When the semicarbazone was prepared by the method previously described,[1] the semicarbazone precipitated directly as fine white needles in 90% yield. The m.p. was 153–155°, unchanged by further recrystallization. Several m.p.'s have been reported for this compound: 160–162° (sample known to be contaminated with the semicarbazone of I),[1] 158–160°[5] and 131–132° (raised to 150° when mixed with a small amount of the semicarbazone of I).[2] The extinction for the ultraviolet absorption in ethanol steadily declined in value from 215 to 270 mμ. Representative values are: 215 mμ, 1330; 240 mμ, 330; 248 mμ, 277; 255 mμ, 217; and 270 mμ, 67. Using our data on the absorption spectra of II, we estimate that the sample of II obtained by Turner and Voitle[1] contained 11% of I, which is in the range estimated by the authors.

Isomerization of 1-Methyl-6-acetylcyclohexene (II) to 1-Methyl-2 and 6-acetylcyclohexenes (I and II).—A solution of 12 g. of 1-methyl-6-acetylcyclohexene (II) in 15 ml. of methanol was treated under nitrogen with 2 g. of sodium methoxide. After 20 hr. the solution was treated with 3 ml. of acetic acid. The color of the solution changes reversibly from yellow in alkali to colorless in acid. The ketones were isolated and distilled to give 11.5 g. of colorless liquid, b.p. 77–87° at 12 mm. The $n^{20}\text{D}$ 1.4825 indicated that the equilibrium mixture contained 65% of I and 35% of II. In the ultraviolet absorption in ethanol, the extinction of the maximum at 248 mμ was 4300, which indicated 61% of I and 39% of II. In preparing the semicarbazone, the first crop of white flakes melted at 209–215° indicating it to be nearly pure semicarbazone of I. The yield was 50%. This yield was in accord with the constitution of the equilibrium mixture stated above. One recrystallization from ethanol raised the m.p. to 226–227.5°, comparable to that reported for the pure semicarbazone of I.[1]

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The Vaporization of Graphite Filaments[1]

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The vapor pressure and, more specifically, the heat of sublimation of carbon based on spectroscopic measurements of the dissociation energy of carbon monoxide have been of a controversial nature for a number of years. These measurements gave values for the ΔE_0° of sublimation of carbon ranging from 125–170 kcal.[2–4] Recently, Brewer, Gilles and Jenkins[5] concluded that the ΔE_0° of sublimation was 170.39 kcal./mole by measuring the effusion rate of powdered graphite at 2700°K. Marshall and Norton[6] determined ΔE_0° as 175 kcal./mole by measuring the rate of evaporation of carbon vapor in a vacuum from graphite rings which were heated by an induction furnace. In both experiments it was assumed that the carbon atoms leaving the surface were in their normal 3p ground state. This assumption is also made in the present research.

It was felt that it would be of sufficient interest to run an independent experiment with the "hot wire method" using graphite filaments. Although in principle this experiment is similar to that of Marshall and Norton in using the equation of Knudsen ($n = \alpha p/\sqrt{2\pi mkT}$) to determine the evaporation rate of carbon atoms from a surface into a vacuum, the experimental technique, however, is quite different in that a cylindrical filament was employed instead of rings which might alter the evaporation rate. By measuring the rate of weight loss of the filament in a vacuum, values of αp, the accommodation coefficient multiplied by the vapor pressure, are obtained from the Knudsen equation. The logarithm of αp was plotted against the reciprocal of the absolute temperature in the range 2400–2900°K. as shown in Fig. 1 and the straight line indicates that α is relatively independent of temperature. The slope was drawn through the points using the method of least squares and the value for ΔE_0° of 176.6 ± 1 kcal./mole was calculated with the aid of the free energy data from Kelley,[7] assuming an accommodation coefficient of 1. From the thermodynamic data of Marshall and Norton for gaseous carbon and graphite, a value of 177.2 ± 1 kcal./mole for ΔE_0° was calculated. The results of the individual experimental measurements are given in Table I.

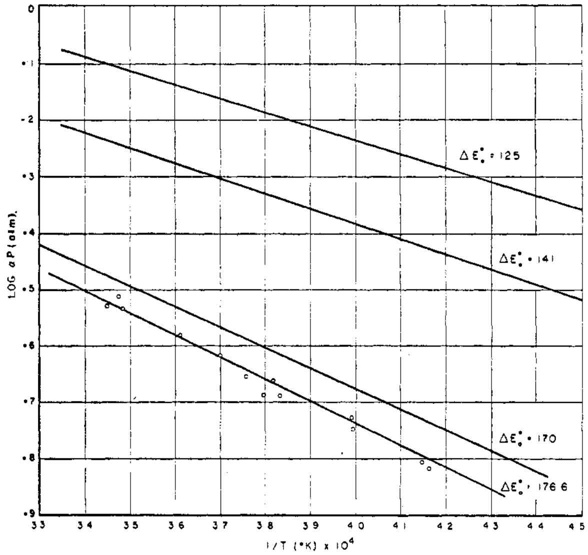

Fig. 1.—The vaporization of graphite filaments.

The question of the value of the accommodation coefficient is still unresolved. Brewer concluded that α was at least 0.3. If this were the case our results would indicate a ΔE_0° of 170, in good agreement with Brewer. Marshall and Norton assumed a value of unity for α in calculating a ΔE_0° of 175 kcal./mole. Recently Goldfinger[8] in Brussells determined the heat of sublimation of graphite by means of the effusion method using very small orifices and obtained a value of 141 kcal./mole for ΔE_0° and concluded that α was of the order of 1/300–1/3000. An α of approximately 1/3000

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[1] This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. DA-04-495-ORD18, sponsored by U. S. Army Ordnance Department.

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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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RECEIVED FEBRUARY 29, 1952

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%).

Acknowledgment.—We gratefully acknowledge assistance of the Research Corporation which made this work possible.

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.

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