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.

[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, 473 (1936).

under reduced pressure yielded 13 g. of a hydrocarbon fraction boiling at 152–154° at 16 mm. pressure, and a remainder (81 g.) of higher boiling products. The lower boiling product, after redistillation over sodium, had the properties compared in Table I with the same properties determined on a similar product formed in the presence of hydrogen fluoride and on three synthetically prepared liquid diphenylbutanes.

TABLE I

PROPERTIES OF DIPHENYLBUTANES AND OF THEIR ACETAMINO DERIVATIVES

Diphenylbutane		From reaction in presence of H₂SO₄	HF	1,1-	1,2-[b]	1,3-
B. p.	° C.	148	124[d]	145	141	291
	mm.	12	4	16	12	760
$n^{20}D$		1.5545	1.5538	1.5664	1.5513	1.5525
d^{20}_4		0.9761	0.9711	0.9928	0.9707	0.9722
Analyses[a]	C, %	91.23	91.84	91.65	91.22	91.03
	H, %	8.72	8.43	7.98	9.00	8.73
Acetamino derivative[2]	M. p., ° C.	219	...	201–203	227	194
	Mixed m. p. with product from present reaction	...	...	195	223	165–170
Analyses, % N[c]		8.86	...	....	8.90	8.47

[a] Calculated: C, 91.37; H, 8.63. [b] Infrared absorption indicates that the product is only 90% pure. [c] Calculated: N_2, 8.64. [d] Infrared absorption spectra agreed with that of 1,2-diphenylbutane.

Reaction of Benzene with Butadiene in the Presence of Hydrogen Fluoride.—This reaction was carried out in a stainless steel autoclave provided with a motor-driven stirrer. The autoclave was charged with 408 g. of benzene (5.25 moles) and 311 grams of hydrogen fluoride (15.5 moles) and cooled to 5°. The contents of the autoclave were stirred and a mixture consisting of 312 g. (4 moles) of benzene and 135 g. (2.5 moles) of butadiene was added from a pressure charger during 3.75 hours. The temperature during the reaction rose to 20° and the pressure was the vapor pressure of the mixture. After all the mixture of butadiene and benzene had been added to the reaction mixture, the hydrogen fluoride was released to a potassium hydroxide scrubber, and the autoclave was heated to 50° to remove the greater part of the hydrogen fluoride dissolved in the hydrocarbons. The autoclave was then cooled, and the reaction mixture removed and treated with potassium hydroxide solution. The reaction product formed an emulsion from which the excess of benzene was removed by steam distillation. High boiling products which remained were separated from the alkaline aqueous layer by extraction with *n*-pentane. The extracted material was washed with water, dried, and vacuum distilled. The fractions so separated had the boiling points and refractive indices shown in Fig. 1.

All of the butadiene entered into reaction. The molar ratio of benzene to butadiene which reacted was 1.2:1. About 50% by weight of the reaction product was diphenylbutane. The higher boiling fraction consisted of a complex mixture among which were products of the interaction of 2 moles of benzene with 2 or 3 moles of butadiene as evidenced by the carbon and hydrogen analyses shown in Table II.

TABLE II

PRODUCTS FORMED FROM BENZENE AND BUTADIENE IN THE PRESENCE OF HYDROGEN FLUORIDE

Fraction no.		3–7	16	21
B. p., ° C., at 760 mm.		280–285	358–374	418–419
Found, %	C	91.84	91.08	90.49
	H	8.43	9.12	9.47
Calcd., %	C	91.37	90.85	90.50
	H	8.63	9.15	9.50
Formula		$C_{16}H_{18}$	$C_{20}H_{24}$	$C_{24}H_{30}$

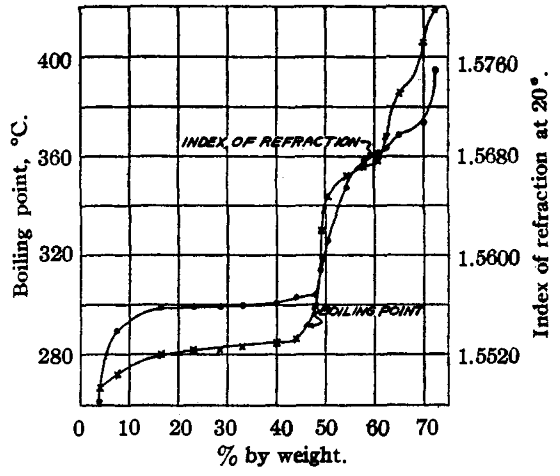

Fig. 1.—Boiling range and index of refraction of the reaction products from benzene and butadiene in the presence of hydrogen fluoride.

Synthesis of Normally Liquid Diphenylbutanes.—The method used for the preparation of diphenylbutanes, illustrated in Table III, consisted in coupling a ketone with a Grignard reagent to form a carbinol which was dehydrated to an olefin by passage over activated alumina at 350°. The olefin was diluted with an equal volume of pentane and hydrogenated at 50° in an Ipatieff rotating autoclave in the presence of a nickel catalyst under 100 atmospheres initial pressure of hydrogen. By this procedure only the olefinic double bond was hydrogenated while the aromatic ring remained unchanged.

TABLE III

SYNTHESIS OF NORMALLY LIQUID DIPHENYLBUTANES

Starting materials			
Ketone	$C_6H_5COC_6H_5$	$C_6H_5CH_2COC_2H_5$	$CH_3COC_6H_5$
Grignard reagent	n-C_3H_7MgBr	C_6H_5MgBr	$C_6H_5C_2H_4MgBr$
Diphenylbutane synthesized			
Isomer	1,1-	1,2-	1,3-
Yield, %	65–70	87	75

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Summary

Reaction of butadiene with benzene in the presence of sulfuric acid and hydrogen fluoride catalysts was studied.

1,2-Diphenylbutane was identified as one of the products of the reaction.

The respective yields of 1,2-diphenylbutane obtained from the reaction of butadiene with benzene catalyzed by sulfuric acid and hydrogen fluoride were 14% and 59% on the basis of the benzene which reacted.

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(2) V. N. Ipatieff and L. Schmerling, THIS JOURNAL, 59, 1056 (1937); 60, 1476 (1938).