[Contribution from the Chemical Laboratory of Harvard University]

Heats of Organic Reactions. IV. Hydrogenation of Some Dienes and of Benzene

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The purpose of this paper is to report upon the heats of hydrogenation of several dienes and of benzene. The technique employed is the same as that described in the earlier papers of this series[1] and needs no further discussion.

Preparation of Compounds

Allene.—Tribromopropane, prepared according to "Organic Syntheses,"[2] was distilled through Column C (see Paper III) at 20 mm. pressure. The boiling point of the product was 105.5–106.5°. The refractive indices of the samples (some twenty fractions) varied from 1.5886 to 1.5888 at 15.2°, and freezing points from 16.25 to 16.40°. Dibromopropene was also prepared by the method of "Organic Syntheses."[3] It was separated from most of the residual tribromopropane by distillation through a one-meter column under reduced pressure. It was finally fractionated in Column B at 75 mm. The boiling points of several fractions varied from 73.2–74.3°, and the refractive indices at 17.3° from 1.5490–1.5562. Obviously the material was not homogeneous. When a refractionation of a portion of this product was attempted, decomposition, together with some polymerization, appeared to take place; only hydrobromic acid and a heavy tar were recovered. Further attempts to purify it were abandoned, and it was converted immediately to allene.

To a vigorously stirred suspension of 900 g. of 30-mesh zinc in 2500 cc. of boiling 95% ethyl alcohol was added 1250 g. of dibromopropene at such a rate that the heat of the reaction caused the alcohol to reflux vigorously. After the addition was complete, the solution was stirred and refluxed as long as any allene was evolved. The crude material, which amounted to approximately 50% of the theoretical, was collected in a trap cooled with Dry-Ice. The product was scrubbed by bubbling through six Friedrich wash bottles, the first three containing 10% sodium hydroxide solution at 0°, and the last three with water at 0°. The gas was partially dried by passage through a tower of potassium hydroxide pellets, and finally condensed in Dry-Ice again. Tests for ethyl alcohol in the last two washing bottles were negative. No precipitate was formed when the gas was allowed to bubble through an ammoniacal solution of silver nitrate. (Acetylene gave a copious precipitate when it was passed through the same solution. This test would seem to indicate that no methylacetylene was present.)

The liquid allene was filtered through a plug of glass wool at −80° and systematically fractionated in the apparatus used for the purification of propylene,[4] except that instead of a 1-meter, a 1.7-m. column was used. A moderate quantity—10–15%—of a low-boiling material was present; the boiling point suggested that it was propylene, but it was not identified definitely. The boiling point of the "best" (No. 1 in Table I) fraction was −34.29 ± 0.01° at 761.6 mm. (0°) and that of another fraction (No. 2 in Table I) was −34.28 ± 0.02° at 761.7 mm. (0°). Both of these are in fair agreement with the vapor pressure data of Livingston and Heisig (760 mm. at −35.0°).[5] The freezing point of No. 1 was at −136.1°.

Butadiene.[6,7]—Cyclohexene, obtained as described in III, was refluxed, the vapor passing over a red-hot spiral made of 1 meter of No. 22 platinum wire. The effluent gases from the reflux condenser were passed through an ice trap, and then into a receiver cooled by Dry-Ice. The apparatus produced up to 50 g. of crude butadiene per hour. The cyclohexene which was carried over into the ice and Dry-Ice traps was recovered and re-used. Some high-boiling material accumulated in the boiling flask and was removed from time to time.

The crude butadiene was distilled twice from bulb to bulb, filtered through a plug of glass wool at −80°, and fractionated twice in Column A. The distillation was not satisfactory; the boiling point fluctuated from −4.58 to −4.49° at 757 mm. (0°). The freezing point determination, Fig. 1, indicated that the compound was not pure; butene-1 may have been present.

A portion of the crude butadiene which had been distilled twice from bulb to bulb was converted to the tetrabromide by allowing it to bubble into a solution of bromine in carbon tetrachloride at room temperature. The overall yield of tetrabromide from cyclohexene was 65%. The product contained approximately one part of the low-melting and three parts of the high-melting isomers. After the crude tetrabromide had been recrystallized twice from alcohol, the capillary melting points of various samples ranged from 115–117°. Further recrystallization of one sample from petroleum ether, chloroform, ether, chloroform, and twice from ether (six additional successive recrystallizations in all) did not alter the melting point substantially.

Butadiene was regenerated from the tetrabromide by the method of Thiele:[8] 660 g. of 30-mesh zinc was stirred rapidly in a 5-liter 3-necked flask fitted with a reflux condenser and containing 2 liters of boiling 95% ethyl alcohol. Heating was stopped and 995 g. of tetrabromide was added at such a rate that the alcohol refluxed vigorously. The addition required about one and one-half hours. The butadiene was collected in a trap cooled with Dry-Ice, the yield being 88%. It was washed in the same manner as butene-1, Sample B,[9] filtered through a

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[1] See preceding paper, III, This Journal, **57**, 137 (1935).

[2] "Organic Syntheses," Coll. Vol. I, p. 507.

[3] *Ibid.*, p. 203.

[4] See II. This Journal, **57**, 877 (1935).

[5] Livingston and Heisig, *ibid.*, **52**, 2409 (1930).

[6] German Patent 252,499.

[7] We wish to thank Professor F. O. Rice for suggesting cyclohexene to us as starting material for the preparation of butadiene.

[8] Thiele, *Ann.*, **308**, 339 (1899).

[9] See II, p. 879.

plug of glass wool at −80°, and distilled through Column A. The boiling point of the middle fraction was −4.51 ± 0.01° at 757 mm. (0°). The freezing point was −108.7° (see Fig. 1).

1,4-Pentadiene.[10]—α-Chloroethyl ether was prepared by bubbling a slight excess over the calculated amount of anhydrous hydrochloric acid into a 3-to-1 mixture of absolute ethyl alcohol and paraldehyde (b. p. 124.1–124.3° at 766 mm.). The mixture was stirred vigorously, and the temperature maintained at −10 to −5°. The yield of crude material, dried, and free from hydrochloric acid, was 91%. Upon distillation at 160 mm. through Column C, the yield dropped to 65%, in accordance with the observation of Shoemaker and Boord. The boiling point was 48.5–49.5°. Most of the loss seemed to be due to the presence of a low-boiling fraction. The chloro ether was converted to the dibromo ether; the yield of material boiling at 70–72° at 15 mm. was 74%. The allyl Grignard reagent was prepared by allowing a solution of 5 moles of allyl bromide (see III) in 3 liters of ether to drop at the rate of 400 cc. an hour on 10 moles of magnesium;[11] the mixture was stirred vigorously. The reagent was filtered off by forcing it through a plug of glass wool; 5 mols of fresh turnings was added to the residual magnesium, and another run made in the same flask.

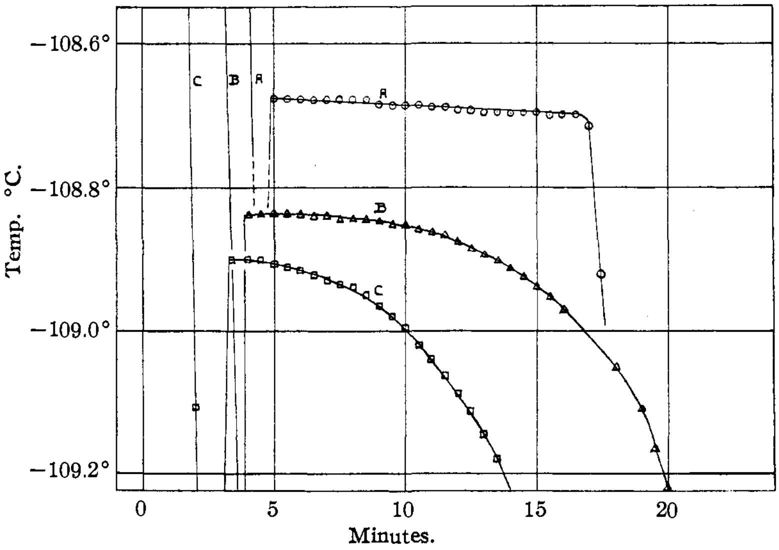

Fig. 1.—Freezing curves of A, 1,3-butadiene from tetrabromide, Sample H + I; B, 1,3-butadiene from cracking, Sample N; C, Sample H + I + 0.5% butene-1.

Dibromoethyl ether diluted with an equal volume of ether was added to the Grignard reagent at 10° during three to five hours until the solution no longer gave a test for Grignard reagent. The upper and lower layers, which had formed, were worked up separately. The solutions were acidified with acetic acid and then stirred vigorously with water; the water layer was removed and the treatment repeated with dilute alkali; the solutions were dried with potassium carbonate, and the ether removed by distillation through Column C. The α-allyl-β-bromoether was not steam distilled but was fractionated directly. Any residual α,β-dibromoether ought to have been decomposed by the previous treatment with water and alkali and in any case the ethyl vinyl ether which it would ultimately yield should be separable in Column A. The product was transferred to a one-meter column, and distilled; the pressure was decreased gradually, and in such a way that some 1,5-hexadiene which had been formed could be collected and recovered. The product was finally distilled in Column C. The boiling point was 70–75° at 16 mm. It changed by about one degree during any one fractionation, but on different runs it varied considerably more. The yield was 51% based on the allyl bromide, and 78% on the dibromoether.

Twelve hundred grams of α-allyl-β-bromoethyl ether, 1500 cc. of *n*-butyl alcohol, and 1500 g. of zinc dust were stirred and refluxed. No reaction occurred after an hour. After the addition of about 3 g. of zinc chloride,[12] 1,4-pentadiene was evolved, slowly at first and then more rapidly. The rate of the reaction could be controlled nicely by the rate of heating and the process required about four hours for completion. The 1,4-pentadiene was collected in an ice trap. The combined products from several runs were distilled through a one-meter column; b. p. 25.8–26.0°. The distillate was mixed with 1 liter of methyl alcohol, and refractionated; b. p. 24.0°. The azeotrope was washed five times with an equal volume of ice water, dried with potassium carbonate, filtered, and distilled. The yield at this stage was 75%. The product was finally fractionated in Column A. The boiling point was 26.27 ± 0.01° at 767 mm. (0°) and the freezing point −148.1°.

1,5-Hexadiene.—Some 1,5-hexadiene was recovered from the intermediate fraction resulting from the distillation of α-allyl-β-bromoethyl ether. A further quantity was prepared by a modification of the method of Lespieau.[13] The products were combined and systematically fractionated. The portion boiling at 59–60° was refluxed with thinly sliced sodium for eight hours, and then distilled. It was finally fractionated in Column A. The boiling point was 59.87 ± 0.01° at 767 mm. (0°) and the freezing point −140.8°.

Cyclohexadiene.[14]—To 2067 g. of cyclohexene and 500 cc. of chloroform cooled with Dry-Ice, 4063 g. of bromine was added at such a rate that the temperature did not rise above −20°. The crude material was heated and a stream of carbon dioxide passed through it until the hydrobromic acid and chloroform were removed. The product was systematically fractionated at 20 mm. in a one-meter column. The boiling range was 110–111°; the yield at

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[10] Shoemaker and Boord, This Journal, **53**, 1505 (1931).

[11] Mallinckrodt turnings "For Grignard Reactions."

[12] We are indebted to Professor E. P. Kohler for suggesting this procedure.

[13] Lespieau, *Ann. chim.*, [8] **27**, 149 (1912).

[14] Hofmann and Damm, *Mitt. schlesischen Kohlenforschungsinst. Kaiser-Wilhelm-Ges.*, **2**, 97–146, Sept., 1925; *C. A.*, **22**, 1249 (1928).

this point was 81%. The fractions were combined, and refractionated in Column B at 30 mm. The boiling point was 117–118°; the indices of refraction of twenty fractions varied from 1.5581 to 1.5583 at 8.2°. The dibromocyclohexane in portions of 4 moles, was converted to a mixture of cyclohexadiene and ethyl-Δ-2,3-cyclohexenyl ether according to the directions of Hofmann and Damm. The alcohol solution, from which the sodium bromide had been removed by filtration, was distilled in Column C; three fractions were taken: to 78° (this consisted largely of the ethyl alcohol–cyclohexadiene azeotrope), 78–85° (this consisted largely of ethyl alcohol), and residues. The first fraction was distilled with water, and crude cyclohexadiene recovered from it. The residues were mixed with about 3 liters of water, and distilled until no more oil came over. The aqueous residues from these steps were combined with the 78–85° fraction; the whole was diluted to 11 liters and boiled until the distillate was not cloudy on dilution with water. The distillate was diluted with water, the oil separated, and the aqueous residues boiled as before. This process was repeated as long as any product could be recovered—usually twice was sufficient. The yield of crude cyclohexadiene was 17%, and of the unsaturated ether, 67%—a total recovery of 84%. The products were washed, dried with anhydrous potassium carbonate, and systematically fractionated. Enough cyclohexadiene was recovered to warrant a distillation in Column A, but the results indicated that the product was decidedly impure and it was discarded.

The portion of ethyl cyclohexenyl ether boiling at 150–155° was refluxed with two portions of sodium; on the second treatment there was practically no reaction. This material was then fractionated in Column B, and the portion boiling at 154.6–154.8° at 760 mm. collected. This was converted to cyclohexadiene by distillation with potassium acid sulfate.[14] The product was washed several times with cold water, and then with dilute alkali. It was dried with potassium carbonate, filtered, and distilled. The yield at this point was 57%. The cyclohexadiene was finally mixed with one and a half its weight of methyl alcohol, and the azeotrope fractionated in Column A. The boiling point was 56.65 ± 0.04° at 762 mm. (0°). The middle fraction was shaken five times with an equal volume of ice water, dried with potassium carbonate, filtered, and distilled. It was then fractionated in Column A; the boiling point was 80.31 ± 0.01° at 757 mm. (0°). The freezing point was −104.8°; $n^{20}\text{D}$ 1.4740.

Benzene.—Merck Blue Label Benzene was purified by partial freezing until the freezing point of the crystals, when separately melted and refrozen, was the same as that of the mother liquor (5.5° on a 0.1° thermometer). This product was distilled in Column A; the boiling point was 80.27 ± 0.01° at 762 mm. (0°) and $n^{20}\text{D}$ 1.5009. The freezing point was +5.45°.

Cyclopentadiene.—Two thousand grams of technical dicyclopentadiene[15] was cracked in a small still equipped with a 91-cm. column filled with glass beads and a partial condensing head; the fraction of the monomer distilling at 40–41° was 1300 cc. This was distilled in Column C and the fraction boiling at 40.1–40.3° at 766 mm. was 850 cc. This fraction was refluxed for ten hours on a steam-bath to polymerize it to the dimer, and was then distilled in Column C at 50 mm. The boiling point of the product was 86.0° and the freezing point was 33.5°. A redistillation through Column C raised the freezing point to 33.6°. The yield was 600 cc. of pure dimer. This was recracked in Column C in an atmosphere of nitrogen. From 381 g. of dimer 266 g. of monomer was obtained which boiled flatly at 40.83° at 772 mm. (0°).

The Results

Due to the variations in the various tests, we shall present the results of each compound separately. The double catalyst experiment, performed in *each* case, will not be mentioned explicitly. The test of completeness of reaction for each run was by the specifically tested bromine absorption method (see II and III) except in the cases of 1,3-cyclohexadiene and benzene. In the former of these two, the sulfuric acid test developed for cyclohexene (see III) proved satisfactory in combination with determinations of refractive index and rough freezing points; for benzene, no chemical test but the two physical tests only were used. With some of the compounds there exists the danger that polymerization might have occurred in the bubbler during the runs. However, in no case did it amount to more than a very few per cent. Because of the difference in the vapor pressures of the monomeric and polymeric forms, none but the former thus was carried into the calorimeter by the hydrogen.

Allene.—In Table I are given all of the calorimetric runs. It is to be observed that the average deviation of these results is somewhat larger than usual. Sample No. 1 seemed to be the best and gave an excellent freezing "flat" without any drift at −136.1°; addition of 0.4% propylene lowered the initial freezing point by *ca.* 0.1° and the curve fell off pronouncedly. The test for irreversible adsorption on the catalyst (see III) was negative. The degradation-polymerization experiment showed by the combustion method that no methane was formed, although extra precautions were taken to remove any possible methane from the condensate. The condensate was fractionally distilled in a small (4-mm., 60 cm.) Podbielniak type[16] column with vacuum jacket; the pot was heated by a bath at 40°. The distillation temperature remained constant at −35° until nothing would come over and then fell. The distillate was collected in two equal portions and these had equal vapor pres-

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[15] Drs. Fraenkel and Landau, Berlin.

[16] See I, THIS JOURNAL, **57**, 71 (1935).

sures (126 mm.) at −80°, indicating no ethane. The constancy of the boiling point at the end of the process showed an absence of butane. The volume of propane collected was 5150 cc. at N. T. P. The residue in the column was carefully removed and found to weigh 0.69 g., to have an approximate boiling point of 62–3°, an approximate freezing point of −143 to −147°, and $n^{20}\text{D}$ 1.3715. The values lead one to conclude that the polymer is isohexane.[17] From the data of Rossini[18] one may compute ΔH of $2\ C_3H_8 \longrightarrow n$-hexane $+ H_2 = +9.5$ Cal. and if, as is the case with n- and isobutane,[19] isohexane is more stable by 1.6 Cal., one finds ΔH of $2\ C_3H_6 \longrightarrow$ isohexane $+ H_2 = +7.9$ Cal. 6.5% of the allene reacting finally forms isohexane and the correction to the observed heat of hydrogenation is −260 cal. The final value for the heat of hydrogenation of allene is −71,280 ± 200 cal. The assigned over-all uncertainty is believed to be sufficient because as Table I shows, the heat of hydrogenation was fairly constant, thus indicating reproducible extent of polymerization under the variable conditions of the gas flow. The uncertainty is sufficiently small not to affect our essential conclusions.

TABLE I

ALLENE

Run	Moles C_3H_4	C_3H_4 flow, moles/min.	H_2 flow, mole/min.	$-\Delta H$ 355°K., cal./min.
1	0.015616	6.32 (10^{-4})	0.0121	70,841
2	.017176	6.38 (10^{-4})	.0127	70,949
3	.015596	6.61 (10^{-4})	.0121	71,123
4	.015612	7.90 (10^{-4})	.0161	71,130
5	.015456	3.42 (10^{-4})	.0116	71,074
			Average	71,023 ± 103

Runs 1 and 2. Sample No. 3

Runs 3, 4 and 5. Sample No. 1

1,3-Butadiene.—The calorimetric data on the two samples are presented in Table II. As Fig. 1 clearly shows, sample H + I is the better one of the two and, indeed, is unquestionably pure. The degradation-polymerization experiment showed the absence of methane, ethane and polymers. The over-all error is estimated at 100 cal.

TABLE II

BUTADIENE

Run	Moles C_4H_6	C_4H_6 flow, moles/min.	H_2 flow, mole/min.	$-\Delta H$ 355°K., cal./mole.
	From tetrabromide (H + I)			
1	0.018561	8.79 (10^{-4})	0.0122	57,063
2	.018543	8.08 (10^{-4})	.0121	57,024
3	.018559	9.89 (10^{-4})	.0062	57,136
4	.018538	7.71 (10^{-4})	.0184	57,050
5	.018441	4.88 (10^{-4})	.0180	57,061
			Average	57,067 ± 28
	From cracking (N)			
1	0.018513	9.87 (10^{-4})	0.0121	57,286
2	.018560	7.79 (10^{-4})	.0121	56,967
3	.018576	8.11 (10^{-4})	.0122	56,947
4	.018542	8.51 (10^{-4})	.0179	57,117
			Average	57,079 ± 122

1,4-Pentadiene.—The sample of 1,4-pentadiene used in the calorimetric experiments (given in Table III) gave a good freezing curve, the "flat" of which occurred at −148.1 to −148.2° up to 80% frozen material; addition of 0.5% n-pentane lowered the initial point by 0.3° and the curve dropped off slowly. The degradation-polymerization experiment gave negative tests for all side reactions. An experiment was performed to test for irreversible adsorption on the copper catalyst: in a run wherein some 8 cc. of pentane was collected, a weight increase of the catalyst of 2.6 mg. was found; this is quite within the limits of error. $n^{20}\text{D}$ of the hydrogenation product was 1.3570. The over-all error is estimated as 150 cal.

TABLE III

1,4-PENTADIENE

Run	Moles C_5H_8	C_5H_8 flow, moles/min.	H_2 flow, mole/min.	$-\Delta H$ 355°K., cal./mole
1	0.018242	6.14 (10^{-4})	0.0129	60,871
2	.018252	5.79 (10^{-4})	.0129	60,676
3	.018104	3.67 (10^{-4})	.0125	60,776
4	.018308	9.69 (10^{-4})	.0130	60,837
			Average	60,790 ± 64

1,5-Hexadiene.—1,5-Hexadiene showed a good freezing "flat" at −140.8° and addition of 0.5% hexane caused a dropping off. The degradation-polymerization experiment gave negative

TABLE IV

1,5-HEXADIENE

Run	Moles C_6H_{10}	C_6H_{10} flow, moles/min.	H_2 flow, mole/min.	$-\Delta H$ 355°K., cal./mole
1	0.018358	6.53 (10^{-4})	0.0132	60,545
2	.018380	6.55 (10^{-4})	.0131	60,465
3	.018220	4.22 (10^{-4})	.0129	60,500
4	.018412	10.41 (10^{-4})	.0138	60,592
			Average	60,525 ± 43

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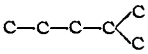
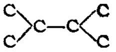
(17) *Cf.* Bruun and Hicks-Bruun, *Bur. Standards J. Research*, **5**, 933 (1930).

	M. p., °C.	B. p., °C.	$n^{20}\text{D}$
C—C—C—C—C—C	− 95	68–9	1.375
	−143	60.4	1.3735
	−128^a ^{a}(see III)	58	1.377

(18) Rossini, *ibid.*, **12**, 735 (1934).

(19) Rossini, *J. Chem. Phys.*, **3**, 438 (1935).

tests for side reactions. In a test of irreversible adsorption in which 10 cc. of hexane was collected, a weight increase of 0.5 mg. was found. $n^{20}\text{D}$ of hydrogenation product was 1.3738. The over-all error is estimated as 150 cal.

1,3-Cyclohexadiene.—Two different copper catalysts were ineffective in promoting complete hydrogenation of 1,3-cyclohexadiene. Instead we used a 75% cobalt–25% nickel catalyst, prepared according to Long,[20] by precipitation and dialysis of the mixed hydroxides from pure nitrates, dehydration of the oxides and reduction with hydrogen beginning at 300° and finally at 450°. The calorimetric results, given in Table V, were obtained with an amount of this catalyst prepared from approximately 40 g. of oxides.

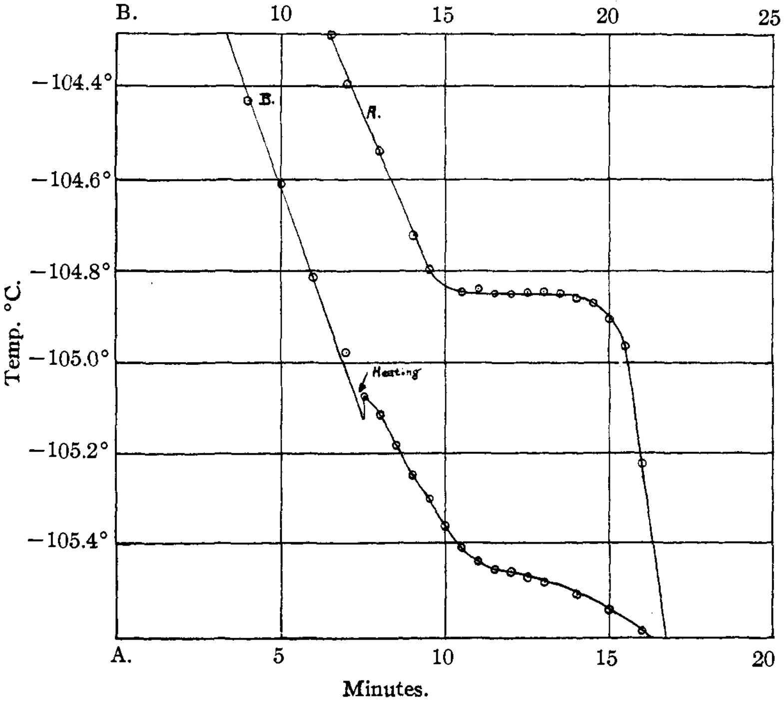


Fig. 2.—Freezing curves of A pure 1,3-cyclohexadiene CHD-6; B with 0.5% cyclohexene.

The freezing curves of pure and contaminated (0.5% cyclohexene) cyclohexadiene are shown in Fig. 2. The hydrogenation product had a well-defined freezing point (no drift) at +6.44 ± 0.03° and $n^{20}\text{D}$ 1.4258 (compare cyclohexane, Paper III). The degradation-polymerization experiment showed no non-condensable gases; this together with the freezing point of the product of hydrogenation may be regarded as good evidence of absence of side reactions. A test for irreversible adsorption on the Co–Ni catalyst was negative, a weight decrease of 0.2 mg. being found in a hydrogenation producing 10 cc. of cyclohexane.

There may be some doubts as to whether the compound studied is the 1,3- or the 1,4-isomer. In favor of the here accepted interpretation are the following facts: (1) the method of preparation is more favorable to the formation of the 1,3-compound; (2) it seems that when both isomers are concurrently produced by other methods, the one here described predominates and thus is probably energetically the more stable one, with a conjugated system; (3) Professor L. F. Fieser has successfully used our compound for Diels–Alder syntheses. Each of these points is in itself not an especially strong argument but together they form a firm basis for our conclusion. The over-all error is estimated as 100 cal.

Benzene.—The same Co–Ni catalyst used for cyclohexadiene was employed in the runs given in Table VI. There was no irreversible adsorption and the freezing point of the product was very sharp at +6.44 ± 0.03°, indicating a very clean reaction. $n^{20}\text{D}$ of product was 1.4260. It may be added that a contamination of our benzene with 0.5% tetramethylethane gave a freezing-point lowering in perfect accord with theory, thus confirming the trustworthiness of our method. The over-all error is estimated as 150 cal.

Cyclopentadiene.—Freshly depolymerized dicyclopentadiene was used for every run and thus the degree of polymerization in the bubbler was kept very low. Nevertheless the results, reported in Table VII, cannot be regarded as comparable in accuracy to those on other com-

TABLE V

1,3-CYCLOHEXADIENE

Run	Moles C_6H_8	C_6H_8 flow, moles/min.	H_2 flow, mole/min.	$-\Delta H$ 355°K., cal./mole
1	0.019922	7.12 (10^{-4})	0.0152	55,279
2	.019864	6.61 (10^{-4})	.0134	55,361
3	.019671	4.02 (10^{-4})	.0125	55,479
4	.019954	10.03 (10^{-4})	.0140	55,348
			Average	55,367 ± 56

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[20] John H. Long, Ph.D. dissertation, Johns Hopkins Univ., 1933, p. 10.

TABLE VI

BENZENE

Run	Moles C_6H_6	C_6H_6 flow, moles/min.	H_2 flow, mole/min.	$-\Delta H$ 355°K., cal./mole
1	0.022165	7.53(10^{-4})	0.0135	49,626
2	.022186	7.48	.0135	49,606
3	.021988	4.85	.0131	49,799
4	.024483	8.72	.0138	49,553
5	.022207	7.13	.0131	49,780
6	.022255	8.29	.0144	49,877
7	.022123	5.21	.0078	49,718
8	.022317	11.60	.0132	49,837
			Average of 5 high figures	49,802 ± 44
			(Over-all average	49,725 ± 86)

Runs 3 and 4, sample No. 4; all other runs, sample Nos. 3 and 5.

The last four runs were performed several months later than the first, with a different sample of the catalyst. We have a strong but unsupported suspicion that the lower results of runs 1, 2 and 4 were due to incomplete reaction since the slow run 3 agreed with the latter four figures for which more conclusive evidence of complete hydrogenation was available. Therefore the higher average is preferable.

pounds. The starting product, because of polymerization, could not be distilled in Column A and only the freezing point of the dimer, higher than any other reported, serves as a criterion of purity. The freezing point of the hydrogenation product, −93.7°, was determined, the "flat" being quite satisfactory with a 0.1° drift to 80% frozen material. Upon contamination with 0.5% cyclopentadiene the substance did not crystallize but formed a glass; thus the test is inconclusive. The experiment testing for degradation and polymerization was entirely negative, indicating that only cyclopentane results in this hydrogenation; $n^{20}D$ 1.4065. The over-all error is estimated as 200 cal..

TABLE VII

CYCLOPENTADIENE

Run	Moles C_5H_6	C_5H_6 flow, moles/min.	H_2 flow, mole/min.	$-\Delta H$ 355°K.., cal./mole
1	0.021971	8.26 (10^{-4})	0.0137	50,929
2	.021602	3.86 (10^{-4})	..00734	50,780
3	.021817	7.38 (10^{-4})	.0128	50,856
4	.021841	9.02 (10^{-4})	.0130	50,894
			Average	50,865 ± 47

Discussion

The preceding compounds were chosen as typical representatives of dienes and it was hoped that from these examples some general relations might become apparent. This, we believe, to be indeed the case.

When two double bonds are separated in the molecule by several single bonds, their interaction is practically zero. Thus the heat of hydrogenation of 1,5-hexadiene is almost identical with double that of propylene or any other singly substituted ethylene (see III). The same is possibly true of 1,4-pentadiene although its heat of hydrogenation is higher by some 300 calories and this difference may be real (even when converted to absolute zero), indicating that there is a slight unstabilization. This effect becomes extremely pronounced in allene, amounting there to some 10,900 calories. Butadiene occupies an anomalous position in this series, being even more stable by some 3300 calories, than the ethylenic hydrocarbons. This is undoubtedly to be attributed to the "resonance" phenomenon, discussed at some length by Pauling and his collaborators.[21]

If there is an unstabilizing effect in 1,4-pentadiene, then by interpolation toward allene one would find a similar effect amounting to some 1500–2000 calories in butadiene. This really should be added to the above 3300 calories in calculating the "true resonance energy."

Before further considering these resonance effects, the results on the six-membered ring systems bear discussion. Two of the experimental values obtained, those with the cyclohexene and the cyclohexadiene, differ more from the "best" thermochemical data,[22] 24.8 and 47.2 Cal., respectively than one would expect considering the accuracy of combustion calorimetry alone. However, in all three cyclic compounds we have been able to identify the hydrogenation product as pure cyclohexane, and therefore the possibility of a distortion of our results by side reactions seems to be out of the question. It is also quite improbable that our cyclohexene contained cyclohexadiene (see Paper III), thus giving a too-high heat of hydrogenation; the same reasoning applies *a fortiori* to cyclohexadiene, because the presence of benzene could not raise the heat of hydrogenation. This reasoning is added merely as further qualitative support for the conclusion reached previously on the basis of freezing curves, which showed purity of the compounds. The thermochemical data, which give lower figures than our results, must have been obtained, therefore, with quite impure materials. This is not astonishing, considering that at the time such measurements were made the technique of fractionating columns was not nearly so well developed as it is now. As a corollary it may be noted that

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(21) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933); Pauling and Sherman, *ibid.*, **1**, 606, 679 (1933).

(22) Kharasch, *Bur. Standards J. Research*, **2**, 359 (1929).

the calculated heat of hydrogenation of benzene, which involves combustion data of two relatively easily purified substances, benzene and cyclohexane, agrees well with the present determination. The latter is found to lie between the data of Richards and those of Roth,[22] namely, 47.7 and 50.0 Cal., respectively.

The very unexpected result that the first step in hydrogenation of benzene is endothermic to the extent of 5600 cal., rather than slightly exothermic as believed heretofore, has many interesting chemical consequences, into the discusssion of which, because of space considerations, we shall not enter.

The magnitude of the stabilization energy in cyclopentadiene is somewhat less certain than that of the other conjugated compounds here discussed because of the larger uncertainty in the calorimetric results and particularly because of the present lack of the heat of hydrogenation of cyclopentene. As a first approximation, we may estimate the latter as equal to that of cyclohexene. The true value will possibly be slightly higher because of increased strain in the unsaturated five-membered ring. On this basis the stabilization energy is found to be 6400 calories or more.

Summarizing, the "resonance" energies of the conjugated systems studied thus far are: 1800 calories for cyclohexadiene, 3400 calories for butadiene, 6400 calories for cyclopentadiene and 36,000 calories for benzene. These figures are computed disregarding the "labilization" effect disclosed by the study of allene and an amendment to include it will raise the three former ones by some 2000 calories. A corresponding correction for benzene would be 6000 calories but it is wholly uncertain. In any case the figures show the disproportionately great stabilization of benzene, which is not at all in quantitative agreement with the calculations of Pauling and his co-workers. They have computed, by approximate wave-mechanical methods, the effective number of resonating electronic structures in benzene and compared it with the experimental stabilization energy. Thus a quantity was obtained which, according to Pauling, relates the amount of stabilization to one effective resonating structure. Using this semi-empirical parameter and applying the same methods to evaluate the number of resonating structures, it becomes possible to calculate the energies of other conjugated systems, such as butadiene and cyclohexadiene. For the latter two (and presumably for cyclopentadiene also) a value of some 8000 calories was given when, as a basis of calculation, 37,300 calories for benzene was taken. As the present resonance energy of benzene is practically identical with the above, the other calculated figures also remain unchanged.

It is thus clear that the resonance calculations in the form adopted by Pauling have only qualitative significance even with the inclusion of the "labilization" effect. This will not improve matters much because it must be applied consistently and thus will increase the basic figure for benzene, thereby also increasing all derived values.

The experimental values of the resonance of the three conjugated dienes show very striking variations which are in contrast to the perfect regularity of the energy relationships in the olefinic series. Apparently individual factors, not included by Pauling in resonance calculations and not of importance in the mono-olefins, play a very determining role in the conjugated dienes. It may be noted that cyclopentadiene, which from the organic point of view is the most "aromatic" of the three, possesses the greatest stabilization energy.

The data presented in this and in preceding papers of this series do not bear out the idea that conjugation is the sole important factor in determining the energetics of the double bonds. Table VIII, in which are given the heats of hydrogenation of the first double bond in some dienes and also some data on mono-olefins, shows this very well:

TABLE VIII

THE HEAT OF HYDROGENATION OF THE FIRST DOUBLE BOND IN DIENES

	ΔH at 355°
Allene + $H_2 \longrightarrow$ Propylene	−41,165
(Ethylene + $H_2 \longrightarrow$ Ethane	−32,825)
1,4-Pentadiene + $H_2 \longrightarrow$ *n*-Pentene-1	−30,660
1,5-Hexadiene + $H_2 \longrightarrow$ *n*-Hexene-1	−30,400
1,3-Cyclohexadiene + $H_2 \longrightarrow$ Cyclohexene	−26,700
1,3-Butadiene + $H_2 \longrightarrow$ *n*-Butene-1	−26,720
(Tetramethylethylene + $H_2 \longrightarrow$ Tetramethylethane	−26,633)
Cyclopentadiene + $H_2 \longrightarrow$ Cyclopentene	−22,200?
Benzene + $H_2 \longrightarrow$ 1,3-Cyclohexadiene	+ 5,570

It will be observed that the heats of hydrogenation of the first double bonds of two conjugated systems fall between the values which we have found for different mono-olefins and even the striking effects in cyclopentadiene and particularly in benzene become less unusual when it is considered that in the direction from allene to tetramethylethylene other than conjugation effects have altered the heat of hydrogenation by some 14 Cal.

In conclusion we wish to thank Dr. J. B. Conant and Prof. E. P. Kohler for their advice and criticism which have materially helped the progress of this work, and Mr. M. A. Dolliver for his able assistance in the preparation of organic materials.

Summary

1. The following heats of hydrogenation have been obtained at 355°K.

	ΔH, cal./mole
Allene + $2H_2$	$-71,280 \pm 103$ (200)
1,3-Butadiene + $2H_2$	$-57,067 \pm 28$ (100)
1,4-Pentadiene + $2H_2$	$-60,790 \pm 64$ (150)
1,5-Hexadiene + $2H_2$	$-60,525 \pm 43$ (150)
1,3-Cyclohexadiene + $2H_2$	$-55,367 \pm 56$ (100)
Benzene + $3H_2$	$-49,802 \pm 44$ (150)
Cyclopentadiene + $2H_2$	$-50,865 \pm 47$ (200)

The uncertainties represent calorimetric precision, while the figures in parentheses are the crudely estimated all inclusive errors.

2. These data are discussed and it is pointed out that two double bonds, when placed close together in the molecule, exert an unstabilizing effect upon one another. The resonance predictions of Pauling are confirmed but qualitatively.

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A Method of Comparison and Critical Analysis of the Physical Properties of Homologs and Isomers. The Molecular Volume of Alkanes*

BY GEORGE CALINGAERT AND JOHN W. HLADKY

Any simple and reasonably accurate method of correlating the physical properties of a compound with its structure is of obvious worth, both for the purpose of evaluating the reliability of the numerical values assigned to the property in question, and in studying the effects of molecular structure on physical properties in general.

There have been numerous attempts to develop correlations of this type, all of which, however, appear to suffer from the disadvantage that either they are not quantitative or that they depend on the calculation of some complex function involving two or more physical constants.

The present paper describes a correlation method involving a simple linear relation between the structure of the molecule and a single physical constant, and uses as illustration the application of the method to the molecular volumes of the straight and the branched-chain alkanes. The method is based on the fact that in an homologous series most of the properties are smooth functions of the molecular weights.

The usefulness of the method is enhanced by the simultaneous addition of 2 features: (a) by a suitable transformation of the ordinate scale, the lines for homologous series are made to plot as straight or nearly straight lines; (b) the properties of isomers are plotted against the number of carbon atoms in the longest chain, thus giving rise to a new set of curves (for isomers). These "homolog" and "isomer" lines form a lattice in which the position of individual compounds can be predicted with far greater accuracy than when family lines alone are used. In addition to permitting a critical evaluation of the data, the method throws considerable light on the effect of structure on the physical properties of homologs and isomers. The method appears to be applicable to a large number of physical properties, and as an illustration the molecular volume of the alkanes will be discussed below.

Molecular Volumes[1]

A. Preparation of Data and Plot.—All the data which can be found in the literature on the densities of all alkanes from C_3 to C_{12}, and on normal alkanes up to C_{16}, are collected and indexed. Whenever data *by the same author* are available at two or more temperatures the values of $\delta d/\delta t$ are calculated and plotted as a function of tem-

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[1] The molecular volumes (M. V.) as used here are defined as: M. V. = Molecular Weight/d^{20}_4, using the atomic weights C, 12 and H, 1. This is used in preference to the densities which are usually reported in the literature, because M. V. are more nearly straight line functions of molecular weight in homologous series.