

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Heats of Organic Reactions. V. Heats of Hydrogenation of Various Hydrocarbons

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In the previous publications of this series¹ there have been reported the heats of hydrogenation of a considerable number of unsaturated hydrocarbons. These data, it has been shown, indicate some rather striking regularities, correlating molecular structure and this thermo quantity. In this paper we shall present some additional determinations and attempt to substantiate and to amplify some of our earlier generalizations. Our next paper will deal with hydrogenations of some oxygen-containing compounds.

Preparation of Materials

Inasmuch as the purity of the compounds is probably the factor limiting the accuracy of our calorimetric determinations, we shall follow our set precedent and report the preparations in some detail.

Ethylbenzene.—Ethylbenzene was prepared from acetophenone by the method of Clemmensen.² Fritche's acetophenone was distilled through Column B of Paper II at 100 mm. pressure. The major portion, which distilled at 132.4–132.7°, was used in this synthesis. The refractive indices of the fractions collected varied from $n^{17.5D}$ 1.5348 to 1.5350.³

The best yield of crude ethylbenzene on any one reduction was 50% of the theoretical; the over-all yield of crude material from 2280 g. of acetophenone was 42.5%. The crude product was washed with potassium carbonate solution, dried over calcium chloride and let stand over sodium for fifteen hours. It was then distilled from the sodium, giving 769 g. of product which was fractionated in Column B; 686 g. of material was obtained which distilled at 136.80 ± 0.05° at 755 mm. This corresponds to a yield of 38% based on the weight of acetophenone used. Upon refractionation through Column A of Paper II a middle fraction of 114 g. distilled at 135.97° at 765 mm. The freezing point of this fraction was -94.7°⁴ and n^{20D} 1.4960.⁴

The total distillate of this fractionation (approximately 515 g.) distilled at 135.98 ± 0.02° at 765 mm.

o-Xylene.—*o*-Xylene ("reinst"), as obtained from Dr. Frankel and Dr. Landau of Berlin, Germany, was fractionated through Column A. The fraction chosen for calorimetric measurements, No. 5, had the following constants; b. p. 144.07–0.08° at 765 mm.,⁵ n^{20D} 1.5055, f. p. -25.10°.

(1) I. Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, *THIS JOURNAL*, **57**, 65 (1935); II. Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935). III, IV, *ibid.*, **58**, 137, 146 (1936).

(2) Clemmensen, *Ber.*, **46**, 1838 (1913).

(3) Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **84**, 20 (1911), give $n^{17.5D}$ 1.5350.

(4) "I. C. T.," Vol. I, p. 219, gives f. p. -92.8°; b. p. 136.5° at 776.7 mm. Brühl, *Ann.*, **235**, 12 (1886), gives n^{20D} 1.49594. Huffman, Parks and Daniels, *THIS JOURNAL*, **52**, 1548 (1930), give -95.1° (178.0°K.). Timmermans and Martin, *J. chim. phys.*, **23**, 247 (1926), give -94.4°.

(5) "I. C. T.," Vol. I, p. 219, gives for *o*-xylene: b. p. 144°, m. p. -27.1°, p. 277, n^{20D} 1.5058; Rossini, *Bur. Standards J. Research*, **11**, 555 (1933), gives f. p. -25.3°.

Fraction No. 5, 90 g., was the only fraction obtained with a flat boiling point; the other fractions were lower boiling and comprised about 66% of the charge of 500 g.

Mesitylene.—Eastman best grade of mesitylene was purified according to the method given in "Organic Syntheses";⁶ 398 g. of mesitylene was recovered from 500 g. of starting material. This was distilled through Column B at 100 mm.; a middle fraction of 323 g. was obtained which distilled flatly at 99.3°; n^{20D} 1.4995;⁷ f. p. -51.4°.⁸

Styrene.—Styrene was prepared from phenylethyl alcohol by the method of Sabetay;⁹ 2074 g. of phenylethyl alcohol in two and three molar runs was dehydrated by heating over a molten 50–50 mixture of sodium and potassium hydroxides (50 g. mixture per mole of alcohol) contained in a round-bottomed flask bearing a downward condenser. Heating was so regulated that the temperature of the distillate did not exceed 140°. The product was separated from the water layer, washed with saturated calcium chloride solution and dried over calcium chloride. Treatment with metallic sodium seemed to cause considerable polymerization, so this procedure was omitted after the first three runs. The yield of styrene to this point was 1627 g. or 92%. Fractionation of the crude material from a small amount of hydroquinone through Column B at 60 mm. gave 1008 g. of material distilling at 66.7 ± 0.05° corresponding to a yield of 57% based on the phenylethyl alcohol used. The refractive indices of the fractions obtained varied from $n^{17.5D}$ 1.5479 to 1.5483. This material was stored over hydroquinone in the dark and redistilled as needed for the calorimeter.

Sample No. 1, 173 g., distilled at 65.15° at 50 mm.; n^{20D} 1.5470.¹⁰ Sample No. 2 distilled at 65.6° at 50 mm.; n^{20D} 1.5470; f. p. -30.5°.¹¹

Indene and Hydrindene.—A pure grade of indene, obtained from Gesellschaft für Teerverwertung, was distilled through Column B; the middle fraction, consisting of Samples 2, 3 and 4, had a flat b. p. of 83.8° at 30.5 mm. The refractive index of the three samples was the same, $n^{19.8D}$ 1.5767.¹² Sample No. 2 had a f. p. of -1.67°.¹³

Part of this fraction was hydrogenated, using the Adams catalyst,¹⁴ to hydrindene using no solvent. Hydrogen was taken up at the rate of about nine liters an hour when 1 g. of catalyst was used for 200 g. of indene. The absorption of hydrogen ceased immediately when the calculated

(6) "Organic Syntheses." Coll. Vol. I, John Wiley and Sons, Inc. 1931, p. 334; note 8, p. 337.

(7) Auwers, *Ann.*, **419**, 92 (1919), gives $n^{17.5D}$ 1.49804.

(8) "I. C. T.," Vol. I, p. 228, gives -52.7°.

(9) Sabetay, *Bull. soc. chim.*, [4] **45**, 69 (1929).

(10) Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **82**, 99 (1910), give n^{20D} 1.5449.

(11) Waterman and de Kok, *Rec. trav. chim.*, **53**, 1133 (1934), give f. p. -33°; n^{20D} 1.5462.

(12) Spilker and Dombrowsky, *Ber.*, **42**, 572 (1909), give $n^{18.5D}$ 1.5773; Ruzicka and Peyer, *Helv. Chim. Acta*, **18**, 676 (1935), give n^{21D} 1.5748.

(13) Weissgerber, *Ber.*, **42**, 569 (1909), gives f. p. -2°.

(14) Adams and Shriner, *THIS JOURNAL*, **45**, 2171 (1923).

amount had been taken up. Practically all of the hydrindene distilled flatly in Column B at 79.0° and 29 mm.; n_{20}^{20} 1.5382;¹⁵ f. p. -51.4°.

Cyclopentene.—Cyclopentanone was prepared from adipic acid by the method of Boedtker¹⁶ with a 90% yield of crude product after it had been washed with potassium carbonate to remove any adipic acid and dried over anhydrous potassium carbonate. The cyclopentanone was fractionated carefully in Column B. The fractions used distilled from 130.2–130.3° at 756 mm.

Cyclopentanol was prepared from cyclopentanone by reduction with the Adams platinum catalyst. It was found that by promoting the catalyst with a small amount of iron¹⁷ the ketone could be reduced very rapidly if the very pure ketone with no solvent was used in the Adams machine. The rate of absorption of hydrogen was about eight liters per hour. Five-tenths gram of catalyst was employed with each two-mole run. The cyclopentanol thus obtained was distilled in Column B giving a middle fraction boiling at 139.8–139.9° at 751 mm.

Cyclopentene was prepared by dehydrating the alcohol with anhydrous oxalic acid,^{17a} washing the product with water and potassium carbonate solution, drying with calcium chloride and finally distilling from sodium metal. A yield of 83% based on alcohol dehydrated was obtained. The cyclopentene was then fractionated in Column A. The fraction used for measurement had the following physical constants: b. p. 44.17 ± 0.01° at 760 mm.; f. p. -134.6°; n_{20}^{20} 1.4223.¹⁸

α-Phellandrene.—The Hercules Powder Company through Dr. E. R. Littmann very kindly supplied us with approximately 250 cc. of α-phellandrene; the material was represented as being the best obtainable. This was purified, following the suggestions of Littmann, by distillation through a three-foot (91-cm.) jacketed, indented column under a pressure of 16 mm. The bulk of the material, about 200 cc., distilled at 62.5–66.5°. This was refluxed for one-half hour over clean metallic sodium and redistilled under 16 mm. pressure, giving a main fraction of b. p. 62.7–64.1°. A second distillation gave a main fraction of 75 cc., b. p. 64.7–65.7°; n_{20}^{20} 1.4746.¹⁹

α-Terpinene.—This compound, also supplied by the Hercules Powder Company, was purified in the same way as was α-phellandrene. The middle fraction from the distillation was taken for calorimetric measurement; it distilled at 81.5–82.0° under 30 mm. pressure; n_{20}^{20} 1.4757.²⁰

Limonene.—Eastman best grade of limonene was distilled through Column B giving a middle fraction, Samples II, III and IV, with b. p. 74.7° at 24 mm. α-Phellandrene, α-terpinene and limonene all formed glasses when chilled in liquid air and no freezing points could be obtained.

Sample II had a refractive index of n_{20}^{20} 1.4721 and for Sample IV n_{20}^{20} 1.4727 was found.²¹

Isopropylethylene.—The sample of isopropylethylene was kindly supplied by Dr. E. P. Carr of Mt. Holyoke College. The constants submitted with the sample were: b. p. 20.18–21° at 760 mm. and n_{20}^{20} 1.3675.²² No freezing point was obtained on this material as it formed a very viscous liquid in liquid air even after repeated warming and cooling; this agrees with the observation of Norris and Reuter.²²

Neo-amylethylene.—This compound was prepared from the Grignard reagent of *t*-butyl chloride and allyl bromide according to the method of Whitmore and Homeyer.²³ The allyl bromide used was a flat cut at 69.75° and 753 mm. The *t*-butyl chloride was of the same grade as was used in making *t*-butylethylene. A 63% yield of the ethylene was obtained, boiling at 71.0–72.8°. This was converted into the dibromide²³ and distilled. The fractions with boiling range of 104.7–105.0° at 16 mm. were treated with zinc in ethyl alcohol to regenerate the hydrocarbon; this was recovered by distillation of the reaction mixture, washing with successive portions of water, and drying with calcium chloride, yield 68%. Systematic fractionation through Column A gave a middle fraction with b. p. 72.63 ± 0.01° at 765 mm., f. p. -136.5°, n_{20}^{20} 1.3919.²⁴

Tertiary Butylethylene.—A good grade of commercial *t*-butyl alcohol was distilled in Column C; a fraction boiling over 0.2° was used for the preparation of *t*-butyl chloride.²⁵ A sample of *t*-butyl chloride boiling flatly at 50.7° (766 mm.) (Column C) was used to prepare the Grignard reagent according to Whitmore.²⁶ Pure acetaldehyde, freshly distilled, was added to this reagent, the reaction mixture broken down and the product recovered in the usual manner. A 58% yield of pinacolyl alcohol was obtained based on *t*-butyl chloride used. This alcohol was converted, after fractionation, to the acetate by treatment with 10% excess acetyl chloride; the chloride was added slowly with stirring and the reaction mixture allowed to stand overnight. The excess acid chloride was then distilled off and the ester fractionated in Column B; a 61% yield was obtained, distilling at 80.5–80.9° at 99 mm.; n_{20}^{20} 1.4020 to n_{20}^{20} 1.4023.

Acetic acid was split out by a method suggested by Dr. Paul L. Cramer of General Motors (private communication), who obtained better yields than found in the original work of Whitmore and Rothrock.²⁷ Pinacolyl acetate was converted into *t*-butylethylene and acetic acid by passage through a reaction tube packed with glass wool in a furnace maintained electrically at 400°. The reaction product was washed free from acetic acid and the *t*-butylethylene separated from unchanged pinacolyl acetate by fractionation. The unchanged pinacolyl acetate was recovered nearly quantitatively and repassed through the

(15) Cotton and Mouton, *Ann. chim.*, [8] **28**, 218 (1913), give n_{20}^{20} 1.5351.

(16) Boedtker, *J. pharm. chim.*, **15**, 225 (1932).

(17) Carothers and Adams, *THIS JOURNAL*, **45**, 1071 (1923).

(17a) Zelinsky and Lewina, *Ber.*, **66**, 477 (1933).

(18) Filipow, *J. Russ. Phys.-Chem. Soc.*, **46**, 1163 (1915) [*Chem. Zentr.*, **86**, I, 1057 (1915)], gives b. p. 44.1–44.6°; n_{20}^{20} 1.42183.

(19) Smith, Hurst and Read, *J. Chem. Soc.*, **133**, 1657 (1923), give the following constants for α-phellandrene from two different sources: b. p. 58–59° at 16 mm., n_{20}^{20} 1.4732; b. p. 62.5–63.5° at 15.5 mm., n_{20}^{20} 1.4744.

(20) Richter and Wolff, *Ber.*, **63**, 1720 (1930), give n_{20}^{20} 1.477.

(21) Richter and Wolff, *ibid.*, **63**, 1724 (1930), give n_{17}^{17} 1.4727 for *l*-limonene; this is probably the most recent figure.

(22) Norris and Reuter, *THIS JOURNAL*, **49**, 2624 (1927), give b. p. 20.10 ± 0.05° at 760 mm.; n_{15}^{15} 1.3675.

(23) Whitmore and Homeyer, *ibid.*, **55**, 4555 (1933).

(24) Whitmore and Homeyer²³ give b. p. 72.35° at 760 mm. and n_{20}^{20} 1.3911.

(25) "Organic Syntheses," Coll. Vol. I, p. 138.

(26) Whitmore and Badertscher, *THIS JOURNAL*, **55**, 1561 (1933).

(27) Whitmore and Rothrock, *ibid.*, **55**, 1106 (1933).

furnace. The *t*-butylethylene thus obtained was then distilled from sodium and finally fractionated through Column A. The product used had the following physical constants: b. p. 41.18 \pm 0.01° at 760 mm.; n_{20}^D 1.3765.²⁸

2,4,4-Trimethylpentene-1 and 2,4,4-Trimethylpentene-2.—Technical diisobutylene was generously supplied us by Prof. George S. Parks of Stanford University. About 4 liters of this material was refluxed over sodium metal chips for one hour and then distilled. The resulting product, 2321 g., was fractionated in two distillations through Column A to give a rough separation of the two isomers. Each isomer was then carefully refractionated, giving the following data.

2,4,4-TRIMETHYLPENTENE-1²⁹ (LOW-BOILING ISOMER)

Charge 473 g., b. p. 101.51–.53°, 765 mm.

Fraction	B. p., °C. (765 mm.)	n_{20}^D	Wt., g.
DIB-27	101.22–.49	1.4075	110
DIB-28	101.49–.53	1.4082	60
DIB-29	101.53–.56	1.4087	77
DIB-30	101.56–.58	1.4089	122
DIB-31	101.58–.58	1.4089	28
Residues			46

2,4,4-TRIMETHYLPENTENE-2²⁹ (HIGH-BOILING ISOMER)

Charge 424 g. Residues from first fractionations

DIB-21	104.30–.74	1.4159	98
DIB-22	104.74–.84	1.4159	67
DIB-23	104.84–.83	1.4159	27
DIB-24	104.83–.85	1.4159	27
DIB-25	104.85–105.63	1.4160	80
DIB-26	105.63–106.56	1.4155	24
Residues			137

The structures of these isomers as assigned to them by Whitmore and Church³⁰ on the basis of ozonolysis were confirmed by the same method; we shall forego a discussion of the tedious details.

Pentadiene-1,3.—Crotonaldehyde from Carbide and Carbon Chemical Corporation was fractionated through Column B; the samples used distilled at 102.3–102.4° at 765 mm.

Methylmagnesium chloride Grignard reagent was made up in 5-molar lots in the usual way and crotonaldehyde, to which had been added about an equal volume of anhydrous ether, was added until a negative test for Grignard reagent was obtained with Michler's ketone. Grignard reagent from 25 moles of magnesium required 23.7 moles of crotonaldehyde. The reaction mixture was decomposed with water and an amount of 30% sulfuric acid added sufficient to neutralize the magnesium hydroxide formed. Upon working up the product, it was found to be not pentene-2-ol-4 but the ether from two moles of the pentenol as described by Baudringheim.³¹

(28) Schurman and Boord, *THIS JOURNAL*, **55**, 4930 (1933), give n_{20}^D 1.3759; Fomin and Sochanski, *Ber.*, **46**, 244 (1913), give n_{20}^D 1.37667; Laughlin, Nash and Whitmore, *THIS JOURNAL*, **56**, 1395 (1934), give n_{20}^D 1.3760.

(29) Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932), give for 2,4,4-trimethylpentene-1, b. p. 100.1 at 737 mm., n_{20}^D 1.4082, and for 2,4,4-trimethylpentene-2, b. p. 103.4 at 737 mm., n_{20}^D 1.4158.

(30) Whitmore and Church, *THIS JOURNAL*, **54**, 3710 (1932).

(31) Baudringheim, *Bull. sci. acad. roy. Belg.*, **15**, 53 (1929).

The crude product was washed with saturated sodium bisulfite solution, and then water. The yield was 1290 g. (8.3 mole) corresponding to 70% based on crotonaldehyde. Fractionation in Column B gave 801 g. of product distilling at 158.5–158.9° at 770 mm., a yield of 44%.

The 801 g. of product was passed over freshly activated alumina for dehydration to pentadiene-1,3; better yields of olefin were obtained when the temperature of dehydration was 280–290°. The crude pentadiene was distilled through a three-foot (91-cm.) jacketed, indented column, giving 510 g. of material (72% yield) boiling at 35–45° and yielding a bromide upon saturating a small sample in carbon tetrachloride with bromine in the cold, that melted at 114–114.5°. The once-distilled pentadiene was fractionated through Column B, giving 353 g. distilling at 41.2–42.6° at 770 mm. and this in turn was fractionated through Column A. Three samples totaling 70% of total charge were collected for use in the calorimeter:

Sample	B. p., °C. (760 mm.) ³²	n_{20}^D	F. p., °C.
P-2	41.85–.87	1.4304	–87.7
P-3	41.88–.90	1.4303	–88.1
P-4	41.91–.93	1.4304	–88.9

2,3-Dimethylbutadiene-1,3.—2,3-Dimethylbutadiene-1,3 was prepared by dehydrating pinacol over activated alumina.

The pinacol hydrate starting material was obtained from Professor L. F. Fieser of this Laboratory. To remove the water of hydration it was distilled at atmospheric pressure in Column C until the temperature of the distillate reached 122°. The residue from 3580 g. of hydrate amounted to 1475 g., a yield of 79%. The crude pinacol was subjected to distillation at 100 mm., giving 1226 g. (65% yield) of product; b. p. 117.4–117.5°; m. p. 43.2–43.4°.

Dehydration of the pinacol was accomplished by passing it through a tube 70 cm. long and 2.5 cm. in diameter filled with activated alumina at 450–500°. The product from 1179 g. of pinacol was distilled through Column B giving 585 g. (71.5% yield) of 2,3-dimethylbutadiene-1,3 distilling at 68.6–69.7° at 765 mm. This was fractionated through Column A; from 304 g. of olefin was obtained 153 g. distilling at 68.70 \pm 0.01° at 765 mm.; f. p. –76.0° and n_{20}^D 1.4390.³⁴

Data and Results

No important variations in calorimetric procedure have been adopted. With some of the higher boiling compounds, in order to obtain a workable rate of temperature rise, it was necessary to keep the device in which the hydrogen becomes saturated with the hydrocarbon at 100°; to ensure against condensation of reactant or product in the flow system, the operating temperature of the calorimeter was raised above the 82°

(32) Beilstein, Vol. I, p. 132, gives 114.5° for 1,2,3,4-tetrabromopentane.

(33) Farmer and Warren, *J. Chem. Soc.*, 3224, (1931), report fractions of piperylene ranging in boiling point from 42.0–42.8° and in refractive index from n_{20}^D 1.4305 to 1.4314.

(34) Kogerman, *Naturforscher-Ges. Univ. Tartu*, **41**, Nr. 3/4 (1934), [*Chem. Zentr.*, **106**, I, 2965 (1935)], gives n_{20}^D 1.43929; b. p. 68.8–68.9° at 753.5 mm.

common to our earlier determinations. For purposes of comparison, all data have been reduced to 82° by use of ΔC_p values of -4 cal./deg. for addition of one H_2 , -8 for $2H_2$, -12 for $3H_2$ and -16 for $4H_2$; errors resulting from this approximation are slight due to the small temperature ranges involved.³⁵

Ethylbenzene + $3H_2$.—The table shows a high degree of precision, even with varied flow rates. The freezing point of the ethylbenzene was very sharp at -94.7° ; addition of 0.5% benzene lowered the initial freezing point by 1.1° and the freezing curve dropped off steadily. A test for irreversible adsorption on the cobalt-nickel catalyst used was negative, as were tests designed to detect ethane and methane in the hydrogenated product. Unfortunately it proved impossible to freeze the product; even with prolonged chilling in liquid air the material remained glassy; n_D^{20} 1.4333, to be compared with n_D^{20} 1.4332³⁶ for ethylcyclohexane. We estimate the over-all accuracy of the determination as 100 cal./mole.

Run no.	Moles C_8H_{10}	Moles H_2 per min.	Moles C_8H_{10} per min.	$-\Delta H_{881}$ cal./mole
1	0.022190	0.0143	5.06 (10^{-4})	49,252
2	.022423	.0136	7.81 (10^{-4})	49,219
3	.022496	.0170	8.38 (10^{-4})	49,217
4	.022549	.0142	11.57 (10^{-4})	49,250
Average				49,235 \pm 17
				$-\Delta H_{355}$ 48,920

***o*-Xylene + $3H_2$.**—This hydrogenation over cobalt-nickel yields a mixture of isomers and no test of purity of the product by the freezing point method was possible; a glass resulted on chilling in Dry-Ice; n_D^{20} 1.4321 to 1.4324.³⁷ The freezing "flat" of the *o*-xylene was not especially good, falling off 0.1° to 70% frozen material; however, addition of 0.5% of the lowest boiling fraction caused a freezing-point lowering of 0.2° and the curve fell off more rapidly than in the case of the pure material. Each run was tested chemically for completeness of hydrogenation by treating 1 cc. of the product with 7-10 small drops of concd. sulfuric acid for one and one-half minutes at 70° ; blanks showed that 0.1% of *o*-xylene in the product caused the formation of a yellow tint. The test for irreversible adsorption was negative. The over-all accuracy is estimated at 200 cal./mole.

Run no.	Moles C_8H_{10}	Moles H_2 per min.	Moles C_8H_{10} per min.	$-\Delta H_{881}$ cal./mole
1	0.021830	0.01653	5.58 (10^{-4})	47,492
2	.021571	.01355	3.49 (10^{-4})	47,440
Average				47,466 \pm 26
				$-\Delta H_{355}$ 47,250

Mesitylene + $3H_2$.—The freezing point of mesitylene was very sharp at -51.4° ; addition of 0.8% benzene lowered the initial freezing point by 1.1° and the temperature

(35) A determination of the heat of hydrogenation of benzene to cyclohexane as a test of the calorimeter one year after the reported values (see IV) gave $\Delta H = -50,021$ at 101.6° ; corrected to 82° with $\Delta C_p = -12$ cal./deg., $\Delta H = -49,788$; this is to be compared with the earlier average of $-49,802$.

(36) Signaigo and Cramer, THIS JOURNAL, 55, 3331 (1933).

(37) "I. C. T.," Vol. I, p. 276, gives 1.430.

dropped off steadily. A chemical test for completeness of reaction similar to that for *o*-xylene was used: 0.1% mesitylene in the product was detectable; all runs were complete. No freezing point of the hydrogenation product as a criterion of purity was possible, as a mixture of isomers results in this experiment; n_D^{20} 1.4280.³⁸ Tests for the presence of methane in the effluent gases and for irreversible adsorption on the cobalt-nickel catalyst were both negative. The over-all accuracy is probably 200 cal./mole, which includes any uncertainty in the purity of the mesitylene. However, the average ΔH represents the formation of an unknown mixture of isomers and thus may have a not well-defined thermodynamic meaning. It would seem from the data of Eisenlohr and Gorr³⁸ that we are getting chiefly the *trans* isomer, but the agreement of the refractive indices may be fortuitous.

Run	Moles C_9H_{12}	Moles H_2 per min.	Moles C_9H_{12} per min.	$-\Delta H_{881}$ cal./mole
1	0.020505	0.0070	2.85 (10^{-4})	47,957
2	.020647	.0112	4.23 (10^{-4})	48,018
3	.020746	.0050	4.94 (10^{-4})	47,827
4	.011447	.0158	3.67 (10^{-4})	47,920
Average				47,930 \pm 57
				$-\Delta H_{355}$ 47,620

Styrene + $4H_2$.—The data on this compound are quite consistent over a two-fold variation of hydrogen and styrene concentration. To ensure against polymerization the samples were stored in Dry-Ice and put into the clean saturating device just before the runs; this procedure was employed with all compounds for which polymerization was suspected. No methane or ethane was formed as concurrent side-reactions on the cobalt-nickel catalyst and no irreversible adsorption occurred. The styrene froze rather sharply at -30.5° ; addition of 0.5% ethylbenzene lowered the initial freezing point by 0.2° and the "flat" was somewhat steeper. The hydrogenation product showed no definite freezing point, yielding a glass; n_D^{20} 1.4333 (compare with product from ethylbenzene). The over-all accuracy is approximately 200 cal./mole.

Run	Sample	Moles C_8H_8	Moles H_2 per min.	Moles C_8H_8 per min.	$-\Delta H_{881}$ cal./mole
1	1	0.014153	0.0065	3.11 (10^{-4})	77,777
2	2	.013755	.0127	4.15 (10^{-4})	77,886
3	2	.013810	.0120	5.38 (10^{-4})	77,955
4	2	.013829	.0103	5.63 (10^{-4})	77,953
Average					77,893 \pm 61
					$-\Delta H_{355}$ 77,480

Hydrindene + $3H_2$.—The tabulated data show fair consistency in the runs. The freezing point of the hydrindene was excellent at -51.4° ; addition of 0.5% hydrogenation product lowered the initial freezing point by 0.3° and the temperature dropped off much more rapidly than with the pure material. A test for completeness of hydrogenation was devised: 1 cc. of the product + 10 small drops of concd. sulfuric acid at room temperature; blanks showed that as little as 0.1% of hydrindene in the product caused the formation of a definite brown color. The test was negative for all the reported runs, as was the test for ir-

(38) Eisenlohr and Gorr, Fortschr. Chem., Physik physik. Chem., 18, H9 (1925), give *cis*-1,3,5-trimethylcyclohexane. n_D^{20} 1.43010; *trans*-1,3,5-trimethylcyclohexane. n_D^{20} 1.42710.

reversible adsorption on the cobalt-nickel catalyst. No freezing point of the product was possible as a mixture of stereoisomers is present; a glass resulted; n^{20}_D 1.4688.³⁹ The over-all accuracy is approximately 250 cal./mole.

Run	Moles C ₉ H ₁₀	Moles H ₂ per min.	Moles C ₉ H ₁₀ per min.	-ΔH ₃₇₃ cal./mole.
1	0.022589	0.01217	5.01 (10 ⁻⁴)	46,061
2	.022652	.01486	4.89 (10 ⁻⁴)	45,867
3	.022490	.01482	4.64 (10 ⁻⁴)	46,055
4	.022652	.01519	5.12 (10 ⁻⁴)	45,966
Average				45,987 ± 71
-ΔH ₃₆₆				45,800

Indene + 4H₂.

Run	Sam-ple	Moles C ₉ H ₈	Moles H ₂ per min.	Moles C ₉ H ₈ per min.	-ΔH ₃₇₃ cal./mole
1	3	0.014836	0.01356	3.48 (10 ⁻⁴)	70,096
2	3	.014877	.01597	3.82 (10 ⁻⁴)	70,089
3	4	.014768	.01691	3.16 (10 ⁻⁴)	70,342
4	4	.014965	.01830	4.35 (10 ⁻⁴)	69,829
5	4	.014711	.01601	2.92 (10 ⁻⁴)	70,448
6	3	.014541	.01568	2.16 (10 ⁻⁴)	70,390
Average					70,199 ± 194
-ΔH ₃₆₆					69,910

The table shows large variation in the calorimetric results. A plot of ΔH versus the reciprocal of the length of the run (or versus rate of flow of indene) shows an irregular increase of ΔH with increased contact time on the catalyst; however, the slowest run, 6, gives almost the same ΔH as the next two, Nos. 5 and 3. Incomplete reaction in the faster runs, as a possible explanation of this difficulty, must be ruled out for the following reasons. (1) Each run's product was tested for completeness by the sulfuric acid test used for hydrindene and gave negative results (blanks with indene proved the validity of the test). (2) The experimental molar refractivity, P, from the determined n^{20}_D 1.4683 and d_{20} 0.8748 of the product from Run 3, is 39.46, and agrees well with the theoretical value, 39.37 calculated from Hückel's⁴⁰ figures for C₉H₁₆. (3) A comparison of the refractive indices of the product of "slow" Run 3 and of a non-calorimetric run faster than Run 4 was made by use of a Zeiss portable laboratory interferometer; this instrument had previously been calibrated with liquids of known index; the test showed the index of the product of the "fast" run only 0.00033 unit (23 scale divisions) higher than that of the "slow" run; this would correspond to about 0.3% incompleteness, while the maximum variation of the heats of hydrogenation is about 1%. (4) Comparison of the indices of the products from indene and hydrindene by means of the Zeiss interferometer shows that the latter is 0.00017 unit higher than the former. (5) Two cubic centimeters of the hydrogenation product from "slow" Run 3 in 30-cc. glacial acetic acid with 0.1 g. of platinum oxide and a trace of ferrous ion was treated in an Adams hydrogenation apparatus;⁴¹ the test was negative as only the empirical amount of hydrogen for the cata-

lyst was absorbed. Addition of 0.1 cc. of hydrindene resulted in the absorption of 60 cc. of hydrogen. This test for incompleteness was repeated with 4.4 cc. of product from a run faster than Run 4 and was likewise negative. Two cubic centimeters of indene was then hydrogenated in the Adams apparatus and approximately the theoretical amount of hydrogen was absorbed, corresponding to formation of octahydrindene.

In view of all this evidence we are completely puzzled and shall give only the over-all average ΔH. Compared with the fairly uniform data for hydrindene it seems entirely unlikely that varying amounts of the isomers of the hydrogenation product or that concurrent side-reactions, such as breakage of the five-membered ring, are causing the difficulty. As in the case of hydrindene, the hydrogenation product formed a glass and a freezing-point test of purity was impossible; n^{20}_D 1.4683. The test for irreversible adsorption on the cobalt-nickel catalyst was negative. The freezing point of the pure indene was very sharp at -1.67°; an initial freezing-point lowering of 0.3° and a pronounced falling off in temperature resulted upon contamination of the indene with 0.5% hydrogenation product.

As a crude estimate of over-all accuracy we shall give 500 cal./mole.

Cyclopentene + H₂.—The freezing point of the cyclopentene was sharp at -134.6° and dropped off markedly on addition of 1% of hydrogenation product (initial f. p. -135.0°). The hydrogenation product froze at -93.4°,⁴² 0.3° higher than that of the diene hydrogenation product (see IV, p. 151), but the trend of the freezing curve was the same as that of the diene. Each run was checked for completeness of hydrogenation by means of the bromine addition test (see II, p. 876). Tests for irreversible adsorption on the cobalt-nickel catalyst were negative; n^{20}_D 1.4064.⁴³ The over-all accuracy is estimated as 60 cal./mole.

Run	Moles C ₅ H ₈	Moles H ₂ per min.	Moles C ₅ H ₈ per min.	-ΔH ₃₆₆ cal./mole
1	0.038936	0.0094	9.93 (10 ⁻⁴)	26,921
2	.038939	.0117	9.94 (10 ⁻⁴)	26,905
3	.039062	.0085	14.01 (10 ⁻⁴)	26,920
4	.039121	.0127	14.19 (10 ⁻⁴)	26,915
Average				26,915 ± 5

α-Phellandrene⁴⁴ + 2H₂.—The data on the three related compounds, α-phellandrene, α-terpinene, and limonene, have no claim to high accuracy as we have such weak data regarding the purity of reactant and product. It probably is fair to assign a variation of 300 cal./mole to each final figure, as even fairly high percentages of other terpenes would not greatly influence the hydrogenation value.

This hydrogenation over cobalt-nickel yielded a product which was a mixture of isomers and formed a glass when chilled; n^{20}_D 1.4376 to 1.4380.⁴⁵

(39) Hückel, Sachs, Yantschulewitsch and Nerdel, *Ann.*, **518**, 155 (1935), give for hydrindane (*cis*) n^{20}_D 1.4713 to 1.4718.

(40) Hückel, "Theor. Grundlagen d. org. Chem.," Akad. Verlag., Leipzig, 2d ed., Vol. II, 1935, p. 86.

(41) We are indebted to Dr. R. B. Hershberg for his kindness in performing these experiments.

(42) "I. C. T.," Vol. I, p. 192, gives -93.3°.

(43) Compare with product from cyclopentadiene, n^{20}_D 1.4065 (see IV); Landolt-Börnstein, Erg. Iib, p. 820, gives n^{20}_D 1.40609 for cyclopentane.

(44) 2-Methyl-5-isopropylcyclohexadiene-1,3.

(45) "I. C. T.," Vol. I, p. 277, gives n^{20}_D 1.437 for para-menthane; a vast variety of values may be found for this compound.

Run	Moles C ₁₀ H ₁₆	Moles H ₂ per min.	Moles C ₁₀ H ₁₆ per min.	-ΔH ₃₅₅ cal./mole
1	0.018026	0.0115	5.88 (10 ⁻⁴)	53,625
2	.018017	.0096	5.88 (10 ⁻⁴)	53,619
Average				53,622 ± 3
				-ΔH ₃₅₅ 53,410

α-Terpinene⁴⁶ + 2H₂.—Each run was tested chemically for completeness of reaction. The product of this hydrogenation over cobalt-nickel formed a glass when cooled in liquid air; *n*²⁰_D 1.4403. We cannot explain the variation of the indices of the three hydrogenation products of these related compounds; it may be due both to varying amounts of impurity and to varying amounts of the isomers of *p*-menthane.

Run	Moles C ₁₀ H ₁₆	Moles H ₂ per min.	Moles C ₁₀ H ₁₆ per min.	-ΔH ₃₅₅ cal./mole
1	0.014402	0.0158	3.50 (10 ⁻⁴)	50,717
2	.014409	.0158	3.26 (10 ⁻⁴)	50,694
Average				50,705 ± 12

Limone⁴⁷ + 2H₂.—A test for completeness of hydrogenation using concentrated sulfuric acid, similar to that developed for hydrindene, was applied to the product from each run; the efficiency of the test was proved with blanks. Irreversible adsorption on the cobalt-nickel catalyst was absent. A glass resulted when the product was chilled in liquid air; *n*²⁰_D 1.4389 to 1.4392.⁴⁸

Run	Sample	Moles C ₁₀ H ₁₆	Moles H ₂ per min.	Moles C ₁₀ H ₁₆ per min.	-ΔH ₃₅₅ cal./mole
1	3	0.019059	0.01433	3.79 (10 ⁻⁴)	54,239
2	4	.019084	.01552	3.61 (10 ⁻⁴)	54,242
3	2	.019143	.01739	5.15 (10 ⁻⁴)	54,295
Average					54,259 ± 24
					-ΔH ₃₅₅ 54,110

Isopropylethylene + H₂.—A controlled freezing point of the product was very satisfactory; the value was -159.6°;⁴⁹ *n*¹⁴_D 1.3567.⁵⁰ Although a satisfactory freezing point suffices as a criterion of singleness of reaction, further independent test showed no degradation to lower hydrocarbons. The bromine test was used with all runs to indicate completeness. Irreversible adsorption on the 5% platinum-on-asbestos catalyst was absent. The over-all accuracy is 60 cal./mole.

Run	Moles C ₈ H ₁₆	Moles H ₂ per min.	Moles C ₈ H ₁₆ per min.	-ΔH ₃₅₅ cal./mole
1	0.035793	0.01160	8.73 (10 ⁻⁴)	30,366
2	.035977	.01000	10.56 (10 ⁻⁴)	30,324
3	.035968	.00912	9.28 (10 ⁻⁴)	30,322
4	.035800	.01230	7.49 (10 ⁻⁴)	30,331
Average				30,336 ± 15

Neo-amylethylene + H₂.—The 4,4-dimethylpentene-1 had an initial freezing point of -136.5° and fell off to -136.8° at 80% frozen material; addition of 0.5% hydrogenation product lowered the initial freezing point to

(46) 1-Methyl-4-isopropylcyclohexadiene-1,3.

(47) 1-Methyl-4-isopropenylcyclohexene-1.

(48) Compare with products from α-phellandrene and α-terpinene. All these materials should yield the same hydrogenation product.

(49) Parks, Huffman and Thomas, *THIS JOURNAL*, **52**, 1032 (1930), give -160.5° (112.6°K.) for 2-methylbutane.

(50) "I. C. T.," Vol. I, p. 193, gives m. p. -159.7°; p. 276 gives *n*²⁰_D 1.355 for 2-methylbutane.

-136.9° and the rate of drift was faster than for the pure material. The hydrogenation product was very satisfactory, as evidenced by a sharp freezing point at -123.9°;⁵¹ *n*²⁰_D 1.3823.⁵² There was no irreversible adsorption on the cobalt-nickel catalyst. The bromine titration test was used to ensure completeness of reaction. 60 cal./mole may be given as the over-all accuracy.

Run	Moles C ₇ H ₁₄	Moles H ₂ per min.	Moles C ₇ H ₁₄ per min.	-ΔH ₃₅₅ cal./mole
1	0.035185	0.01258	5.81 (10 ⁻⁴)	29,525
2	.035618	.01314	11.42 (10 ⁻⁴)	29,538
3	.035405	.01307	7.89 (10 ⁻⁴)	29,533
Average				29,532 ± 5

***t*-Butylethylene + H₂.**—The freezing point determination of *t*-butylethylene was very unsatisfactory; even with carefully controlled cooling, the material would supercool, heat to an initial freezing point and the temperature would then gradually drop off at an almost linear rate. Even hydrocarbon subjected to two fractional recrystallizations in liquid air-baths behaved in this manner, and the initial freezing point was not appreciably changed. This material has been sent to Prof. Parks for his estimate of the situation.^{53a} Likewise difficulty was experienced with the hydrogenation product: a glassy solid resulted even after many attempts. The test for irreversible adsorption on cobalt-nickel was negative, as were all the bromine addition tests for incompleteness of reaction; *n*²⁰_D product 1.3688.⁵³ We estimate the over-all accuracy as 150 cal./mole.

Run	Moles C ₆ H ₁₂	Moles H ₂ per min.	Moles C ₆ H ₁₂ per min.	-ΔH ₃₅₅ cal./mole
1	0.034537	0.01273	8.90 (10 ⁻⁴)	30,349
2	.034648	.00612	11.11 (10 ⁻⁴)	30,366
3	.034380	.01261	6.16 (10 ⁻⁴)	30,307
Average				30,341 ± 22

2,4,4-Trimethylpentene-1 + H₂.—Parks, Todd and Shomate⁵⁴ have estimated the purity of this hydrocarbon, Sample DIB-30, as 99.5%. The hydrogenation product froze well at -107.4°;⁵⁵ *n*²⁰_D 1.3917.⁵⁶ All runs were complete as shown by the bromine titration method and the test for irreversible adsorption on cobalt-nickel was negative. The over-all accuracy is approximately 60 cal./mole.

Run	Sample DIB	Moles C ₈ H ₁₆	Moles H ₂ per min.	Moles C ₈ H ₁₆ per min.	-ΔH ₃₅₅ cal./mole
1	31	0.038412	0.00768	8.23 (10 ⁻⁴)	27,250
2	30 + 31	.038469	.01060	8.73 (10 ⁻⁴)	27,231
3	30 + 31	.038551	.00911	10.12 (10 ⁻⁴)	27,235
4	30	.038584	.01160	11.00 (10 ⁻⁴)	27,229
Average					27,236 ± 7

(51) Parks, Huffman and Thomas, *THIS JOURNAL*, **52**, 3242 (1930), give -125.0° (148.1°K.) for freezing point of 2,2-dimethylpentane.

(52) Edgar and Calingaert, *ibid.*, **51**, 1540 (1929), give *n*²⁰_D 1.38233, f. p. -125.6° for 2,2-dimethylpentane.

(52a) Prof. Parks informs us that his tests have been unavoidably delayed; they will be reported in one of his papers.

(53) Maman, *Compt. rend.*, **198**, 1323 (1934), gives *n*²⁰_D 1.37054 for 2,2-dimethylbutane. "I. C. T.," Vol. I, p. 276, gives *n*²⁰_D 1.369.

(54) Parks, Todd and Shomate, *THIS JOURNAL*, **58**, 2505 (1936).

(55) Parks, Huffman and Thomas, *ibid.*, **52**, 1032 (1930), give -106.8° (165.3°K.) for 2,4,4-trimethylpentane; Bruun and Hicks-Bruun, *Bur. Standards J. Research*, **9**, 269 (1932), give -107.41°.

(56) Smyth and Stoops, *THIS JOURNAL*, **50**, 1883 (1928), give *n*²⁰_D 1.39163 for 2,4,4-trimethylpentane.

2,4,4-Trimethylpentene-2 + H₂.—Parks, Todd and Shomate⁵⁴ estimate the purity of this hydrocarbon, Samples DIB 23 + 24, as 98%; this lower purity was suspected by us in view of the distillation data (see Preparations). It seems likely that there exists another compound boiling only slightly above this isomer; this point is strongly supported by an examination of the distillation curves of Fenske, Quiggle and Tongberg.⁵⁷ The table shows that Run 1 on Sample DIB-25, from just above the "flat," gives a ΔH markedly different from those of Runs 2, 3 and 4 which are with Samples DIB-22 and -23 from the region of the "flat."⁵⁸

Run	Sample	Moles C ₅ H ₁₀	Moles H ₂ per min.	Moles C ₅ H ₁₀ per min.	— ΔH_{298} cal./mole
1	DIB-25	0.037106	0.0112	7.97 (10 ⁻⁴)	28,232
2	DIB-22	.036906	.0098	7.48 (10 ⁻⁴)	28,398
3	DIB-22	.036952	.0116	8.79 (10 ⁻⁴)	28,398
4	DIB-23	.036963	.0137	9.10 (10 ⁻⁴)	28,379
Average 2, 3, 4					28,392 = 8

n^{20}_D of product: from 1, 1.3932; from 2, 3, 4, 1.3918.⁵⁹ The usual tests for completeness of reaction and for irreversible adsorption on the cobalt-nickel catalyst were negative. The initial freezing point of the hydrogenation product was -108.2° (compare with 2,4,4-trimethylpentene-1) and the freezing curve had a pronounced downward trend. This freezing-point depression and dropping-off shows that the impurity present is not the low-boiling isomer, which should yield the same saturated hydrocarbon upon hydrogenation, but rather some other material. In view of this evidence it is difficult to estimate the over-all accuracy of this determination.

Crawford and Parks⁶⁰ have determined the heat of hydrogenation of the mixture of diisobutylenes in the liquid phase; $\Delta H_{298} = -28,580$ (≈ 800) cal./mole. Assuming with Fenske, Quiggle and Tongberg⁵⁷ that the pentene-1 is four times as abundant as the pentene-2, our data give for the heat of hydrogenation in gas phase of the mixed isomers at 298°K. $\Delta H = -27,240$. The agreement is fair, considering neglect of heats of vaporization.

Pentadiene-1,3 + 2H₂.—The small amount of material available prevented an attempt to separate the *cis-trans* isomers of this diene. However, several hydrogenations over copper were made on the three main samples; these are listed in the table. The trend is the same as found with the butenes-2, suggesting that the *cis*-isomer is the higher boiling one. The various samples represent far from pure materials as the freezing points given are initial ones and in each case the curve fell off rapidly; addition of 0.5% pentane to Sample P-2 lowered the freezing point to -87.8° but the trend of the curve was essentially unaltered. However, 15 cc. of the hydrogenation product from several samples of the diene gave an excellent freezing "flat" at -129.6° ,⁶¹ showing conclusively that the starting material can only consist of 5-C straight-chain compounds. Thus it is fairly certain that the diene is a

(57) Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

(58) Sample DIB-24 was not used in our calorimetric experiments as it was sent to Prof. Parks for his measurements.

(59) Compare with product from low-boiling isomer.

(60) Crawford and Parks, *THIS JOURNAL*, **58**, 373 (1936).

(61) Parks and Huffman, *ibid.*, **52**, 4381 (1930), give -129.7° (143.4° K.) for *n*-pentane.

Run	Sample	Moles C ₅ H ₈	Moles H ₂ per min.	Moles C ₅ H ₈ per min.	— ΔH_{298} cal./mole
1	P-2	0.019887	0.0143	7.80 (10 ⁻⁴)	54,008
2	P-2	.019982	.0153	10.40 (10 ⁻⁴)	53,963
3	P-4	.019830	.0139	7.54 (10 ⁻⁴)	54,208
4	P-4	.019888	.0098	10.40 (10 ⁻⁴)	54,174
5	P-3	.019791	.0141	6.33 (10 ⁻⁴)	54,208
Average for P-2					53,986 = 23
Average for P-4					54,191 = 17
Over-all average of runs					54,112 = 101

mixture of pure isomers, as presence of a mono-olefin is eliminated by the preparation. The bromine titration was used to show completeness of reaction; no degradation, polymerization or irreversible adsorption on the copper catalyst occurred. We have struck an average of all the ΔH values and present it as we did the value for the mixture of pentenes-2. The over-all accuracy is approximately 150 cal./mole.

2,3-Dimethylbutadiene-1,3 + 2H₂.—The freezing point of the diene was sharp at -76.0° and addition of 0.5% hydrogenation product caused a lowering of 0.4° , although not much change in the freezing "flat" was noted. It proved impossible to freeze the hydrogenation product; a glass resulted in all attempts (contrast with results on products from *unsym*-methylisopropylethylene and tetramethylethylene; see III, p. 143); n^{20}_D product, 1.3748.⁶² The bromine titration tests for completeness, tests for degradation to methane and for irreversible adsorption on the 5% platinum-on-asbestos catalyst were all negative. The over-all accuracy is approximately 150 cal./mole.

Run	Moles C ₆ H ₁₀	Moles H ₂ per min.	Moles C ₆ H ₁₀ per min.	— ΔH_{298} cal./mole
1	0.020092	0.0123	6.36 (10 ⁻⁴)	53,867
2	.020160	.0109	8.48 (10 ⁻⁴)	53,871
3	.020155	.0085	8.42 (10 ⁻⁴)	53,898
4	.020206	.0103	10.56 (10 ⁻⁴)	53,853
Average				53,872 = 13

Discussion

In order to conserve space we shall not attempt here a comparison of our data with those obtained by the combustion method. It is, however, noteworthy that in general combustion data on the more easily purified compounds agree much better with the present determinations than those made on difficult substances. This suggests that one of the major sources of error in those measurements is the inadequate purification of the materials.

With the three newly added monosubstituted ethylenes, isopropyl, neo-amyl and *t*-butyl ethylenes, the number of representatives of this group of hydrocarbons has been increased to six. It will be noted that with the exception of the neo-amyl group, the rest agree well among themselves,

(62) Compare with indices of product from *unsym*-methylisopropylethylene, n^{20}_D 1.3746; product from tetramethylethylene, n^{20}_D 1.3747 (omitted from III); "I. C. T.," Vol. I, p. 276, gives n^{20}_D 1.3783 for 2,3-dimethylbutane.

averaging $30,200 \pm 100$ cal./mole. The neo-amyl group, however, gives a distinctly lower result but the suggestion in paper III that branched-chain substituents are generally more effective in lowering the heat of hydrogenation can no longer be supported. Instead it must be concluded that introduction of branched-chains near the double bond leads to heats of hydrogenation which cannot be so accurately represented by the simple rules postulated in paper III as is possible with straight-chain alkyls. This is shown very clearly by the isomeric diisobutylenes. The lower boiling, 2,4,4-trimethylpentene-1, agrees still quite well with predictions. Its heat of hydrogenation is some 800 to 1000 cal. lower than those of other unsymmetrical disubstituted ethylenes (see III), whereas neo-amylethylene has a value which is lower by 600 to 800 cal. than those of other monosubstituted compounds. The 2,4,4-trimethylpentene-2, however, is completely anomalous. The same rules would predict for it a value of some 27,000 cal. (as in trimethylethylene) and in any case a value lower than that of its isomer. Instead, 28,400 cal. is found. Two per cent. impurity found by Parks, Todd and Shomate⁵⁴ does not explain the discrepancy unless the impurity is supposed to be a diene, perhaps C_7H_{12} , formed by splitting out of methane in the process of manufacture, boiling at nearly the same temperature. This is admittedly not very probable, but the structure of this hydrocarbon has been determined reliably by ozonolysis. Because of the good applicability of the hydrogenation rules as tested heretofore with pure compounds of established structure the possibility of diene impurity cannot be ignored.

However, Samples DIB-23 and 24 were returned to us by Professor Parks for further tests. At his suggestion we tested for peroxides by means of potassium iodide-starch solutions with negative results. Also, thirty-two grams of this material was treated with 0.65 g. of maleic anhydride on a steam-bath at 50° for thirty minutes; the diisobutylene was distilled off under reduced pressure at 35° , washed with potassium carbonate solution and dried with potassium carbonate. It was then subjected to a fractional distillation in a small Podbielniak-type column at a 10:1 reflux ratio; from 30 g. of material there was obtained 25 g. boiling at 104.8° (760 mm.). A calorimetric run was made on this

sample and its heat of hydrogenation found to be $-28,337$ cal./mole. Thus it seems that, if the discrepancy regarding this compound is to be attributed to a diene impurity, at least the diene present cannot be a conjugated one, capable of reacting with maleic anhydride.

With substituted conjugated dienes the introduction of alkyl groups also results in a lowering of the heat of hydrogenation, but the regularities are not very clear cut. Thus the change from butadiene to cyclohexadiene (equivalent to substitution on both ends of the chain) (see IV) lowers the heat by 1700 cal., butadiene to 1-methylbutadiene-1, 3 results in 3000 cal. change, and an introduction of two methyl groups in 2,3-positions causes 3100 cal. lowering. These apparent irregularities are probably connected with small changes of the conjugation resonance energy. If one assumes that precisely the same rules hold for substitution of alkyls in dienes as do in mono-olefins the resonance energies are found to vary from 4000 to 1800 cal.

The study of the terpenes was undertaken chiefly to verify the data on cyclohexadiene-1,3 in view of the importance of this compound in the light of a considerable disagreement with the older thermochemical data. The new results confirm the heat of hydrogenation of cyclohexadiene as well as can be expected considering the somewhat uncertain state of purity of the new substances. In α -phellandrene one of the double bonds receives an additional methyl substituent as compared with cyclohexadiene. Taking for this effect the value of 1500 cal. (difference between butene-2-*cis* and trimethylethylene), we calculate 53,800; obsd. 53,400. α -Terpinene has two new substituents on both double bonds; hence its heat of hydrogenation according to the same rule should be 52,300 whereas 50,700 is found. Limonene is not conjugated; to calculate its heat of hydrogenation we take the figure for methylisopropylethylene (28,000) and add to it monosubstituted cyclohexene (27,100) obtaining 55,100; found 54,100 for $-\Delta H$. Roth^{62a} has stated, on the basis of the heats of combustion of α -phellandrene (1435 Cal.) and 1,3-dimethyl-5-ethenecyclohexene-3 (1455 Cal.), that a shift of a double bond from a side chain into the ring in a conjugated position liberates ca. 20 Cal. Our values for α -phellandrene and limonene do not confirm this. The discrepancy may well be attrib-

(62a) Roth, *Z. Elektrochem.*, 17, 789 (1911).

uted to the purity of the compounds used in the combustion measurements.

Benzene derivatives show a general lowering of their heats of hydrogenation as compared with parent substance. The lowering is rather small, being 900, 1300 and 700 cal. per substituent group in ethylbenzene, *o*-xylene and mesitylene, respectively. These figures are distinctly lower than those for the third substituent in aliphatic compounds, but the trend is in general the same. It is to be noted that the substituents on the benzene ring have little effect on the resonance energy. The heat of hydrogenation of the ethylenic group in styrene can be calculated readily by comparison with ethylbenzene and is found to be 28,560 cal. It is noteworthy that the conjugation energy with the benzene ring is quite small, amounting to only 1600 cal. This is a case where the use of thermochemical data has led to quite different results.⁶³ The heat of combustion, however, undoubtedly was falsified by the presence of polymerized material, which fortunately does not affect the present method as the high-boiling polymer is not carried by the passing gas stream into the calorimeter.

We now come to compounds containing five-membered carbon rings and it is desirable to consider them from a unified point of view. In paper IV the heat of hydrogenation of cyclopentadiene was reported as 50,865 cal., which is 4500 cal. lower than that of cyclohexadiene-1,3. This was interpreted as due to increased resonance energy but present measurements do not bear out this point of view. Indeed the heat of hydrogenation of cyclopentene, 26,915 cal., is 1680 cal. lower than that of cyclohexene and thus the resonance energies in the two cases are practically the same. The uniformly lower values in the five-membered ring systems, however, are very puzzling. If it is assumed tentatively that the entire difference between the six- and the five-membered series is due to strain and that the six-membered rings, whether saturated or unsaturated, are practically strainless,⁶⁴ then it follows that with increasing saturation of the five-membered rings the strain increases. Namely, to explain the lowered heat

of hydrogenation one must suppose that in the process of hydrogenation part of the available energy is retained by the molecule as increased strain instead of being liberated as heat.

The reliability of these experimental findings receives independent support from the study of indene and hydrindene. Unfortunately at present there are no values of 1,2-dihydronaphthalene⁶⁵ to be compared with indene but we may use the data on styrene and correct them for substitution according to the rules previously developed. Correcting for orthosubstitution on the benzene ring of styrene (difference between ethylbenzene and *o*-xylene) and for second substitution on the side chain double bond, we arrive at 73,700 cal. The observed value for indene is 69,900 and while both may be rather considerably in error, the magnitude of the difference is much too large to be explained away on this basis.

Quite similar are the results obtained with hydrindene. It may be compared directly to *o*-xylene because, as we have found earlier, the change from methyl to longer chain radicals does not affect appreciably the heat of hydrogenation. Hence, if the five-membered ring acts in all respects as an aliphatic chain the two figures should be identical. Actually it is found that hydrindene has a 1400-cal. lower heat of hydrogenation. For the logical validity of this comparison it is not necessary to fix the double bonds in the benzene ring. The physical facts are that after hydrogenation we have a five-membered saturated (substituted) ring and that in the process of hydrogenation this system has been obtained from one which lacked two hydrogens in adjacent positions common to the benzene ring. By comparison with *o*-xylene we note that the introduction of these two hydrogens into the five-membered ring releases less heat than a similar process when the ring is not closed as in *o*-xylene. (We are supposing here that the other hydrogenated positions in the benzene ring are less affected by the five-membered ring than these particular two atoms; for this we have complete justification from all data on the heats of hydrogenation.)

It is seen thus that indene and hydrindene fall in line with cyclopentadiene and cyclopentene, namely, there is less heat evolution when these compounds take up hydrogen and become

(63) Pauling and Sherman, *J. Chem. Phys.*, **1**, 684 (1933), give 6900 cal. (calcd.); 6700 (obsd.).

(64) Cyclohexane and cyclohexene are entirely strainless on the basis of the tetrahedral carbon atom model if one allows non-planar rings. Cyclohexadiene, even when planar, is under a very slight strain, when accepted internuclear distances are used. Perhaps this explains the slightly lower magnitude of the resonance energy found by us for cyclohexadiene as compared with other conjugated dienes.

(65) Data on this and related compounds may soon be available from determinations of heats of hydrogenation in the liquid phase made by Dr. R. B. Williams of this Laboratory.

saturated five-membered rings than when the corresponding process occurs in open chains or six-membered rings.

The data on cyclopentane and cyclopentadiene can be summarized by stating that the former has a strain smaller by some 1600 cal. and the latter one smaller by *ca.* 4000 cal. than cyclopentane. And since the latter, as combustion data⁶⁶ indicate, is itself under a strain of about 4000-5000 cal., there appears to be no strain in cyclopentadiene and a very small one in cyclopentane.

These facts are quite difficult to reconcile with tetrahedral angle carbon atom models. Construction of diagrams of the five-membered rings readily shows that the strain in these rapidly increases with increasing unsaturation. The use of 1.53 Å. for the single bond and 1.36 Å. for the double bond distances, together with tetrahedral angles, reveals that in cyclopentane the formation of the planar pentagon produces a strain due to the closure of a gap of 0.16 Å. In cyclopentane the gap has increased to 1.34 Å. and in cyclopentadiene it is 2.06 Å. In this last case the gap is hardly larger than in the model of cyclobutane, which latter compound, as it is known, is under a severe strain. Indeed, on studying these models, one wonders how cyclopentadiene, if it has this theoretical stereochemical structure, could ever have been found in the distillation of coal.

The discrepancy can be, of course, formally ascribed to some other, as yet unstudied, competing effects which overshadow the strains. Such an attitude, however, is very unsatisfactory since the strain theory itself was introduced to explain the instability of certain atomic configurations in organic compounds and one rather must conclude that the magnitude of strains cannot be evaluated in some special cases, at least, on the basis of the tetrahedral angle model. The problem is one of great interest and further work on small, unsaturated rings, in particular on lactones and acid anhydrides, is planned.

Some comments concerning the fixation of double bonds in benzene rings are in order.

(66) Hückel, "Theor. Grundlagen d. org. Chem." Akad. Verlag, Leipzig 2d ed., Vol. I, 1935, p. 60, gives 5000 cal. Consistent use of Swietoslowski's data on cyclopentane and cyclohexane [as given by Kharasch, *Bur. Standards J. Research*, **2**, 359 (1929)] and Rossini's very reliable data on the straight-chain compounds [*ibid.*, **13**, 21 (1934)] corrected from gas to liquid state, gives -13,200 and -9700 as the heats of formation of the straight-chain compounds from the cyclic ones; the strain in cyclopentane is thus 3500 cal.

From the conclusions as to the relative strains in the five-membered rings one cannot, of course, arrive at definite conclusions about the positions of double bonds in the attached benzene ring. One point is quite clear, however, if in the tetralin molecule the saturated ring does not prevent the free resonance between the two Kekulé formulas, in hydrindene such resonance cannot be hindered in favor of a single bond being made a part of the five-membered ring. This is evident because more heat is evolved when an unsaturated six-membered ring is converted into a saturated one than when this happens to a five-membered ring. The entropies of the two processes are unknown but one might surmise, with a considerable degree of certainty, that they are not far different from one another. Hence there will be less driving force for the five-membered ring in hydrindene to become saturated than for the six-membered one in tetralin. This is in decided disagreement with conclusions reached by Mills and Nixon,⁶⁷ Sidgwick and Springall⁶⁸ and Fieser and Lothrop⁶⁹ from their studies of other phenomena. As these phenomena are rather complex it is somewhat questionable whether their conclusions are the only plausible ones.

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ERRATA AND ADDENDA

(1) In III, p. 143, there should be recorded the n_D^{20} of the product from tetramethylethylene = 1.3747.

(2) In IV, p. 150, 5% Pt-on-asbestos was the catalyst used in the hydrogenation of cyclopentadiene.

(3) Parks, Todd and Shomate⁶⁴ have given the following estimates of purity: in III, heptene-1, 99.85%; in III, tetramethylethylene, "probably of similar high order"; in IV, 1,4-pentadiene, 99.90%.

Summary

The heats of hydrogenation of the following substances have been determined:

(67) Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).

(68) Sidgwick and Springall, *Chemistry and Industry*, **55**, 476 (1936).

(69) Fieser and Lothrop, *THIS JOURNAL*, **58**, 2050 (1936).

Substance + xH ₂	°K.	ΔH , cal./mole	Deviation, cal.	Over-all accuracy, cal.	ΔH_{100}° , 82° C., cal./mole
Ethylbenzene + 3H ₂	381	-49,235	±17	±100	-48,920
<i>o</i> -Xylene + 3H ₂	373	-47,466	±26	±200	-47,250
Mesitylene + 3H ₂	381	-47,930	±57	±200	-47,620
Styrene + 4H ₂	381	-77,893	±61	±200	-77,480
Hydrindene + 3H ₂	373	-45,987	±71	±250	-45,800
Indene + 4H ₂	373	-70,199	±194	±500	-69,910
Cyclopentene + 1H ₂	355	-26,915	±5	±60	-26,915
α -Phellandrene + 2H ₂	381	-53,622	±3	±300	-53,410
α -Terpinene + 2H ₂	355	-50,705	±12	±300	-50,705
Limonene + 2H ₂	373	-54,259	±24	±300	-54,110
Isopropylethylene + 1H ₂	355	-30,336	±15	±60	-30,336
Neo-amylethylene + 1H ₂	355	-29,532	±5	±60	-29,532
<i>t</i> -Butylethylene + 1H ₂	355	-30,341	±22	±150	-30,341
2,4,4-Trimethylpentene-1 + 1H ₂	355	-27,236	±7	±60	-27,236
2,4,4-Trimethylpentene-2 + 1H ₂	355	-28,392	±8	?	-28,392
Pentadiene-1,3 + 2H ₂	355	-54,112	±101	±150	-54,112
2,3-Dimethylbutadiene-1,3 + 2H ₂	355	-53,872	±13	±150	-53,872

1. The previously discussed rules correlating the heat of hydrogenation with the structure of unsaturated hydrocarbons have been extended. It has been found that branched-chain substituents do not follow the rules as well as do the straight chains.

2. The evidence of the heats of hydrogenation

of the five-membered carbon ring systems points to a strain which decreases as unsaturation increases. This is quite contrary to conclusions which may be drawn from tetrahedral angle carbon atom models. The implications of these results are discussed.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

Dibenzylideneglucose and Dibenzylideneglucuronic Acid from 6-Benzoyldiethylmercaptoglucose. Synthesis of Another Dibenzylideneglucose from 4,6-Benzylideneglucose

BY PHILIPPOS E. PAPADAKIS

It is known that acetals of aromatic aldehydes and sugars are obtainable in pure crystalline form. Benzylidene derivatives of sugars which have part of their hydroxyl groups blocked are convenient starting materials in synthetic work.¹ The application of catalytic hydrogenation to such acetals of aromatic aldehydes and sugars for the splitting of the benzylidene residue, wherever the acid hydrolysis is objectionable, constitutes another advantage in favor of their use.

The present author had occasion in the past to prepare 6-benzoyldiethylmercaptoglucose in pyridine solution at 0°. This was used as a starting material for the preparation of a dibenzylidene derivative of glucose. The method

adopted was similar to that used by L. Zervas¹ in the preparation of 4,6-benzylideneglucose. In the course of the experimental work it was found that the ethyl mercaptal groups were split off and a monobenzoyl dibenzylidene derivative of glucose resulted which does not reduce Fehling's solution. It is thought that the compound may be 1,2,3,5-dibenzylidene-6-benzoyl- α -*D*-glucofuranose. If that be the case then by hydrolyzing the benzoyl group one may obtain 1,2,3,5-dibenzylidene- α -*D*-glucofuranose. The latter by subsequent oxidation should yield 1,2,3,5-dibenzylideneglucuronic acid which could be changed into glucuronic acid. The benzoyl residue of the monobenzoyldibenzylideneglucose was split off by means of either alcoholic potassium hydroxide solution and heat or by means of the calculated amount of sodium methoxide in chloroform at 0°. The resulting

(1) L. Zervas, *Ber.*, **64**, 2289 (1931); P. Brigl and R. Schinle, *ibid.*, **66**, 325-30 (1933); P. Brigl and H. Gruner, *ibid.*, **65**, 1428 (1932); P. Brigl and O. Widmaier, *ibid.*, **69**, 1219 (1936); P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **53**, 431 (1922); *ibid.*, **57**, 319 (1923).