melted after two recrystallizations from glacial acetic acid at 217–218.5°. A mixed melting point with the quinone obtained by oxidation of 3-acetylphenanthrene showed no depression.

Summary

1. The action of oxalyl chloride on phenanthrene described by Liebermann and Zsuffa has been shown to yield not phenanthrene-9-carboxylic acid as the main product, but phenanthrene-3-carboxylic acid, accompanied by smaller quantities of the 2- and 9-isomers and an acid of melting point 123–125° whose structure has not yet been determined.

2. A good preparative method for phenanthrene-9-carboxylic acid is described.

3. The influence of bromine substitution in the 9-position on Friedel–Crafts reactions in this series has been investigated.

4. 9-Bromophenanthrene-3(or 6)-carboxylic acid and 9-bromo-3(or 6)-acetylphenanthrene are described.

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PRODUCTION OF BUTENES BY PYROLYSIS OF THE NORMAL MONOCHLOROBUTANES

BY PAUL E. WESTON[1] AND H. B. HASS

Introduction

In recent years normal butane has become available in large quantities at a low price. It is conceivable that this butane can be converted into more valuable substances through the butenes as intermediates, for example into sec.-butyl alcohol, by chlorination of the n-butane, splitting off hydrogen chloride from the monochlorobutanes, and hydration of the resulting butenes. In addition to the direct economic importance, this method of producing the butenes is of fundamental importance to the general chemistry of the olefins, for the butenes are the simplest substances in which it is possible to have the shifting of a hydrogen atom from one carbon atom to another (shifting of a double bond), stereomutation between cis and trans forms and shifting of a methyl group. A survey of the literature has shown that almost no information at all is available concerning the conditions governing these changes.[2] Lucas and his associates[3] have been at-

[2] Egloff, Schaad and Lowry, J. Phys. Chem., 35, 1825, 1860, 1866 (1931).

[3] Young and Lucas, THIS JOURNAL, 52, 1964 (1930); Dillon, Young and Lucas, ibid., 52, 1953 (1930); Lucas, Dillon and Young, ibid., 52, 1949 (1930).

tacking this problem through the pyrolysis of the butyl alcohols, while we have been attacking it through the pyrolysis of the monochlorobutanes.

The splitting off of hydrogen halides from ethyl, propyl, isobutyl, iso-amyl, hexyl and heptyl halides to form olefins has been accomplished, using pumice, soda lime,[4] bivalent metallic chlorides, and alumina as catalysts. The reactions are reversible, and therefore the hydrogen halide must be removed, or the products cooled quickly, to prevent recombination. The catalysts gradually lose their activity by the formation of a carbonaceous deposit on them.

We have found that the pyrolyses of 1-chlorobutane and 2-chlorobutane in a glass tube are homogeneous vapor phase reactions, 1-chlorobutane giving all 1-butene, and 2-chlorobutane giving a mixture of 1-butene, cis-2-butene, and trans-2-butene. When calcium chloride was used as a catalyst, 2-chlorobutane gave almost entirely the 2-butenes, and 2-chloro-butane gave very largely 2-butenes also.
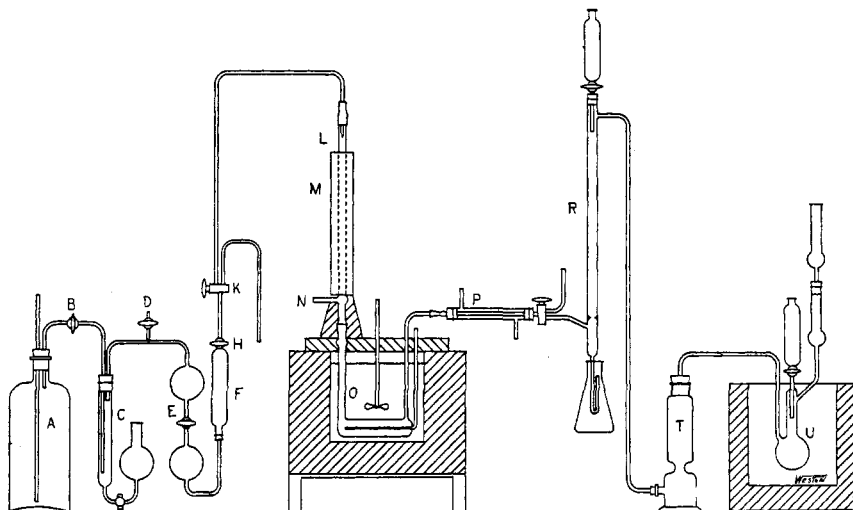

Fig. 1.—Apparatus for studying the pyrolysis of the monochlorobutanes.

Experimental Part

The apparatus is shown in Fig. 1. The parts A to L were designed to obtain a constant rate of flow of chlorobutane. Water from a source having a constant head (about 4.56 meters) flowed into the 2-liter bottle, A, compressing the air to a constant pressure. This air bubbled through mercury in C, and exerted pressure on some very viscous oil in the upper bulb of E. The rate of flow of oil could be adjusted by the stopcock, E. The oil displaced mercury in the lower bulb of E, which in turn displaced the chloro-butane from the graduated 50-ml. separatory funnel, F, into the vaporizer, M. As the mercury rose in F, the back pressure increased, and so to prevent a decrease in the

4 Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, p. 125; Faragher and Garner, THIS JOURNAL, 43, 1715 (1921).

rate of flow, the pressure on the oil in E was increased by allowing an equivalent amount of mercury to escape from C.   Since the oil had a high viscosity, the opening in the stop-cock had to be relatively large, and therefore small solid particles would not block the opening and alter the rate of flow, as would be the case if an attempt were made to control the flow of chlorobutane directly.

The chlorobutane was vaporized in the electrically heated tube, M.   Indentations in the walls of the tube caused turbulent flow and better heating.   The temperature of the vapor, as it entered the reaction tube, was about 100° as indicated by a thermometer inserted in the opening, N.

The reaction tube, O, of Pyrex glass, was immersed in an electrically heated bath of sodium nitrate and potassium nitrate.   The temperature was kept uniform by stir-ring, and was controlled by a Leeds and Northrup potentiometer controller actua-ted by a thermocouple immersed in the bath.   A well sealed into the reaction tube contained two thermocouples, one at each end.   A loosely fitting glass plug placed in the entrance tube, O, caused the vapor to flow close to the hot walls and become heated quickly.   The products were cooled quickly to reduce the extent of the reverse reaction by leading them through a capillary into the water cooler, P.   The reaction tube could be removed by separating the ground joints.

The extent of reaction was determined by dissolving the hydrogen chloride in stand-ard sodium hydroxide solution as it trickled over glass beads in the tower, R, and titrating the excess alkali.   Unreacted chlorobutane which collected with the alkali did not react with it, or interfere with the titration in any way.   From the moles of hydrogen chloride evolved and the moles of chlorobutane used, the extent of reaction was calculated. The exposure time, or duration of the reaction, was calculated from the rate of intro-duction of the chlorobutane, the volume of the reaction tube (53 ml.) and the mean of the entering and leaving volumes of gas, as calculated from the extent of reaction and the gas laws.   This of course does not give the true reaction time.

The butenes were analyzed by converting them into the bromides and determining, for the bromides, the densities and reaction rates with potassium iodide in methanol, exactly as described by Dillon, Young and Lucas.   The butenes were dried with calcium chloride in the tower, T, liquefied, and allowed to react with bromine in the bath, U, at −15 to −20°.   The bromides were distilled under reduced pressure before being analyzed, to remove small amounts of chlorobutanes and butadiene tetrabromide.

Both 1-chlorobutane and 2-chlorobutane were prepared by the thermal chlorination of *n*-butane.   Butane and chlorine were used in the ratio of 10:1 by volume, at a reaction temperature of 400–475°.   The product consisted of 90.3% monochlorides and 9.7% poly-chlorides by weight.   The monochlorides consisted of 63% 2-chlorobutane and 37% 1-chlorobutane.   Unreacted butane was recycled.   The chlorides were separated by recti-fication.   The 1-chlorobutane used in this research had a boiling point of 77.6–77.7° at 743 mm., or 78.3–78.4° corrected to 760 mm.[5]   The 2-chlorobutane had a boiling point of 67.2–67.3° at 740 mm., or 68.0–68.1° corrected to 760 mm.   If the butane used above con-tained any isobutane, the 2-chlorobutane made from it would have been contaminated with isobutyl chloride, for the boiling points of these isomers are only one degree apart; therefore some 2-chlorobutane was also prepared from the alcohol and hydrochloric acid. This 2-chlorobutane[6] had a boiling point of 67.4° at 743 mm., or 68.0° corrected to 760 mm.

Discussion of the Rate of Reaction

The thermal decompositions of 1-chlorobutane at 550° and 2-chloro-butane at 500° in a glass tube are homogeneous vapor phase reactions.

[5] "International Critical Tables," Vol. III, p. 246.

[6] "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. V, 1925, p. 27.

The data to support this conclusion are given in Table I and Fig. 2. The reactions were run under three different conditions, namely, in a clean reaction tube (cleaned by burning the carbonaceous deposit with air), in a tube coated with the carbonaceous deposit which slowly formed from side reactions, and in a tube stuffed with glass wool. All of the points fit the curves equally well, indicating that the glass surface and the carbonaceous deposit did not alter the rate of reaction. In the table, two reaction temperatures are given, the first being the temperature at the entrance and the second at the exit of the reaction tube. Different temperatures were obtained at different rates of flow, and the temperatures inside the tube never equaled the temperature of the bath because these reactions are endothermic. The 2-chlorobutane from the alcohol reacted slightly, but definitely faster than the 2-chlorobutane from chlorination of butane, probably because the latter contained some isobutyl chloride, a primary chloride. It can be seen from the curves that 1-chlorobutane, a primary

TABLE I

RATE OF PYROLYSIS OF THE MONOCHLOROBUTANES (PLOTTED IN FIG. 2)

Expt.	Reaction temp., °C.	Moles BuCl	Moles HCl	Duration of expt., min.	Reaction, %	Exposure, seconds	Chlorobutane	Reaction tube
1	499–9	0.1665	0.0166	31.0	10.0	8.9	1-	Clean
2	547–7	.1020	.0331	12.0	32.4	4.8	1-	Clean
3	548–8	.0956	.0418	18.0	43.7	7.3	1-	Clean
4	548–9	.1160	.0633	33.0	54.5	10.6	1-	Clean
5	546–6	.1870	.0469	15.0	25.1	3.4	1-	Carbonized
6	545–7	.0986	.0398	16.0	40.4	6.4	1-	Carbonized
7	544–4	.1940	.0442	14.0	22.8	3.1	1-	Glass wool
8	547–7	.0977	.0414	17.0	42.4	6.8	1-	Glass wool
9	547–7	.1010	.0484	22.0	48.0	8.3	1-	Glass wool
10	493–7	.0765	.0660	15.0	86.3	6.8	2-	Clean
11	492–8	.0929	.0776	17.0	83.7	6.5	2-	Clean
12	490–5	.1221	.0850	15.0	69.5	4.6	2-	Clean
13	490–5	.1480	.0901	13.0	60.9	3.4	2-	Clean
14	490–5	.1480	.0899	13.0	60.6	3.4	2-	Clean
15	488–92	.1708	.0619	7.0	36.2	1.75	2-	Clean
16	490–3	.1711	.0846	11.0	49.4	2.6	2-	Clean
17	493–9	.0994	.0860	21.0	86.6	7.4	2-	Carbonized
18	491–6	.1141	.0790	13.0	69.1	4.2	2-	Carbonized
19	490–5	.1540	.0835	11.0	54.1	2.8	2-	Carbonized
20	492–6	.1151	.0886	17.0	76.9	5.4	2-	Carbonized
21	490–6	.1022	.0829	15.0	81.0	5.3	2-ex alc.	Clean
22	491–5	.1250	.0798	11.0	63.7	3.4	2-ex alc.	Clean
23	488–93	.1693	.0785	9.0	46.4	2.2	2-ex alc.	Clean
24	490–7	.1200	.0790	11.0	65.9	3.5	2-	Glass wool
25	489–93	.1560	.0777	10.0	49.8	2.4	2-	Glass wool
26	492–8	.1192	.0891	17.0	74.6	5.3	2-	Glass wool
27	489–94	.1095	.0803	13.0	73.1	4.4	2-ex alc.	Glass wool
28	492–8	.0976	.0860	19.0	88.0	6.8	2-ex alc.	Glass wool

chloride, reacted much more slowly than 2-chlorobutane, a secondary chloride. The amount of carbonaceous deposit which formed was very small, being only about 0.01 g. per 380 g. of chlorobutane decomposed.
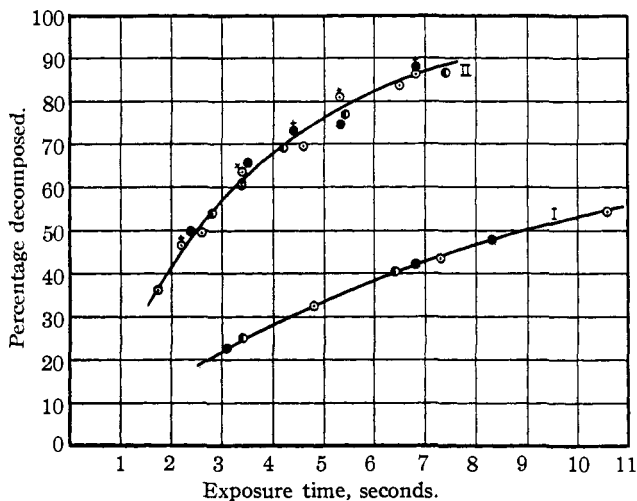

Fig. 2.—Rate of pyrolysis of the monochlorobutanes: I, 1-chlorobutane at 550°; II, 2-chlorobutane at 500°; ⊙, clean reaction tube; ◐, carbonized reaction tube; ●, tube stuffed with glass wool; +, indicates that the 2-chlorobutane was made from the alcohol.

Discussion of the Composition of the Butenes

The compositions of the butenes obtained under various conditions are given in Table II. In the absence of a catalyst at 550°, 1-chlorobutane gave only 1-butene (Expt. 1), but 2-chlorobutane gave a mixture of all three normal butenes (Expt. 3). The butenes from 2-chlorobutane were about two-thirds 2-butenes, and of these, two-thirds was the lower-boiling isomer (*trans*). If the butenes were formed by the simple splitting off of a molecule of hydrogen chloride followed by rearrangement of the radical to a more stable form, it seems obvious that 1-chlorobutane should yield almost entirely 1-butene while 2-chlorobutane should yield a mixture of the isomers. The 1-butene does not rearrange easily under these conditions to 2-butenes, for in Expt. 2 the reaction time allowed was almost twice that in Expt. 1, but still 1-chlorobutane yielded all 1-butene. Under prolonged exposure, some of the 1-butene decomposed into butadiene, and the tetrabromide formed from the butadiene impaired the accuracy of the analysis, but even so, if there was a rearrangement of the 1-butene, it occurred to a very small extent.

The composition of the butenes did not change with the reaction temperature, for at 450, 490, 500 and 550° (Expts. 3 to 10) the mean composi-

tion was 1-butene 35 ± 3%, *cis*-2-butene 22.5 ± 3.5%, and *trans*-2-butene 43 ± 4%, except No. 8, which was 6% low. In all of these experiments the results were the same with 2-chlorobutane prepared either from the alcohol or by chlorination of butane.

TABLE II

COMPOSITION OF BUTENES

Expt.	t, °C.	BuCl and source	Reaction time, sec.	Bromides d_{20}	K_{76}	Butenes, % 1-	Cis-2-	Trans-2-
1	550	1-	6	1.8028	0.0782	100	..	..
2	550	1-	10	1.8051	.0769	100	..	..
3	550	2-*ex* Cl₂	2	1.7889	.0572	35	20	45
4	500	2-*ex* Cl₂	6	1.7891	.0577	37	19	44
5	500	2-*ex* alc.	6	1.7886	.0558	33	21	46
6	500	2-*ex* Cl₂	6	1.7891	.0555	33	25	42
7	490	2-*ex* Cl₂	..	1.7894	.0555	34	26	39
8	490	2-*ex* Cl₂	..	1.7898	.0564	38	26	37
9	490	2-*ex* Cl₂	..	1.7888	.0557	32	23	45
10	450	2-*ex* Cl₂	11	1.7891	.0576	37	19	44
11	450	1-	Catalyst	1.7893	.0490	22	42	36
12	450	2-*ex* Cl₂	Catalyst	1.7884	.0468	13	44	43
13	450	2-*ex* alc.	Catalyst	1.7888	.0468	16	45	39
14	400	2-*ex* Cl₂	Catalyst	1.7858	.0456	0	35	66
15	250	2-*ex* Cl₂	Catalyst	1.7869	.0458	5	39	56

When anhydrous calcium chloride was used as a catalyst at 450° the butenes produced from both 1-chlorobutane and 2-chlorobutane were largely 2-butenes. Enough catalyst was used to fill the reaction tube entirely and the chlorobutanes were run slowly enough to obtain a high yield of butenes. The catalyst became covered with a dark gray deposit and lost most of its activity in two hours. Only 22% 1-butene was obtained from 1-chlorobutane with the catalyst compared to 100% 1-butene without a catalyst (Expts. 1 and 11), and only 13–16% 1-butene from 2-chlorobutane compared to 33% (Expts. 12, 13). At still lower temperatures, 400 and 250°, 2-chlorobutane gave almost no 1-butene at all when the catalyst was used (Expts. 14, 15). It is unknown whether the butenes rearranged in contact with the catalyst, or whether the catalyst caused the reaction to go in such a way that principally the 2-butenes were formed directly from the chlorobutanes, but Ipatiev and Zdzitovetsky[7] state that zinc chloride does not cause rearrangement of either the *n*-butenes or isobutene. A study of the behavior of these butenes in contact with various catalysts would aid in explaining the results obtained by Dillon, Young and Lucas with the butyl alcohols, as well as these results with the chlorobutanes.

Summary

A study has been made of the thermal decomposition of 1-chlorobutane and 2-chlorobutane in the absence of a catalyst, and using anhydrous

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[7] Ipatiev and Zdzitovetsky, *Chem. Abstracts*, **2,** 259 (1908).

calcium chloride as a catalyst.   The extent of reaction was determined by titrating the hydrogen chloride evolved, and the mixtures of butenes were analyzed by determining for their bromides, the densities and the reaction rates with potassium iodide in methanol.

In the absence of a catalyst, the decompositions of 1-chlorobutane at 550° and of 2-chlorobutane at 500° are homogeneous gaseous reactions. 1-Chlorobutane gave only 1-butene, but 2-chlorobutane gave a mixture of 1-butene, *cis*-2-butene and *trans*-2-butene.   The composition of the product from 2-chlorobutane was the same at 450, 500 and 550°.

In the presence of the catalyst at 450°, both chlorobutanes gave mixtures of all three butenes, there being relatively little 1-butene, however.

It is unknown whether the butenes rearranged in contact with the catalyst, or whether the catalyst caused the reaction to go in such a way that principally the 2-butenes were formed directly from the chlorobutanes.

WEST LAFAYETTE, INDIANA

NATURAL AND SYNTHETIC RUBBER. X. CONSTITUENTS OF THE RUBBER HYDROCARBON

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE AND MARY W. RENOLL

It has been shown in the seventh paper of this series,[1] that nitrogen-free rubber hydrocarbon can be prepared by fractional precipitation of natural rubber from a mixture of alcohol and benzene.   This fractionation method is now applied to the rubber hydrocarbon itself to determine whether it is a single individual or a mixture of various components, and, in the last event, to isolate these constituents.

Some criterion is needed to follow the progress of any fractionation. The measurement of a well-defined physical property is best.   In the present research, use is made of a standardized precipitation point (abbreviated to s. p. p. in the text), which is defined as follows.   The standard precipitation point of a rubber specimen is the temperature at which a sudden increase of turbidity occurs in a slowly cooled solution of 0.85% rubber, 28.55% absolute alcohol and 70.60% benzene.   The manner in which the s. p. p. is determined is described in the experimental part of this paper.

Procedure

Two hundred and fifty grams of crepe rubber was dissolved in benzene and fractioned into primary cuts.   The method of fractionation was a duplication of that reported in the seventh paper.   The technique, however, was improved to prevent alteration of the specimen by light or oxygen.   The flasks containing the rubber solu-

[1] Midgley, Henne and Renoll, THIS JOURNAL, **53**, 2733 (1931).