

Four hundred mg. of reagent P was dissolved in 20 cc. of ethanol-acetic acid (9:1) solution and the mixture refluxed for 24 hours. At the end of this period 200 mg. of estrone was added and the heating continued for two additional hours. Following the usual work-up, the non-ketonic fraction yielded, after one recrystallization from dilute ethanol, 73 mg. (36.5%) of estrone azine, m.p. 290–300° (dec.).

When Girard reagent T was used instead of reagent P and the reaction carried out as described above for two hours, no azine was formed; however, upon prolonging the heating period for 24 hours, a 10% yield of azine was obtained.

**The Formation of Other Steroid Azines during Girard Separation. Dehydroisoandrosterone Acetate.**—350 mg. of dehydroisoandrosterone acetate was refluxed with 700 mg. of Girard reagent P in acetic acid-ethanol solution for two hours. After the customary work-up, 25 mg. of the crystalline azine melting at 265–268° was obtained in the non-ketonic fraction. The sample was prepared for analysis by sublimation in high vacuum at 250–275°.

*Anal.* Calcd. for  $C_{22}H_{30}O_2N_2$ : C, 76.80; H, 9.21; N, 4.27. Found: C, 77.52; H, 9.05; N, 4.25.

The azine of dehydroisoandrosterone was prepared in a similar way and melted at 256°. Acetylation with acetic anhydride and pyridine gave the same diacetoxy derivative, m.p. 265°, as described above.

**Pregnenolone.**—500 mg. of  $\Delta^4$ -pregnen-3 $\beta$ -ol-20-one was treated with Girard reagent P (1 g.) in the usual way for two hours. The crystalline azine found in the non-ketonic fraction weighed 40 mg. (96 mg. of azine was obtained when the reaction was carried out for 24 hours). The sample was sublimed in high vacuum at 250–300° and then recrystallized from ethyl acetate-acetone, m.p. 290–295°.

*Anal.* Calcd. for  $C_{22}H_{34}O_2N_2$ : C, 80.20; H, 10.26; N, 4.45. Found: C, 80.05; H, 10.57; N, 4.65.

A sample of pregnenolone azine, prepared from pregnenolone and hydrazine hydrate, did not depress the melting point of the above product. Both samples yielded the same diacetoxy derivative, m.p. 253–257° (Kofler block) (plates from benzene-ligroin).

**Testosterone.**—548 mg. of testosterone was treated for 48 hours with 1 g. of reagent P as described above. Two hundred mg. of the yellow azine was obtained in the non-ketonic fraction. It was recrystallized twice from chloroform-methanol, m.p. 257.5–260° (dec.). For analysis it was dried at 100° for 16 hours.

*Anal.* Calcd. for  $C_{28}H_{42}O_2N_2$ : C, 79.68; H, 9.85; N, 4.89. Found: C, 79.64; H, 10.01; N, 5.25.

Its ultraviolet spectrum had two maxima, one at 262  $m\mu$  (log  $E$  4.41) and the other at 300  $m\mu$  (log  $E$  4.40). A sample of testosterone azine prepared by the reaction of testosterone with hydrazine hydrate exhibited the same ultraviolet spectrum, log  $E_{262\ m\mu}$  4.41 and log  $E_{300\ m\mu}$  4.42. It did not depress the melting point of the product obtained from the reaction of testosterone with Girard reagent P.

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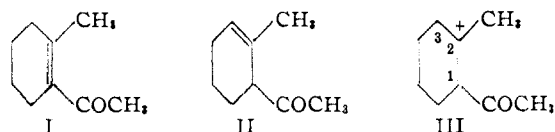
### Acetylation of 1-Methylcyclohexene

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Yields of about 50% have frequently been reported for the stannic chloride catalyzed acetylation of 1-methylcyclohexene with acetyl chloride. However, the product obtained after the customary alkaline treatment is an equilibrium mixture of 1-methyl-2-acetylcyclohexene (I) and 1-methyl-6-acetylcyclohexene (II).<sup>1,2</sup>

In studying the acetylation of 1-methylcyclohexene with zinc chloride in acetic anhydride, a surpris-



ingly simple result was found. Pure 1-methyl-6-acetylcyclohexene (II) was formed in 70% yield. The purity was indicated by the following observations. Silver nitrate failed to give any precipitate which indicated the absence of chloro compounds. The product remained colorless indefinitely. The index of refraction ( $n_D^{20}$  1.4740) was similar to that previously reported for II.<sup>1</sup> The semicarbazone formed in 90% yield and the m.p. (153–155°) was unchanged by recrystallization. In the ultraviolet absorption, the extinction at 248  $m\mu$  ( $\epsilon$  277) was lower than previously reported for II.<sup>1</sup> This indicated that little if any of the conjugated ketone (I) was present. Actually from our data it can be estimated that the sample of II prepared by Turner and Voitle<sup>1</sup> contained 11% of the conjugated ketone I. This is within the range estimated by these authors.

Treatment of the pure 1-methyl-6-acetylcyclohexene (II) with sodium methoxide in methanol gave a 95% yield of the equilibrium mixture, which was shown to contain 63% of I and 37% of II.

The reaction conditions used for acetylating methylcyclohexene differed from those of previous workers not only in the use of zinc chloride in place of stannic chloride, but also in the avoidance of prolonged treatment with alkaline reagents. It is entirely possible that II is also the principal product from the stannic chloride catalyzed reaction, but the presence of chloro compounds obscures the exact composition of the initial product.

The exclusive formation of II in the acetylation has an important bearing on the behavior of carbonium ions. The acetylation probably proceeds through the intermediate carbonium ion, III. This carbonium ion must then eject the hydrogen at C-3 rather than the more acidic hydrogen at C-1.

From a consideration of the chlorination of olefins, Taft<sup>3</sup> stated as a general principle (applicable to formation of olefins from carbonium ions) that the most electron-rich carbon, adjacent to the positive carbon, loses the proton. In the present case this is equivalent to stating that the least acidic hydrogen is lost. It is evident that the formation of II from the carbonium ion (III) follows this principle.

#### Experimental

**1-Methyl-6-acetylcyclohexene (II).**—The procedure was similar to that published for the acetylation of diisobutylene.<sup>4</sup> To a solution of 20 g. of 1-methylcyclohexene in 60 g. of acetic anhydride was added 25 g. of powdered anhydrous zinc chloride. The addition of the solid was completed in 20 min. The temperature rose to 43° during the addition. After stirring for 20 hr., the clear solution was chilled and the excess anhydride decomposed by adding ice and water. Ether (100 ml.) was added and the ether extract washed three times with water, once with dilute potassium hydroxide, and then with water until the washings were neutral. The ether solution was dried over sodium sulfate and distilled to give 20 g. (70%) of colorless 1-methyl-6-acetylcyclohexene (b.p. 77–80° (12 mm.);  $n_D^{20}$  1.4740). The product remained colorless on standing.

(1) R. B. Turner and D. M. Voitle, *THIS JOURNAL*, **73**, 1408 (1951).

(2) E. A. Braude, E. R. II. Jones, II. P. Koch, R. W. Richardson, F. Sondheimer and J. B. Toogood, *J. Chem. Soc.*, 1895 (1949).

(3) R. W. Taft, Jr., *THIS JOURNAL*, **70**, 3364 (1948).

(4) A. C. Byrns and T. F. Doumani, *Ind. Eng. Chem.*, **35**, 349 (1943).

When the semicarbazone was prepared by the method previously described,<sup>1</sup> 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),<sup>1</sup> 158–160° and 131–132° (raised to 150° when mixed with a small amount of the semicarbazone of I).<sup>2</sup> The extinction for the ultraviolet absorption in ethanol steadily declined in value from 215 to 270 m $\mu$ . Representative values are: 215 m $\mu$ , 1330; 240 m $\mu$ , 330; 248 m $\mu$ , 277; 255 m $\mu$ , 217; and 270 m $\mu$ , 67. Using our data on the absorption spectra of II, we estimate that the sample of II obtained by Turner and Voite<sup>1</sup> 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  $n_D^{20}$  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 m $\mu$  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.<sup>1</sup>

(5) K. Dimroth and O. Luderitz, *Ber.*, **81**, 242 (1948).

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## The Vaporization of Graphite Filaments<sup>1</sup>

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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  $\Delta E_0^\circ$  of sublimation of carbon ranging from 125–170 kcal.<sup>2–4</sup> Recently, Brewer, Gilles and Jenkins<sup>5</sup> concluded that the  $\Delta E_0^\circ$  of sublimation was 170.39 kcal./mole by measuring the effusion rate of powdered graphite at 2700°K. Marshall and Norton<sup>6</sup> determined  $\Delta E_0^\circ$  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.

(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.

(2) L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1939.

(3) A. G. Gaydon, "Dissociation Energies," John Wiley and Sons, Inc., New York, N. Y., 1947.

(4) G. Herzberg, "Molecular Spectra and Molecular Structure," Prentice-Hall, Inc., New York, N. Y., 1939.

(5) L. Brewer, P. W. Gilles and F. A. Jenkins, *J. Chem. Phys.*, **16**, 797 (1948).

(6) A. L. Marshall and F. J. Norton, *This Journal*, **78**, 2166 (1950).

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  $\alpha p$ , the accommodation coefficient multiplied by the vapor pressure, are obtained from the Knudsen equation. The logarithm of  $\alpha p$  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  $\alpha$  is relatively independent of temperature. The slope was drawn

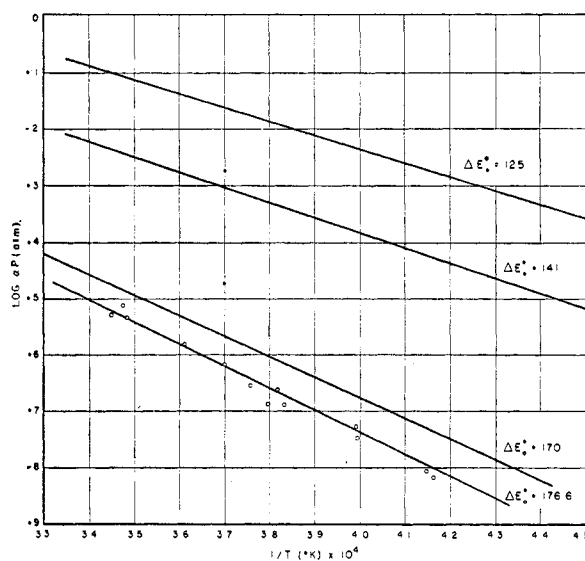


Fig. 1.—The vaporization of graphite filaments.

through the points using the method of least squares and the value for  $\Delta E_0^\circ$  of 176.6  $\pm$  1 kcal./mole was calculated with the aid of the free energy data from Kelley,<sup>7</sup> assuming an accommodation coefficient of 1. From the thermodynamic data of Marshall and Norton for gaseous carbon and graphite, a value of 177.2  $\pm$  1 kcal./mole for  $\Delta E_0^\circ$  was calculated. The results of the individual experimental measurements are given in Table I.

The question of the value of the accommodation coefficient is still unresolved. Brewer concluded that  $\alpha$  was at least 0.3. If this were the case our results would indicate a  $\Delta E_0^\circ$  of 170, in good agreement with Brewer. Marshall and Norton assumed a value of unity for  $\alpha$  in calculating a  $\Delta E_0^\circ$  of 175 kcal./mole. Recently Goldfinger<sup>8</sup> in Brussels 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  $\Delta E_0^\circ$  and concluded that  $\alpha$  was of the order of 1/300–1/3000. An  $\alpha$  of approximately 1/3000

(7) K. K. Kelley, U. S. Bur. Mines Bull. 383 (1935).

(8) Th. Doehard, P. Goldfinger and F. Wealbroeck, *J. Chem. Phys.*, **20**, 787 (1952).