[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Debromination of Pentaerythrityl Bromide by Zinc. Isolation of Spiropentane[1]

BY M. J. MURRAY AND EUGENE H. STEVENSON

When Gustavson[2] first debrominated pentaerythrityl bromide he assigned to the reduction product the structure vinyltrimethylene. Zelinsky,[3] however, concluded that the spirocyclane (spiropentane) configuration would more nearly account for the chemical reactions and for the synthesis of the compound. Shortly thereafter Philipov[4] was convinced that the reduction product was a mixture of methylenecyclobutane and methylcyclobutene. In 1923 Ingold[5] stated that "the simplest possible *spiro*-compound has never yet been isolated or even transiently formed as an unstable intermediate product." Rogowski,[6] however, in 1939, interpreted the results of an electron diffraction study on the reduction product as proving spiropentane to be the correct formula. Whitmore and Williams[7] painstakingly fractionated a large quantity of the reduction product and proved by ozonolysis that it consisted of a mixture of 2-methyl-1-butene and methylenecyclobutane. The ratio found was about one of the former to eleven of the latter. No evidence could be obtained for the presence of any other compound. Bauer and Beach[7] made an electron diffraction study of the high-boiling fraction obtained by Whitmore and Williams and concluded that it could not possibly be spiropentane and that the methylenecyclobutane structure was the correct one.[8]

The present work began with a Raman spectroscopic investigation of the product obtained when pentaerythrityl bromide was reduced by zinc in aqueous methanol. Two Raman lines which could be assigned neither to the main product, methylenecyclobutane (I), nor to 2-methyl-1-butene (II) showed that a third compound (III) was present. Modified conditions of reduction resulted in the formation of a much larger proportion of the third component and made possible its isolation. A preliminary study of the compound lends considerable support to the opinion that it is the long-sought spiropentane.

Discussion

The spectroscopic results obtained in this work are listed in Table I. For purposes of comparison the spectra of 2-methyl-1-butene and cyclobutanone were taken from the literature.

The high-boiling fraction (41.6–41.9°) of the product obtained from the reduction in aqueous methanol shows a strong, polarized Raman line near 960 cm.$^{-1}$. This line is present also in the spectra of cyclobutanone and methylcyclobutane and is characteristic of the cyclobutane ring. Cyclobutanone has very nearly the same symmetry, mass, and force constants as would be present in methylenecyclobutane, and there is excellent correspondence in a majority of the lines of this ketone with those of the high-boiling fraction of the reduction product.

In ordinary, unconjugated ketones the carbonyl frequency is near 1720 cm.$^{-1}$. The value of 1774 cm.$^{-1}$ found by Kohlrausch and Skrabal for cyclobutanone indicates that the carbonyl is attached to a ring that is not strain free. Similarly, the spectrum of the high-boiling fraction has an olefinic frequency at 1679 cm.$^{-1}$, an unusually high value for an unsymmetrical disubstituted ethylene which normally has this vibration near 1650 cm.$^{-1}$. This is excellent evidence that the olefin is exocyclic. Furthermore, if the olefinic linkage were within the strained ring itself (methylcyclobutene), it would be expected to exhibit a much lower frequency—probably near 1600 cm.$^{-1}$.[9] On the basis of these considerations the authors feel that the spectrum of the high-boiling fraction is thoroughly consistent with the methylenecyclobutane structure.

After eliminating the lines due to methylenecyclobutane from the spectrum obtained for the low-boiling fraction, the remaining lines, with two exceptions, are found to be the more prominent lines in the spectrum of 2-methyl-1-butene. This gives spectroscopic confirmation to the chemical evidence of Whitmore and Williams on the occurrence of this compound. The absence of any trace of line at 1338 cm.$^{-1}$ precludes the possibility that any significant amount of 2-methyl-2-butene exists in the mixture. The appearance of the substantial line at 1033 cm.$^{-1}$ and of the somewhat weaker line at 581 cm.$^{-1}$, however, proves that a third component is present. The quantity of the third compound cannot be estimated with any degree of certainty until the scattering ability of the substance is known, but it seems rather likely that the crude reduction product may contain between 1 and 5% of the compound.

A careful study of the Raman spectra of the crude reduction product and of various fractions obtained in its distillation revealed that the com-

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(1) For a communication regarding this work see Murray and Stevenson, THIS JOURNAL, **66**, 314 (1944)

(2) Gustavson, *J. prakt. Chem.*, [2] **54**, 97 (1896).

(3) Zelinsky, *Ber.*, **46**, 160 (1913).

(4) Philipov, *J. prakt. Chem.*, [2] **93**, 163 (1916).

(5) Ingold, *J. Chem. Soc.*, **123**, 1710 (1923).

(6) Rogowski, *Ber.*, **72**, 2021 (1939).

(7) See footnote to an article by Bauer and Beach, THIS JOURNAL, **64**, 1142 (1942).

(8) In a recent article Shand, Schomaker and Fischer (*ibid.*, **66**, 636 (1944)) also conclude that the main product of the reduction is methylenecyclobutane.

(9) The two methylcyclobutenes would exhibit different olefinic frequencies; the one having the methyl group attached to the doubly bound carbon would have the slightly higher value.

TABLE I

RAMAN SPECTRA OF THE DEBROMINATION PRODUCTS OF PENTAERYTHRITYL BROMIDE COMPARED WITH THE SPECTRA OF RELATED COMPOUNDS

2-Methyl-1-butene[a] $\Delta\nu$ cm.$^{-1}$	I	Low-boiling fraction $\Delta\nu$ cm.$^{-1}$	I^b	Methylenecyclobutane $\Delta\nu$ cm.$^{-1}$	I^b		Cyclobutanone[c] $\Delta\nu$ cm.$^{-1}$	I	Methylcyclobutane[d] $\Delta\nu$ cm.$^{-1}$	I^b	III (Spiropentane) $\Delta\nu$ cm.$^{-1}$	I^b
252	0											
		354	17	354	23	0.8			320	1	305	4
393	2b	371	15	373	13		403	3	416	0.4		
433	2b	428	w				458	6				
485	1											
530	1											
											581	16
		581	6						603	1.4		
		659	12	657	20	0.3	674	4			613	4
709	1								743	5.0		
773	5	770	12						772	0.5	779	4
		871	16	873	14	0.9			872	4	872	30
890	2	904	18	907	20	0.8	898	5b	914	12		
964	1	955	65	957	72	0.2	957	8	962	14		
1020	1b	1033	14				1013	00?	1066	1	1033	50
1091	3	1082	1						1100	4		
							1141	00?	1159	1	1150	1
		1193	7	1191	11	0.9	1196	2	1217	2		
									1256	1		
									1339	1		
1390	0	1390	16	1391	20	0.7	1398	4b	1377	w	1397	5
1413	3	1415	w									
1433	3	1429	28	1428	20	0.8	1442	00?	1447	8	1426	10
1654	5	1651	21									
		1679	36	1679	48	0.3	1774	3				
				2826	4				2724	0.3	2836	0.4
2856	3	2861	2	2861	4		2882	0	2861	34		
											2891	w
2893	5b	2901	68	2902	60	0.2			2907	73		
2917	4	2921	74	2921	75		2929	12b				
2942	4	2954	73	2952	88	0.4			2958	100		
2971	2	2987	100	2986	100	0.4	2970	6b				
2984	3										2991	100
		3076	18	3072	18	0.8	2994	2			3065	30

[a] Thompson and Sherrill, THIS JOURNAL, **58**, 746 (1936). [b] Intensity measured on a Gaertner microdensitometer. Values of ρ for methylene cyclobutane were also measured on this instrument. Lines listed as w were too weak for intensity measurements. [c] Kohlrausch and Skrabal, *Z. Elekt.*, **43**, 282 (1937). [d] The sample used was not fractionated. It contained some III, hence lines known to belong to that compound have been deleted.

pound responsible for the 1033 and 581 cm.$^{-1}$ lines should boil within a few degrees of 37°. This observation sharply narrowed the list of compounds to be considered. A number of other compounds were eliminated because of the absence of Raman lines in certain positions. For example, the lack of a line in the 2100–2200 cm.$^{-1}$ region proved that the compound was not an acetylene. Still other substances were eliminated because they were known not to exhibit Raman lines at 1033 and 581 cm.$^{-1}$. In this way it was possible tentatively to conclude that III was no compound whose properties were known to the authors. (Methylcyclobutane was eliminated only after its spectrum was obtained—see Table I.)

At this point the authors were convinced that there was excellent chance that III was spiropentane.

In the isolation of the new compound there appeared to be two possible procedures. One was the tedious concentration, either by chemical means or by fractional distillation, of the small amount of the substance in the crude reduction product which was obtained when aqueous methanol was employed as solvent. The other was the use of different conditions for the debromination. Fortunately the latter method proved successful and the authors were able, by carrying out the reduction by zinc in molten acetamide[10,11,12] containing sodium iodide and sodium carbonate, to obtain a product consisting of about 40% of the new compound.

Spectroscopically this method of reduction was

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(10) Hass, McBee, Hinds and Gluesenkamp, *Ind. Eng. Chem.*, **28**, 1178 (1936).

(11) McBee, Hass and Tarrant, Abstracts of the 97th meeting, 1939, Am. Chem. Soc., Organic Section, p. 29. (1939).

(12) Whitmore, Popkin, Bernstein and Wilkins, THIS JOURNAL, **63**, 124 (1941).

shown to yield the same volatile products as did the debromination in aqueous methanol.

While separation of the components of the crude mixture by fractionation should be possible in an efficient column, the amount of hydrocarbon mixture available at the moment (18 g.) was not sufficient for this purpose.

Distinct enrichment of III was accomplished easily by repeated extraction with cool, almost saturated, aqueous silver nitrate. The hydrocarbon recovered by heating the separated silver nitrate layer showed spectroscopically that practically no III was absorbed in the extraction. Further purification was carried out by extraction with almost saturated silver perchlorate.

There are certain definite advantages to the use of silver ions for the separation of an olefin from other organic compounds, whenever the extraction is a possible one. The coördinating action of silver ion on olefins is so mild as to cause no detectable rearrangement,[13] a fact which is in direct contrast to the results often obtained with sulfuric acid. Bromine and alkaline permanganate give new products that require separation, and in the latter case the solid manganese dioxide creates experimental difficulties. Finally the silver nitrate method of extraction allows one to recover the olefin merely by warming the solution for low molecular weight substances or by diluting for high-boiling compounds.

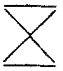
On the other hand, the formation of the silver ion-olefin complex is an equilibrium process[13] which makes it increasingly difficult to extract the olefin as its concentration in the organic layer becomes smaller. Furthermore, the ease of coördination differs markedly with various olefins. In the present case it was found to be much easier to extract from III a larger amount of methylenecyclobutane than the somewhat smaller amount of 2-methyl-1-butene. It was necessary to complete the purification process by reaction of the olefin with bromine. Analysis showed the compound to be C_5H_8. The Raman spectrum of the final sample is listed in Table I.

Throughout the early stages of purification of III the hydrocarbon mixture always had the sharp, characteristic odor of low molecular weight, unsaturated compounds. The odor remained practically unchanged until the final extractions with concentrated silver perchlorate solution. The organic layer then had an odor similar to that of chloroform.

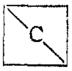
It was felt at first that the observed boiling point of the new compound, 38.3-38.5°, was too high for spiropentane. However, Dr. H. I. Bernstein called the authors' attention to the fact that the boiling point of 1,1-dimethylcyclopropane is about 10° higher than that of neopentane. Closure of the second ring would undoubtedly increase the boiling point considerably.

The value of the highly polarized frequency, 1033 cm.$^{-1}$, is nearer to that for a cyclobutane ring (960 cm.$^{-1}$) than that for a cyclopropane ring (1200 cm.$^{-1}$). That spiropentane should show an abnormal cyclopropane ring frequency is definitely not out of order. First, the addition of a second ring in the gem position would give rings with strain characteristics quite different from the one ring system; and, second, the almost pure inner vibration obtained for those hydrocarbons with one ring would probably be replaced by a more highly coupled vibration involving both rings more intimately. This may be considered similar to an effect observed in the Raman spectra of olefins. The C=C vibration is always represented in the spectrum by a prominent line near 1600 cm.$^{-1}$ except when another double bond carbon is attached to the first to form an allene. The interaction of the two double bonds in this type of compound is sufficient to move the vibration completely out of the 1600 cm.$^{-1}$ region.

Raman spectra considerations and the nonreactivity with bromine eliminate acetylenes, diolefins and monocyclic olefins and leave of the C_5H_8 isomers only the dicyclic compounds

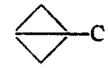

IV


V



VI

VII



VIII

as structural possibilities.

There are at present two reasons why the authors believe structure IV to be the most plausible:

1. In the presence of sodium iodide and sodium carbonate the reduction of 1,3-dihalides in molten acetamide has been found to produce good yields of the normally expected compounds (cyclopropane and derivatives) when the starting products were 1,3-dichloropropane,[10] 1,3-dichlorobutane[11] and 1,3-dibromo-2,2-dimethylpropane.[12] The formation from pentaerythrityl bromide of any condensed ring system other than spiropentane could occur only through an extensive series of rearrangements—a phenomenon which would be expected to occur *less* in acetamide than in aqueous methanol.

2. The carbon-hydrogen Raman lines between 2800 and 3100 cm.$^{-1}$ can be cited as favoring structure IV. Both compounds V and VI have hydrogen attached to cyclobutane rings, whereas IV has the hydrogen combined only with cyclopropane groups. Kohlrausch and Skrabal,[14] who have made a comprehensive study of cyclobutyl and cyclopropyl compounds by means of the Raman effect, found that hydrogen atoms attached to cyclobutane rings produced several intense frequencies near those of aliphatic hydrocarbons; *i. e.*, between 2850 and 3000 cm.$^{-1}$. On the other hand, cyclopropane and those derivatives with hydrogens attached only to three-membered rings (carbocyclic) produce no intense Raman lines in

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(13) Winstein and Lucas (THIS JOURNAL, 60, 836 (1938)) found that neither *cis*- nor *trans*-2-butene underwent isomerization in the aqueous solution.

(14) Kohlrausch and Skrabal, *Monatsh.*, 70, 44, 377 (1937).

this region much below 3000 cm.$^{-1}$. In the new compound the only intense Raman lines between 2800 and 3100 cm.$^{-1}$ occur at 2991 and 3065 cm.$^{-1}$. Although 2991 cm.$^{-1}$ might belong to a substance having either a cyclobutane or a cyclopropane ring, the former structure would show several intense lines below this figure, whereas only the latter structure could give rise to the 3065 cm.$^{-1}$ frequency. This appears to the authors to be quite conclusive as to the absence of a cyclobutyl and as to the presence of a cyclopropyl compound. The weak lines at 2836 and 2891 cm.$^{-1}$ in the spectrum of the sample studied may be due to a trace of impurity or they may actually belong to the pure compound. Their occurrence, since they are so weak, appears to the authors to be beside the point as far as structural arguments are concerned. Structures VII and VIII are ruled out because each has a methyl group and hence would exhibit strong carbon–hydrogen vibrations between 2850 and 2980 cm.$^{-1}$.

The chemical stability of the new compound is remarkable. Its reaction with bromine at 25° in the dark is negligible. It is not hydrogenated over Raney nickel at room temperature. It appears not to be isomerized at 300° when passed over aluminum oxide. With alkaline permanganate the reaction is very slow, and what reaction there is may be caused by a small amount of impurity.

The Raman effect is a method *par excellence* for the study of a problem of this nature and throughout the investigation close check was kept on the changing composition caused by varying factors. One difficulty, however, should be mentioned. Because of the very great differences in scattering ability of various compounds, error is likely to be made in estimations of the composition of mixtures when unknown compounds are concerned. For example, the scattering power of III is high while that of 2-methyl-1-butene is quite low. Consequently there is a tendency for one to estimate the amounts of the former as too high and of the latter as too low until the spectra of the pure compounds have been obtained under similar conditions.

Experimental

Pentaerythrityl Bromide.[15]—The pentaerythritol used was an Eastman Kodak Company product, m. p. 254°. The only modification made in the procedure given in "Organic Syntheses" for the preparation of the bromide was the substitution of acetone for ethyl alcohol in the extraction of the impure reaction product. When acetone was used it was found that the extraction went at a much faster rate and with a smaller volume of solvent, and yielded a product having a m. p. 160° (not recrystallized) which is the same as that obtained by the use of ethyl alcohol. Furthermore, samples extracted by the two methods upon reduction gave products with identical spectra.

Reduction of Pentaerythrityl Bromide in Aqueous Methanol.—Five hundred sixty grams of the pentaerythrityl bromide was mixed with 380 g. of zinc dust, and 1200 ml. of 50% methyl alcohol was poured over the mixture. The volatile product, 57 g., was caught in a dry-ice trap and then dried over calcium chloride. It was fractionated using an 85-cm. Ewell column. Several fractions were obtained and examined spectroscopically. The only one showing Raman lines for a single compound was the high-boiling fraction, b. p. 41.6–41.9° at 752 mm., d^{20}_4 0.7326, n^{25}D 1.4158.

Reduction of Pentaerythrityl Bromide in Acetamide.—Into a 500-ml. three-necked flask was placed 190 g. of Eastman Kodak Company practical grade acetamide, 10 g. of sodium iodide, 30 g. of sodium carbonate and 90 g. (1.4 mole) of zinc dust. The flask was provided with a mercury-seal mechanical stirrer, a reflux condenser from the top of which a tube led to a dry-ice trap, and a device for slowly adding 90 g. (0.23 mole) of solid pentaerythrityl bromide. The flask was heated in an oil-bath at 170–180°. Each addition of the bromide resulted in the evolution of fumes. Carbon dioxide, which formed in the reaction from the sodium carbonate, escaped from the exit tube of the trap. Nine grams of crude material was caught in the dry-ice trap. The Raman spectrum of this material after straight distillation showed the 1033 line to be more intense than the 957 cm.$^{-1}$ line of the methylenecyclobutane. Several lines of 2-methyl-1-butene were also present.

Purification of the Non-olefinic Constituent.—The separation of the olefinic constituents of the mixture from the compound showing the 1033 cm.$^{-1}$ Raman line was accomplished largely by the use of silver salts. Loss of the highly volatile hydrocarbon during extraction was avoided by use of a cylindrical separatory funnel constructed of 18 mm. glass tubing and having a stopcock attached to each end. The positions of the aqueous and hydrocarbon layers were noted for each extraction in order to determine when the process had reached the point of diminishing returns. The contents of the tube were cooled under the tap.

In this apparatus 18 g. of the hydrocarbon mixture was extracted ten times with 5-ml. portions of nearly saturated aqueous silver nitrate. The volume of the hydrocarbon layer decreased 47%. Then followed four extractions with 5-ml. portions of almost saturated aqueous silver perchlorate. Precautions were, of course, taken in the use of the perchlorate solutions, but no vigorous reaction was noted in any case. In the first and second extractions with perchlorate three layers were obtained. The top was the hydrocarbon, the middle probably contained the greater amount of the olefin, and the bottom contained most of the water. The middle layer showed some slight discoloration, but the other two layers remained water-white. The third and fourth extractions gave only two layers each. In spite of several transfers of material, two fractionations for determining constancy of boiling point, and the removal of samples for chemical and spectroscopic tests, the amount of hydrocarbon remaining at this point was 5 g. It appeared by bromination to contain about 6% olefins.

The hydrocarbon layer was then washed thoroughly with water and dried over calcium chloride. It was cooled in an ice–hydrochloric acid-bath, and bromine was added dropwise with stirring until a very faint color of bromine persisted. This color did not noticeably decrease in half an hour. The slight excess of bromine was removed by blowing a trace of olefin vapor from a capillary pipet into the solution. Distillation was through a six inch (length) column packed with glass helices. The main fraction, 38.3–38.5°, was collected at 750 mm.; n^{20}D 1.4117; d^{20}_4 0.755; mol. ref. calcd. for spiropentane, 22.32; found, 22.43. *Anal.*[16] Calcd. for C_5H_8: C, 88.17; H, 11.83. Found: C, 87.91; H, 11.53. The amount finally isolated was only about 1 g. but this was partly because a number of preliminary tests were made with small amounts of the sample before final purification with bromine and partly because of loss in the column which was not equipped with control of reflux ratio.

Stability of the Hydrocarbon.—The method of purification indicates the stability of the product toward bromine. In another experiment several drops (capillary) of the

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(15) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 476.

(16) Thanks are due Dr. T. S. Ma, Univ. of Chicago, for a painstaking analysis of this highly volatile liquid.

hydrocarbon were added to carbon tetrachloride containing a little bromine. In three days at room temperature in the dark there was but little change in the color of the solution.

A few drops (capillary) of the hydrocarbon when shaken with a very dilute aqueous permanganate solution caused no noticeable color change in fifteen minutes. When alkali was added a very slow reaction took place. At the present time it is not certain whether this might be caused by a small amount of impurity or whether it represented a *bona fide* oxidation of the hydrocarbon.

A mixture of methylenecyclobutane, 2-methyl-1-butene and the compound in question was added to cold concentrated sulfuric acid. After dilution and distillation the Raman spectrum showed the presence of both the 1033 and the 581 cm.$^{-1}$ lines.

Passage of a mixture of methylenecyclobutane and the compound thought to be spiropentane over aluminum oxide at 300° resulted in isomerization of almost all of the methylenecyclobutane to isoprene but did not noticeably affect the intensity of the 1033 cm.$^{-1}$ Raman line in the treated sample.

Methylcyclobutane.—Five grams of methylenecyclobutane (containing a small amount of the compound having a Raman line at 1033 cm.$^{-1}$) was hydrogenated over Raney nickel at atmospheric pressure and at room temperature. The Raman spectrum of the material was taken after a straight distillation into the Raman tube without any attempt at fractionation.

Recovery of Olefins.—The combined silver nitrate layers were heated on a water-bath and the olefins collected in a dry-ice trap. A Raman spectrum of the sample showed only lines for methylenecyclobutane and for 2-methyl-1-butene. There was no more than a faint trace of line at 1033 cm.$^{-1}$, the position of the strong Raman-active frequency of III. This, coupled with the fact that treatment of the hydrocarbon layer with silver salts failed after several extractions to dissolve appreciable material from the organic layer, showed that III was practically unaffected by this reagent.

Hg 4358 Å. was used for exciting the Raman spectra. Exposure times were of the order of four hours and the slit width was 0.08 mm. The experimental details of obtaining the spectra are given elsewhere.[17]

Summary

1. Reduction of pentaerythrityl bromide by zinc in aqueous methanol yields a mixture of methylenecyclobutane, 2-methyl-1-butene and a small amount of a third component with Raman lines at 1033 and 581 cm.$^{-1}$.

2. Reduction of pentaerythrityl bromide by zinc in molten acetamide in the presence of sodium carbonate and sodium iodide yields a mixture containing a relatively large amount of the new compound, together with methylenecyclobutane and 2-methyl-1-butene.

3. The new compound was isolated by removal of the olefins with aqueous solutions of silver salts and with bromine.

4. The method of synthesis as well as the Raman spectrum of the substance leads to the belief that the compound is spiropentane.

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[17] Cleveland, Murray, Haney and Shackelford, *J. Chem. Phys.*, 8, 153 (1940); Cleveland and Murray, *ibid.*, 7, 396 (1939).

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Benzene with Butadiene in the Presence of Sulfuric Acid and Hydrogen Fluoride Catalysts

BY V. N. IPATIEFF, HERMAN PINES AND R. E. SCHAAD

The large number of theoretically possible reaction products, some of which may have important applications in the synthesis of valuable materials, prompted us to study the reaction between benzene and butadiene.

We have found that benzene reacts with butadiene in the presence of sulfuric acid or hydrogen fluoride. In order to favor reaction with benzene and to decrease polymerization of butadiene, it was considered advisable to use a large excess of benzene. Under these conditions one mole of butadiene reacted with an average of approximately 1.5 moles of benzene in the presence of sulfuric acid and with 1.2 moles of benzene in the presence of hydrogen fluoride.

The hydrocarbon of lowest boiling point obtained from this reaction was 1,2-diphenylbutane, which was formed by the interaction of two molecules of benzene with one molecule of butadiene. The proof of the structure of this compound was based on the comparison of its physical constants, infrared absorption spectrum, and the melting points and mixed melting points of the acetamino derivative with those of synthetically prepared (liquid) 1,1-, 1,2- and 1,3-diphenylbutanes. The primary product of the reaction was probably 1-phenylbutene-2 formed by the 1,4-addition of benzene to butadiene-1,3 in the presence of the investigated catalysts. Under these conditions phenylbutene then reacted with another molecule of benzene to form the diphenylbutane obtained.

Experimental Part

Reaction of Benzene with Butadiene in the Presence of Sulfuric Acid.—Benzene (156 g.) and 96% sulfuric acid (50.2 g.) were stirred at 0–5° in a 500-cc. flask of the type described[1] by us and 20.0 g. of butadiene (98% pure) was introduced to the stirred mixture as gas from a weighed aluminum bomb during 1.25 hours. The butadiene was added through an opening in the reflux condenser in order that it would be diluted before coming in contact with the sulfuric acid. After the addition of butadiene was completed, the stirring was continued for 0.25 hour while the temperature of the reaction mixture was maintained at 0–5°.

The dark brown product of the reaction consisted of 178 g. of an upper hydrocarbon layer and 46 g. of a lower acid layer. The upper layer, neutralized by sodium hydroxide solution, was steam-distilled to remove the excess of benzene (82 g.). The higher boiling material when distilled

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[1] Ipatieff and Pines, *J. Org. Chem.*, 1, 478 (1936).