

6. A portion of 0.0314 g. of acid having a rotation of  $-179^\circ$  in pyridine was added to 3 cc. of acetic anhydride. The mixture was heated to boiling during one minute to effect solution and then immediately cooled to  $20^\circ$ . The rotation of the acetic anhydride solution was zero. The acetic anhydride was removed below  $20^\circ$  by means of a stream of air under vacuum and the residue dissolved in 2 cc. of pyridine. The rotation of the pyridine solution was zero.

The material recovered from the pyridine solution was recrystallized from benzene and had a melting point of  $179-180^\circ$ . It was insoluble in cold alkali and but slowly soluble in hot alkali, from which solution the original acid of m. p.  $306-307^\circ$  was obtained upon acidification. An analysis proved it to be the mixed acid anhydride of one molecule of 8,8'-dicarboxy-1,1'-dinaphthyl and two molecules of acetic acid.

*Anal.* Subs., 5.063 mg.:  $\text{CO}_2$ , 13.66 mg.;  $\text{H}_2\text{O}$ , 1.89 mg. Calcd. for  $\text{C}_{26}\text{H}_{18}\text{O}_6$ : C, 73.21; H, 4.25. Found: C, 73.58; H, 4.18.

When this mixed acid anhydride was heated above its melting point ( $180^\circ$ ) bubbles were evolved from the light yellow liquid and at  $198-202^\circ$  the liquid was converted to a red colored solid. After washing with hot dilute sodium hydroxide and recrystallization from chloroform this material melted at about  $340^\circ$ . This compound proved to be the anthanthron which was previously prepared by Kalb<sup>4</sup> by the action of concentrated sulfuric acid on 8,8'-dicarboethoxy-1,1'-dinaphthyl. Solution in concentrated sulfuric acid caused a bright green coloration.

*Anal.* Subs.: 2.619 mg.:  $\text{CO}_2$ , 8.26 mg.;  $\text{H}_2\text{O}$ , 0.77 mg. Calcd. for  $\text{C}_{22}\text{H}_{10}\text{O}_2$ : C, 86.25; H, 3.29. Found: C, 86.01; H, 3.29.

### Summary

1. 8,8'-Dicarboxy-1,1'-dinaphthyl has been resolved into optical isomers by fractionation of the monoquinine salt from benzene.
2. This compound is the first  $\alpha, \alpha'$ -disubstituted diphenyl derivative which has been resolved.
3. The optically active acids were readily racemized.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 74]

## SIGNIFICANT TEMPERATURES IN THE PYROLYSIS OF CERTAIN PENTANES AND PENTENES<sup>1</sup>

BY JAMES F. NORRIS AND GEORGE THOMSON

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Previous determinations in this Laboratory of the temperatures at which certain ethers<sup>2</sup> and a number of alkyl derivatives of malonic acid<sup>3</sup> begin to decompose when heated under definite conditions showed that these temperatures could be determined in independent experiments that gave results which agreed within  $\pm 2$  degrees. The values obtained made it possible to correlate the temperatures at which certain bonds were broken

<sup>1</sup> From the thesis presented by George Thomson in partial fulfillment of the requirement for the degree of Doctor of Philosophy, 1930.

<sup>2</sup> Norris and Young, *THIS JOURNAL*, **52**, 753 (1930).

<sup>3</sup> Norris and Young, *ibid.*, **52**, 5066 (1930).

by pyrolysis with the rates at which these bonds were broken in a chemical reaction. The results showed, also, the effect of the structure of the alkyl radicals present on the temperature of pyrolysis.

The satisfactory results obtained in the earlier experiments led to the study in a similar way of the temperatures at which certain pentanes and pentenes begin to decompose when heated. With this information it would be possible to effect the pyrolysis of the hydrocarbons at or near their cracking temperatures and thus obtain the products first formed in their decomposition. It was expected that the results would lead to a better understanding of the mechanism of pyrolysis and to added knowledge of the effect of structure on the lability under the influence of heat of the carbon-carbon and carbon-hydrogen bonds in hydrocarbons.

This method of investigating the cracking of hydrocarbons seemed worthy of study, because previous work in this field has been carried out at such temperatures that profound decomposition resulted, and the number of products formed was so large that it was impossible to draw any definite conclusions as to the mechanism of the many reactions involved. For example, the pyrolysis of pentane and isopentane have been studied by Calingaert<sup>4</sup> at 600° and by Hague and Wheeler<sup>5</sup> at temperatures between 600 and 850°. Calingaert determined quantitatively eight products of the pyrolysis.

It is shown in this paper that normal pentane begins to pyrolyze at 391° and isopentane at 383°. Experiments now in progress indicate that at ten degrees above these temperatures a simple decomposition takes place as the result of the breaking of a single carbon-carbon linkage in each case. These experiments will be reported later. This paper is confined to the consideration of the temperatures at which the hydrocarbons begin to pyrolyze and the rates at which the reactions proceed at different temperatures.

In the determination of the temperature at which pyrolysis begins, the hydrocarbon was heated for about one hour, at a definite temperature, in a glass apparatus in which the expansion that occurred under approximately atmospheric pressure could be measured. At temperatures below that of decomposition no expansion was evident after thermal equilibrium had been established. As the temperature at which the vapor was held was raised, *step by step*, a temperature was reached at which expansion due to pyrolysis continued throughout the hour. From the increase in the volume of the vapor in a measured time, the rate of expansion at this temperature was calculated. The values of these rates at different temperatures were plotted against the temperatures. Figure 1 shows the results of an experiment when *n*-pentane was used.

<sup>4</sup> Calingaert, *THIS JOURNAL*, **45**, 130 (1923).

<sup>5</sup> Hague and Wheeler, *J. Chem. Soc.*, 378 (1929).

It is seen that intersecting straight lines can be drawn through the points. In the case of this hydrocarbon at temperatures up to  $389^{\circ}$  there was no expansion when the hydrocarbon was held at these temperatures for an hour. Above  $389^{\circ}$  expansion continued throughout the hour at the rates indicated.

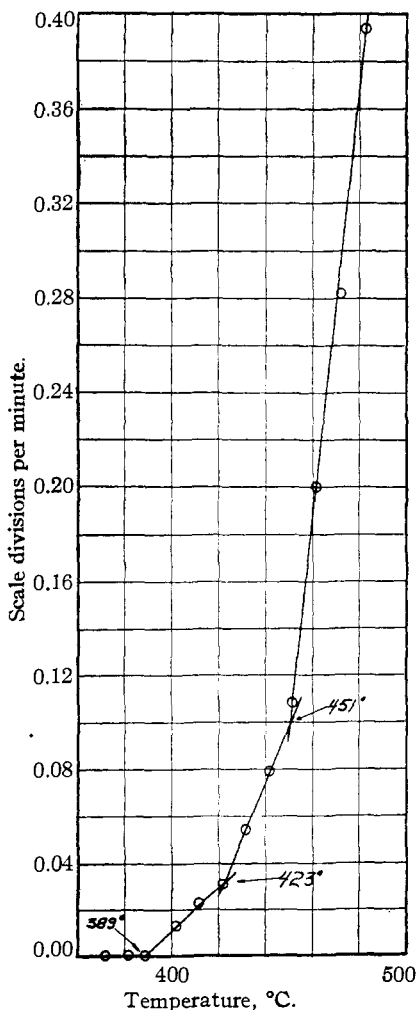


Fig. 1.—*n*-Pentane cracking rate curve:  
1 Scale div. = 0.09 cc. at  $40^{\circ}$ .

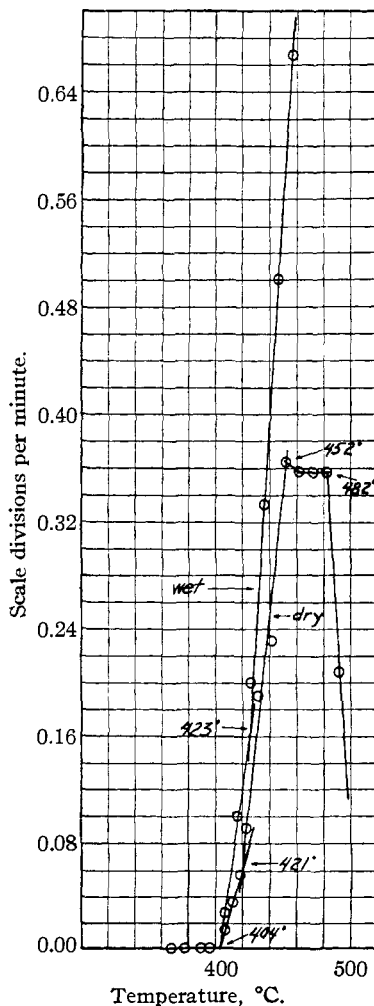


Fig. 2.—Pentene-2 cracking rate curve:  
1 Scale div. = 0.09 cc. at  $40^{\circ}$ .

It appeared probable that between  $389^{\circ}$  and  $423^{\circ}$  one type of decomposition was taking place and that between  $423^{\circ}$  and  $451^{\circ}$  another type had set in. Above  $451^{\circ}$  the increased rate indicated more profound decomposition.

To determine whether or not the breaks in the lines represent real changes in the way in which the hydrocarbon undergoes pyrolysis, Mr. George Standley is now investigating the products formed at temperatures within the ranges indicated. It can be said at this time that the results are in accord with the view put forward above.

In the case of the unsaturated hydrocarbons the results were similar to those obtained with the paraffins, except that an additional significant temperature was observed. Above a certain temperature the rates of expansion either remained constant, or decreased as the temperature was increased. It is evident that at these higher temperatures two types of reactions are taking place simultaneously, namely, pyrolysis, which causes expansion, and another change which leads to contraction.

The examination of the cooled vessel in which the hydrocarbon had been pyrolyzed above the temperature at which the rate of expansion began to decrease (reversal temperature) showed that there had been formed a yellowish-brown oil less volatile than the hydrocarbon used. Below the reversal temperature there was little or no high-boiling oil formed. These observations indicate that the decrease in the rate of expansion is associated with the formation of polymers.

The behavior of pentene-2 is shown in Fig. 2 by the lines marked "dry," which record the rates of decomposition when the hydrocarbon was free from moisture. By plotting the rates it is possible to discover a temperature at which no expansion occurs (reversal temperature), since at this temperature the rates of the two types of reactions are the same.

The reversal temperatures of the three pentenes studied were from 53 to 65° above the temperatures at which the hydrocarbons began to decompose.

The influence of a trace of water in the pyrolysis of pentene-2 was investigated. The results are shown in Fig. 2. There appeared to be no influence on the pyrolysis temperature, but the rate of decomposition was doubled. Reversal in the rate, indicating polymerization, did not occur with the wet hydrocarbon at about ten degrees above the reversal temperature of the dry hydrocarbon.

The results obtained with the hydrocarbons studied are given in Table I.

The tabulated results show that *n*-pentane begins to decompose at a temperature higher than that at which its isomer with a branched chain begins to decompose; that pentane-2 and pentene-1 crack at about the same temperature; that pentene-2 is more stable to heat than pentene-1, and that the increase in the number of radicals joined to doubly linked carbon atoms in trimethylethylene leads to increased thermal stability.

In Table II are given for each hydrocarbon the percentage expansion per hour at ten degrees above the significant temperatures recorded in Table I and the increase in these values per ten degrees within the stated temperature intervals.

TABLE I  
SIGNIFICANT TEMPERATURES IN THE PYROLYSIS OF THE HYDROCARBONS LISTED

	Initial cracking temp., °C.	Second break, °C.	Third break, °C.	Reversal temperature, °C.
Isopentane	383	419	449	
	383	426	450	
	383 Average	423 ± 3.3	450 ± 0.5	
Pentene-1	387	418		457
	388	420		455
	391	421		456 ± 1.0
	389 ± 1.4	420 ± 0.8		
<i>n</i> -Pentane	389	423	451	
	391	423	446	
	393	431	452	
	391 ± 1.1	426 ± 3.0	450 ± 2.0	
Pentene-2	404	419		
	404	421		
	398	425		452
	398	421		452
	396	420		454
	400 ± 2.4	421 ± 1.0		453 ± 0.8
Trimethylethylene	432	452	472	486
	432	446	477	495
	434	447		497
	433		475 ± 2.4	
		448 ± 2.0		493 ± 3.6
	433 ± 0.6			

TABLE II  
THE FIGURES REFER TO THE ACTUAL EXPANSION OF THE HYDROCARBON VAPOR AT THE TEMPERATURE INDICATED

Hydrocarbon	Expansion 10° above initial break, %/hr.	Expansion increase per 10°, %/hr.	Expansion 10° above sec. break, %/hr.	Expansion increase per 10°, %/hr.	Expansion 10° above third break, %/hr.	Expansion increase per 10°, %/hr.	Maximum expansion, %/hr.
Isopentane	0.22	0.22 (383-423°)	1.6	0.7 (423-450°)	4.6	1.7 (450-485°)	
Pentene-1	.67	0.67 (389-420°)	4.4	2.1 (420-456°)			10.4 (456°)
<i>n</i> -Pentane	.22	0.22 (391-426°)	1.6	0.7 (426-450°)	5.1	2.5 (450-482°)	
Pentene-2	.68 (Dry)	0.68 (Dry) (400-421°)	3.7 (Dry)	2.4 (421-453°)			8.8 (453°)
	1.36 (Wet)	1.36 (Wet)	6.3 (Wet)	3.6 (421-459°)			9.9 (493°)
Trimethyl-ethylene	1.2	1.2 (433-448°)	4.1	2.2 (448-475°)			

The results show that pentene-1 and pentene-2 decompose three times as rapidly as *n*-pentane and isopentane when the hydrocarbons are heated ten degrees above their respective cracking temperatures. Trimethylethylene

decomposes about twice as fast as the straight-chain olefins and six times as fast as the paraffins at ten degrees above their respective cracking temperatures. Within the same temperature range (433–448°), it decomposes about twice as fast as the pentanes. Other significant facts which can be drawn from the table will be considered in a subsequent paper in which the study of the products of pyrolysis will be reported.

The work is being extended to other hydrocarbons. It is planned to investigate the influence of increased surface per volume of vapor, and of the presence of catalytic agents on the temperatures of pyrolysis. The theoretical aspect of the subject will be considered later.

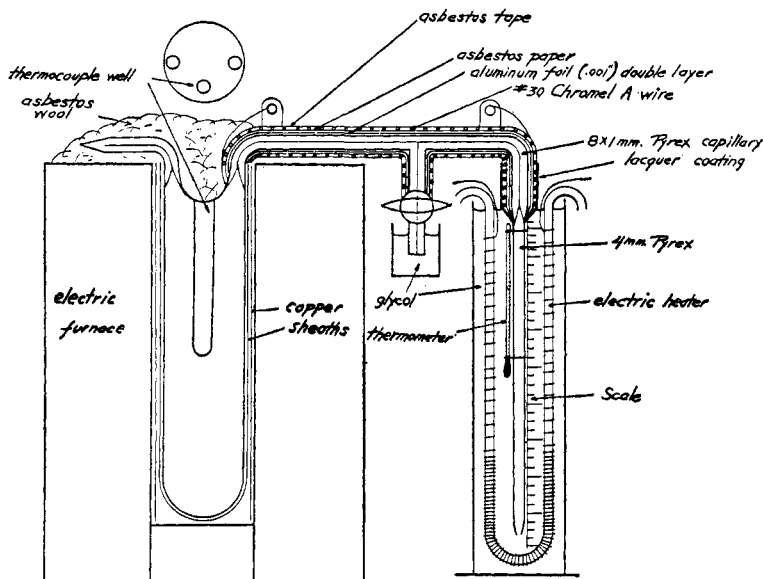


Fig. 3.

### Experimental Part

**Apparatus.**—The apparatus consisted of an electric furnace in which was inserted a Pyrex bulb of about 52 cc. capacity connected by capillary tubing to a manometer arrangement as shown in Fig. 3. The bulb contained a thermocouple well and had another capillary opening to facilitate cleaning. Two copper sheaths surrounding the bulb in the furnace produced uniform temperature distribution. A double layer of aluminum foil underneath the electric heater on the capillary tube leading to the manometer served the same purpose.

The manometer tube was made of 4-mm. Pyrex tubing and was immersed in a hydrometer jar filled with ethylene glycol kept at a constant temperature of 40° by an electric heater. An experiment had shown that the vapors of the hydrocarbons were insoluble in glycol. The hydrometer jar was provided with a scale for reading the liquid level in the manometer tube. To prevent the glycol from soaking up into the electric heater on the capillary tube, the end of the heater was covered with several coats of lacquer.

In order to bring the manometer level to the zero mark, the stopcock on the capillary tube could be opened and gas allowed to escape.

A calibrated chromel-alumel thermocouple connected to a Leeds and Northrup portable potentiometer was used to measure the temperature of the hydrocarbon gas.

Since the olefins absorb oxygen to form peroxides on standing in bottles containing air, and the saturated hydrocarbons absorb some moisture, each hydrocarbon was distilled over sodium, just before each determination, directly into an 8 mm.  $\times$  14 cm. tube until from 1 to 1.5 cc. of hydrocarbon had collected. Chips of freshly cut sodium were then dropped in until there was enough to reach the surface of the liquid. The tube was then slipped over the end of the manometer tube on the apparatus and made tight with a short piece of pressure tubing. After surrounding the hydrocarbon with carbon dioxide snow and acetone, the apparatus was evacuated to less than 1 mm. pressure while at the same time the electric heater on the side arm was turned on and the bulb baked out with a Bunsen burner for several minutes. The heater was then turned off and the bulb allowed to cool. It was then immersed in ice and water and the carbon dioxide snow and acetone substituted by glycol at about the same temperature as the boiling point of the hydrocarbon. This caused the hydrocarbon to distil slowly over and condense in the bulb, which was then inserted in the electric furnace and the tube containing the sodium residue immersed in the hydrometer jar filled with warm glycol so that the rubber connection was just covered. As soon as the temperature of the bulb reached the boiling point of the hydrocarbon, this tube with its rubber connection was pushed off with a pair of tongs and the hydrometer jar raised to the position shown in the sketch. The sweeping action of the excess hydrocarbon boiling out was an added assurance of the absence of air.

When pentene-2 was run wet, the hydrocarbon was distilled over sodium into the 8 mm. tube as before but instead of adding chips of sodium a drop of water was added. The rest of the procedure was the same as when dry.

If, after holding the bulb at constant temperature for one hour, no expansion occurred, the temperature was raised  $10^\circ$  and again held constant for one hour. Eventually a temperature was reached at which expansion was appreciable. Scale readings were then taken over a period of sixty to eighty minutes. As the rate became greater this period was shortened until at  $80$  to  $100^\circ$  above the initial temperature readings were taken over a period of twenty minutes. These readings (4 at the higher temperatures, 8-9 at the lower temperatures) when plotted against time fell on straight lines the slopes of which were plotted against the corresponding temperatures. The intersection of this curve with the zero rate line fixed the initial temperature more accurately.

## Materials

**Pentene-1** was prepared in this Laboratory by Dr. R. L. Wakeman from ethylmagnesium bromide and allyl bromide. Final distillation over sodium gave a boiling point of  $30.0$ - $30.1^\circ$  (corr.),<sup>6</sup>  $d_4^{20}$  0.641.

**Pentene-2** was made by dehydrating secondary amyl alcohol with sulfuric acid according to the method of Norris ["Organic Syntheses," Vol. VII, p. 76]. After drying and distilling over sodium it boiled at  $36.3$ - $36.4^\circ$  (corr.).

**2 Methylbutene-2** was obtained from tertiary amyl alcohol by dehydrating with oxalic acid. The mixture of 2-methylbutene-2 and 2-methylbutene-1 after many distillations through a Davis' column gave about a 12% yield of 2-methylbutene-2, b. p.  $38.3$ - $38.4^\circ$  (corr.).

<sup>6</sup> Kirrmann, [*Bull. soc. chim.*, **39**, 988 (1926)] gives the b. p. as  $30.5$ - $31.0^\circ$  but Hyman and Wagner, [*THIS JOURNAL*, **52**, 4346 (1930)] found the b. p. to be  $30.0^\circ$  (corr.).

<sup>7</sup> H. S. Davis, [*Ind. Eng. Chem., Analytical Edition*, **1**, 61 (1929)].

*n*-Pentane.—By hydrogenating the above pentene-2, using nickel catalyst and purifying the product with sulfuric acid, very pure pentane was obtained, boiling at 36.1–36.2° (corr.).

Isopentane was obtained in a manner similar to that used for *n*-pentane but using the amylene mixture from the dehydration of *tert.*-amyl alcohol. The final product boiled at 27.9–28.0° (corr.).

### Summary

1. The temperatures have been determined at which *n*-pentane, isopentane, pentene-1, pentene-2 and trimethylethylene begin to decompose when heated in a Pyrex glass vessel for one hour.

2. The determination of the rates at which these hydrocarbons decompose showed that for each hydrocarbon the increase in rate per ten degrees was constant within certain temperature limits and that this increase in rate was greater within the higher temperature limits. It appears probable that the limiting temperatures of the several ranges are the temperatures at which certain bonds undergo pyrolysis.

3. It was found that a trace of moisture had no effect on the cracking temperature of pentene-2, but that it doubled the rate at which the hydrocarbon decomposed.

4. When the olefins were heated at increasing temperatures, a temperature was found at which no expansion took place. The results indicate that at this point the expansion which results from pyrolysis is equal to the contraction resulting from polymerization.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

## THE STRUCTURE AND SOME DERIVATIVES OF PARA-DIMETHYLAMINO-PARA-CHLOROBENZOIN

BY SANFORD S. JENKINS<sup>1</sup>

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The object of this report is to present the experimental evidence in support of a structure which is assigned to *p*-dimethylamino-*p*-chlorobenzoin<sup>2</sup> and to describe the preparation and some properties of a number of related compounds.

The starting material was prepared by condensing *p*-dimethylaminobenzaldehyde and *p*-chlorobenzaldehyde by means of potassium cyanide. The substance thus prepared melts at 128° and is readily oxidized with Fehling's solution to the corresponding benzil, which fuses at 144.5°.

Several methods have been employed for determining the structures

<sup>1</sup> Grafflin Scholar, 1930–1931.

<sup>2</sup> Staudinger, *Ber.*, **46**, 3538 (1913).