to 100°, and 54 g. of residue. The distillate (n^{25}D 1.4490) was largely unreacted 11-chloroundecene-1. Addition of petroleum ether to the residue resulted again in two layers. The lighter petroleum ether layer was separated from the heavy brown oil and, after removal of solvent, the residue was distilled using an unpacked, vacuum-jacketed column, 3 inches in length and 2 cm. in diameter. Two fractions were taken as follows: (a) 6 g., b.p. 100° (0.005 mm.) with bath temperatures up to 150°, n^{25}D 1.4690; and (b) 32 g., b.p. 100–130° (0.005–0.01 mm.) with bath temperature 150–200°. Fraction (a) together with the starting material recovered in the first distillation was redistilled. The small amount of residue remaining after removal of the starting material was combined with fraction (b) and again distilled. Bromochloroundecene was obtained at b.p. 106–120° (0.001 mm.) at bath temperature 150–160°, n^{25}D 1.4945, in 27 g. yield, which amount corresponded to a 13% yield uncorrected for recovered excess 11-chloroundecene-1. The yield based on N-bromosuccinimide was 40%; the yield based on 11-chloroundecene-1 not recovered was approximately the same. Five and one-half grams of higher boiling material, n^{25}D 1.5030, b.p. 120–130° (0.001–0.004 mm.) with bath temperature 160–200°, which was probably the dibrominated product (see below), was also obtained.

In an experiment similar to this but in which equimolar amounts of reactants were used, the monobromination product, n^{25}D 1.4945, was obtained in 12% yield, b.p. 110–125° (0.003 mm.) at bath temperature 140–150°.

Anal. Calcd. for $C_{11}H_{20}BrCl$: C, 49.4; H, 7.5. Found: C, 49.2; H, 7.4.

Also obtained (15%) was a higher boiling material, n^{25}D 1.5062, b.p. 135–150° (0.01 mm.) with bath temperature 160–220°, which proved to be a dibromochloroundecene.

Anal. Calcd. for $C_{11}H_{19}Br_2Cl$: C, 38.4; H, 5.9. Found: C, 38.6; H, 5.4.

A number of variations were tried in an effect to improve the yield of the bromochloroundecene but without success. In all experiments appreciable amounts of tarry residue were found after each distillation, and generally (especially at high bath temperatures) evolution of gas was evident. Dispensing entirely with carbon tetrachloride and using excess 11-chloroundecene-1 as solvent offered no advantage. The presence of benzoyl peroxide[7] led to a very vigorous reaction but to no improvement in yield.

Coupling of Bromochloroundecene with *n*-Pentylmagnesium Bromide.—*n*-Pentyl bromide was converted to the Grignard reagent, and the filtered ethereal solution analyzed

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[1] Department of Chemistry, Boston University, Boston, Massachusetts.

[2] W. J. Gensler, E. M. Behrmann and G. R. Thomas, THIS JOURNAL, **73**, 1071 (1951).

[3] First synthesized by K. Ahmad, F. M. Bumpus and F. M. Strong, *ibid.*, **70**, 3391 (1948).

[4] F. M. Bumpus, W. R. Taylor and F. M. Strong, *ibid.*, **72**, 2116 (1950).

[5] W. F. Huber, *ibid.*, **73**, 2730 (1951).

[6] Melting points and boiling points are uncorrected. Analyses by Shirley Golden, Microchemical Laboratory, Department of Chemistry, Harvard University.

[7] H. Schmid and P. Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

in the usual manner.[8] To 290 ml. of the Grignard solution (0.33 mole) in a flask fitted with a moisture-protected reflux condenser was added 54 g. (0.20 mole) of bromochloroundecene. After the initial vigorous reaction had subsided, the mixture was boiled overnight. Hydrolysis was carried out with dilute sulfuric acid. The ether layer was washed with dilute aqueous sodium bicarbonate and with water, and was dried over magnesium sulfate. Removal of solvent left the crude coupling product which was purified by fractionation under reduced pressure. Material boiling at 100–108° (0.7 mm.) with bath temperature 165–200° was collected (22 g. or 51%) as 16-chlorohexadecene-7, $n^{25}D$ 1.4570.

Anal. Calcd. for $C_{16}H_{31}Cl$: C, 74.3; H, 12.0. Found: C, 74.1; H, 12.0.

Judging from the absence of characteristic vinyl group absorption at 10.05 μ, this material was free of branched chain products.

Alkylation of Malonic Ester with 16-Chlorohexadecene-7.—Sodium ethoxide was prepared by dissolving 2.3 g. (0.10 atom) of sodium in 250 ml. of ethanol. Malonic ester (20 g. or 0.12 mole), potassium iodide (2 g.) and 16-chlorohexadecene-7 (III) (22 g. or 0.085 mole) were added and the mixture boiled under a moisture-protected condenser for 24 hours. Precipitated solids were removed by filtration and the filtrate, after concentration, was diluted with 100 ml. of ether. The ethereal solution was washed with water until the washings were neutral to litmus and finally dried over magnesium sulfate.

Ether and excess malonic ester were removed by distillation first at atmospheric pressure and then at 15 mm. Further fractionation yielded 24 g. (74%) of hexadecenylmalonic ester, b.p. 170–172° (0.3 mm.); $n^{25}D$ 1.4493.

Anal. Calcd. for $C_{23}H_{42}O_4$: C, 72.2; H, 11.0. Found: C, 71.8; H, 10.7.

Vaccenic Acid.—The malonic ester was saponified by stirring a mixture of 25 g. of sodium hydroxide, 250 ml. of water, 100 ml. of alcohol and 24 g. (0.063 mole) of the ester for 3 hours at steam-bath temperature. The mixture first became homogeneous and then deposited a precipitate. The alkaline mixture was allowed to stand overnight.

After one extraction with ether, the cold (0°) aqueous solution was brought to *p*H 1 by addition of dilute sulfuric acid, and the acid mixture shaken several times with ether. All traces of sulfuric acid were removed from the ether by thorough washing with water, and the ether solution dried with anhydrous magnesium sulfate. Evaporation of all solvent left 19 g. (93%) of the solid malonic acid.

Decarboxylation was carried out by holding test-tubes containing 1 to 9 g. portions of the malonic acid in a metal-bath at 180° for 12 minutes. In every case the decrease in weight due to loss of carbon dioxide corresponded to that calculated. The combined decarboxylation products were dissolved in approximately 80 ml. of acetone, and the solution cooled to −20°. The resulting precipitate was collected by rapid filtration through a precooled sintered glass funnel. A second crop was obtained in the same way from the concentrated mother liquor. The combined solids (8.3 g.) after two crystallizations from acetone at −20° weighed 7.4 g. (42%). The melting point, 44.5–45°, agreed with published values for synthetic vaccenic acid (43–44°[3]; 45–45.5° sintering at 44.5°[2]; 42.5–43.5°[4]; 43.5–44.5°[5]) and was not depressed when the material was mixed with a sample of vaccenic acid prepared before.[2]

Hydroxylation and Cleavage of Vaccenic Acid.—Application of the hydroxylation method of Swern and co-workers,[9] to a mixture of 0.20 g. (0.002 mole) of vaccenic acid, 1 ml. of 25% hydrogen peroxide and 17 ml. of 87% formic acid afforded 0.230 g. of 11,12-dihydroxystearic acid, m.p. 125–126°. Two crystallizations from ethanol brought the melting point of the acid, either before or after admixture with the same material (m.p. 127.5–128.3°) prepared by Ahmad, Bumpus and Strong,[3,10] to 126.5–128°.

The expected products were obtained from the 11,12-dihydroxystearic acid on cleavage with periodic acid.[3–5] Heptanal 2,4-dinitrophenylhydrazone melted at 104.8–105.5° and, when mixed with authentic material (m.p. 106–107°), at 105–107°. The 2,4-dinitrophenylhydrazone of 10-formyldecanoic acid, after crystallization from aqueous alcohol, melted at 93–95° with some sintering noted at 86°.

Anal. Calcd. for $C_{17}H_{22}N_4O_6$: C, 53.7; H, 6.3. Found: C, 53.8; H, 6.4.

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[8] H. Gilman, *et al.*, THIS JOURNAL, **45**, 150 (1923).

[9] D. Swern, G. N. Billen, T. W. Findley and J. T. Scanlan, *ibid.*, **67**, 1786 (1945).

[10] We are indebted to Dr. Strong for his kindness in supplying a sample of this dihydroxystearic acid.

The Reduction of Carbon Dioxide to Formic Acid with Lithium Aluminum Hydride

BY ALBERT E. FINHOLT AND EUGENE C. JACOBSON

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An extensive study has been made of the reaction of carbon dioxide with lithium aluminum hydride to form methanol.[1–4] Side reactions have been reported to give formic acid, formaldehyde and methyl formate. It has been suggested[3] that the reduction of carbon dioxide may proceed first to a formate, then to the methylene glycol salt and finally to the alcoholate. Thus at least three reactions seem possible, each of which represents a definite degree of reduction

$$4CO_2 + LiAlH_4 \longrightarrow LiAl(OCH_3)_4 \quad (1)$$

$$2CO_2 + LiAlH_4 \longrightarrow LiAl(OCH_2)_2 \quad (2)$$

$$4CO_2 + 3LiAlH_4 \longrightarrow LiAl(OCH_3)_4 + 2LiAlO_2 \quad (3)$$

Hydrolysis or alcoholysis of the salts would give formic acid, formaldehyde or methanol. The plausibility of the suggested mechanism has been strengthened in this work by the preparation of formic acid in good yield according to equation (1). A similar reduction of carbon dioxide to a formate in yields of 69–88% has been accomplished with lithium borohydride[5] although the reaction takes a different course with the formation of diborane as a by-product.

A high ratio of carbon dioxide to hydride is essential for a good yield of formate. This was maintained by the experimental techniques described below. Dilute hydride solutions and highly purified lithium aluminum hydride were other surprisingly critical conditions for good yields.

The importance of concentration may be seen in Table I. A diethyl ether solution containing 0.44% lithium aluminum hydride gave an 81% yield of formic acid, whereas a 3.53% solution gave only a 43% yield. The results were similar with diethylene glycol diethyl ether as a solvent. Under the experimental conditions employed in this study, the dilute solutions probably contributed to maintaining a high ratio of carbon dioxide to hydride at any reaction site.

The yields of formic acid were erratic, varying from 59 to 84%, unless the lithium aluminum hydride was carefully purified. Hydride originally over 95% pure gradually deteriorated after several months of exposure to light and occasional opening

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[4] H. I. Schlesinger and A. E. Finholt, unpublished work.

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