Reaction between Benzene and Butadiene in the Presence of Silico-phosphoric Acid Catalyst

By V. N. Ipatieff, R. E. Schaad, Herman Pines and G. S. Monroe

Previously we described the reaction of butadiene with benzene in the presence of sulfuric acid and hydrogen fluoride catalysts.[1] In batch-type operations the lowest boiling reaction product obtained was 1,2-diphenylbutane.

The present paper deals with a similar reaction, carried out in the presence of a silico-phosphoric acid (solid phosphoric acid)[2] catalyst in continuous-type operation, both at atmospheric pressure and at a pressure of 27 atmospheres. The primary product, a mixture of phenylbutenes, was formed by the interaction of one molecule of benzene with one molecule of butadiene, and amounted to 41 mole % based upon the butadiene charged.

The molar ratio of benzene to butadiene used in most of the reactions was of the order 4:1. This high ratio was necessary in order to prevent both the formation of high-boiling hydrocarbons and the polymerization of butadiene. The products obtained based on the benzene reacted contained 59 mole % of phenylbutenes as compared with 34% when the ratio of benzene to butadiene was one. The type of products obtained, as judged from determination of physical constants, was the same in both instances. The active life of the catalyst was high, especially in the experiment made at superatmospheric pressure. After a run of ten hours, the activity and appearance of the catalyst were unchanged.

When the reaction was carried out at atmospheric pressure about half of the charged butadiene reacted and the catalyst was covered with gummy, high-boiling hydrocarbons which upon extraction with benzene, were recovered as a viscous brown oil. The physical properties and composition of this oil were practically the same as those of the oil recovered in the high-boiling fraction of the alkylation product. The difference in the activity of the catalyst at atmospheric and superatmospheric pressure was apparently due to the fact that under pressure the system was for the most part in the liquid phase which washed the catalyst and prevented the deposition thereon of high-boiling organic materials such as heavy polymers and alkylation products.

In view of the fact that the reaction between butadiene and benzene at superatmospheric pressure gave better yields of phenylbutenes than did similar experiments at atmospheric pressure,

this paper mentions only the data obtained in the experiments made at superatmospheric pressure.

1-Phenyl-1-butene was one of the products formed since on selective hydrogenation, the phenylbutene fraction yielded n-butylbenzene which was identified by means of a solid acetamino derivative. The position of the double bond was determined by ozonization and identification of benzaldehyde from the ozonization products.

The dibutenylbenzene formed also by the interaction of benzene with butadiene at superatmospheric pressure was hydrogenated to 1,4-dibutylbenzene, which on oxidation yielded terephthalic acid.

The reaction products which boiled between 261 and 274° contained dicyclic hydrocarbons formed by the interaction of two molecules of butadiene with one molecule of benzene.

The still higher boiling compounds consisted of tricyclic hydrocarbons formed by the interaction of two molecules of butadiene with two molecules of benzene. The existence of these types of hydrocarbons was demonstrated by means of elementary analysis of: (a) the original compounds, (b) compound formed by the selective hydrogenation and (c) compound obtained by complete hydrogenation of the double bond and of the aromatic nucleus.

Experimental

The **apparatus** used consisted of: (1) a calibrated pressure charger for holding the mixture of benzene and 1,3-butadiene; (2) a conventional laboratory differential pressure pump with the suction attached to the charger and the discharge attached to the upper inlet end of the vertical catalyst tube; (3) a metal block furnace with automatic temperature control; (4) a stainless steel catalyst tube, 19 mm. in diameter and 90 cm. long; (5) a pressure regulator actuating a needle-type valve attached to the outlet end of the catalyst tube; (6) a stabilizer connecting the outlet valve to a dry-ice trap and maintained at a temperature level of about 50° to ensure separation of any unreacted butadiene from the liquid reaction product; and (7) a wet-test meter attached to the outlet end of the dry-ice trap to measure any uncondensed gas.

The **operating** procedure was essentially the same as that usually followed with this type of apparatus and for this reason need not be given in detail. The catalyst tube was placed under the desired nitrogen pressure and its temperature was raised to the desired operating level before the material to be reacted was pumped.

A mixture consisting of 86.7% by wt. of benzene and 13.3% of butadiene (4.5 moles of benzene per 1 mole of butadiene) was passed over 50 g. (70 cc.) of solid phosphoric acid catalyst in the form of 5 × 5 mm. cylindrical pieces at a pressure of 27.2 atmospheres and at an average liquid feed rate of 238 cc. an hour. The average block temperature was 209° while that of the catalyst was 216°; the run was of nine-hour duration. In order to determine whether or not the catalyst would lose its activity, hourly determinations of the percentage of benzene in the re-

(1) V. N. Ipatieff, H. Pines and R. E. Schaad. This Journal, 66, 816 (1944).

(2) V. N. Ipatieff (to Universal Oil Products Co.), U. S. Patents 1,993,512, 1,993,513 (March 5, 1935); 2,018,065, 2,018,066 (October 22, 1935); 2,020,649 (November 12, 1935); 2,057,433 (October 13, 1936); 2,060,871 (November 17, 1936).
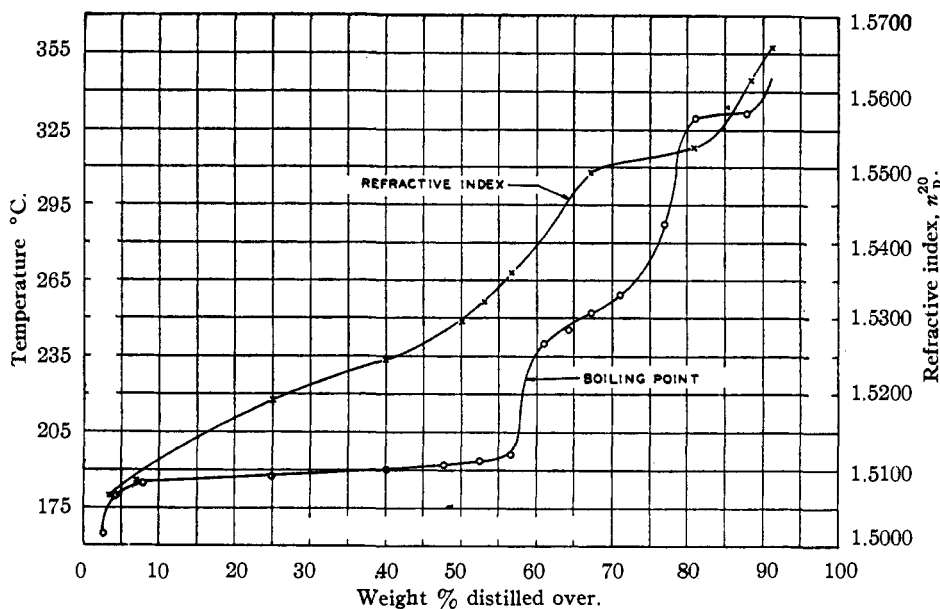
Fig. 1.

covered reaction products were made by distillation. The results obtained are given in Table I.

TABLE I

DETERMINATION OF UNREACTED BENZENE AND REACTION PRODUCT IN PERIODS 2, 4, 6, AND 8, RESPECTIVELY

Period no.		2[a]	4	6	8
Charge, g.		87.2	88.0	87.6	87.9
Distillate to 85°	g.	58.9	62.4	60.9	61.0
	wt., %	67.5	70.9	69.5	69.5
Residue	g.	26.5	24.7	25.6	25.6
	wt., %	30.4	28.1	29 2	29.1
Loss	g.	1.8	0.9	1.1	1.3
	wt., %	2.1	1.0	1.3	1.4

[a] Recovery of benzene in Period 2 was relatively lower than in the other three periods (4, 6, 8). This was probably caused by the fact that, owing to the flooding of the fractionating column, it was necessary to interrupt the distillation, remove the column, and rearrange the wire spiral therein, this procedure increasing the loss over that obtained in the other periods.

A weight balance of the entire experiment referred to in Table I is as follows:

	Grams
Total amount of benzene passed	1555
Total amount of butadiene passed	239
Benzene recovered	1313
Butadiene recovered	None

Accordingly, the mole ratio of benzene to butadiene which reacted was 0.7:1.0. After the reaction the catalyst weighed 53 g. Its physical appearance was no different from that of fresh catalyst and no gummy deposit was observed thereon.

The boiling range of the reaction products is presented in Fig. 1. From the distillation through a column with about twenty theoretical plates and further analysis it was found that 50% of the benzene which reacted was converted into phenylbutenes, while the remainder of the consumed benzene reacted with two or more molecules of butadiene to form a complex mixture consisting of polycyclic hydrocarbons and polybutenylbenzenes.

The main fraction boiling between 187 and 194° consisted of phenylbutenes, which on selective hydrogenation yielded n-butylbenzene, the latter being characterized by means of its acetamino derivative.

Selective Hydrogenation of 187–194° Fraction.—In order to hydrogenate the double bond without affecting the benzene ring, 5.74 g. of this liquid fraction, 1.0 g. of active nickel catalyst,[3] and 15 g. of n-pentane were contacted twelve hours at 16–22° at an initial hydrogen pressure of 100 atmospheres in a rotating autoclave of 125-cc. capacity. After the hydrogenation, the pentane was removed by distillation and a hydrocarbon was obtained which was stable to potassium permanganate, boiled mainly at 182–184°; had d^{20}_4 0.8870; n^{20}D 1.5026, and a composition as calculated for butylbenzene.

Anal.[4] Calcd. for $C_{10}H_{14}$: C, 89.50; H, 10.50. Found: C, 89.82; H, 10.04.

This hydrocarbon yielded a diacetamino derivative[5] melting at 212–213°. This result and the fact that nitration[6] of this diacetamino derivative yielded yellow crystals melting at 180–181° showed that the hydrogenation product contained n-butylbenzene.

Ozonolysis.—A fraction boiling at 187–194° at 760 mm., and with d^{20}_4 0.8996, and n^{20}D 1.5169, was ozonized. Decomposition of the ozonide yielded benzaldehyde which was identified by its 2,4-dinitrophenylhydrazone, m. p. 232–234°. Treatment of a part of the benzaldehyde by silver oxide, followed by acidification produced benzoic acid. These facts evidenced the presence of 1-phenyl-1-butene in the reaction product.

Analyses and Hydrogenations of Higher-boiling Fractions.—Fraction 100–115° at 5 mm. (240–260° at 760 mm.): *Anal.* Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.29; H, 10.09; n^{20}D 1.5272; d^{20}_4 0.9323.

Forty-five grams of the fraction boiling at 100–115° at 5 mm. was hydrogenated at 50° in the presence of six grams of a nickel-kieselguhr catalyst and at an initial hydrogen pressure of 100 atmospheres. Two moles of hydrogen was absorbed per mole of hydrocarbon charged. The hydrogenated material which was free from olefins as

(3) V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

(4) Microanalyses made by Dr. T, S. Ma, University of Chicago.

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

(6) V. N. Ipatieff and L. Schmerling, unpublished results.

determined by means of potassium permanganate solution, distilled as follows:

Cut	B. p. at 5 mm., °C.	% by weight	$n^{20}D$
1	78- 90	12.9	1.5019
2	90- 93	31.6	1.5046
3	93- 96	28.5	1.5408
4	96-109	22.0	1.5067

Cut 2, *Anal.* Calcd. for $C_{14}H_{22}$ (dibutylbenzene): C, 88.35; H, 11.65. Found: C, 88.70; H, 11.47; d^{20}_4 0.9068; molecular refraction, 62.0.

Seven-tenths of a gram of the above-indicated Cut 2 was oxidized by heating at 165° in a sealed tube in the presence of 40 cc. of dilute nitric acid (15 cc. of 72% nitric acid and 25 cc. of water) and 0.1 g. of terephthalic acid was obtained which was identified as dimethyl terephthalate melting at 139.5–140° and showing no depression of melting point when mixed with a synthetic sample.

Fraction, 261–274° at 760 mm., $n^{20}D$ 1.5420: On selective hydrogenation at 40° in the presence of pentane as a solvent this fraction absorbed 1 mole of hydrogen per mole of hydrocarbon charged. The hydrogenated material with boiling point of 115–122° at 4 mm. and $n^{20}D$ 1.5290, analyzed as follows: *Anal.* Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74; for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.70; H, 10.28.

Complete hydrogenation of the product at 100° in the absence of solvent yielded a saturated hydrocarbon which did not react with a nitrating mixture and which analyzed as follows: *Anal.* Calcd. for $C_{14}H_{24}$: C, 87.42; H, 12.58; for $C_{14}H_{26}$: C, 86.56; H, 13.44. Found: C, 87.19; H, 12.85; $n^{20}D$ 1.4850.

These analytical results indicate that the original product consisted probably of a mixture of dicyclic and tricyclic hydrocarbons probably formed by the interaction of two moles of butadiene with one mole of benzene.

Fraction 164–180° at 5 mm. (330–352° at 760 mm.): *Anal.* Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15; mol. wt., 264. Found: C, 90.41; H, 9.29; $n^{20}D$ 1.5635; mol. wt., 267.

Seven and three-tenths grams of this fraction was hydrogenated at 100° in the presence of a nickel–kieselguhr catalyst and at an initial hydrogen pressure of 100 atmospheres. A saturated hydrocarbon stable to a nitrating mixture was obtained boiling at 120–130° at 0.4 mm. (325–338° at 760 mm.), d^{20}_4 0.9274; and $n^{20}D$ 1.4920. *Anal.* Calcd. for $C_{20}H_{36}$: C, 86.87; H, 13.13; mol. wt., 276. Found: C, 86.63; H, 13.05; mol. wt., 266.

These analytical data show that the original product has resulted from the combination of two molecules each of benzene and butadiene in such a way as to form a tricyclic compound.

Summary

On passing a 4.5 : 1 molecular mixture of benzene and butadiene through a layer of silico-phosphoric acid catalyst at 216° and at 27 atmospheres pressure, 0.7 molecular proportion of benzene and all of the butadiene reacted forming a liquid product containing about 50% of phenyl-*n*-butenes and smaller amounts of 1,4-dibutenylbenzene, a dicyclic hydrocarbon formed by interaction of two molecules of butadiene with one molecule of benzene, and a tricyclic hydrocarbon formed by interaction of two molecules of butadiene with two molecules of benzene.

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The Kinetics of the Decomposition of Trichloroacetates in Ethyl Alcohol

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It has been suggested previously, in a study of the decomposition of trichloroacetates in several solvents,[1] that the rate-determining step in this decomposition is a unimolecular decomposition of the trichloroacetate ion, forming carbon dioxide and the anion of the acid chloroform, CCl_3^-. The similar hypothesis for the decomposition of trinitrobenzoates—that the trinitrobenzoate ion decomposed to carbon dioxide and the anion of the acid trinitrobenzene—was examined for the case of solutions in ethyl alcohol[2] and in mixtures of dioxane and water[3] and found to agree with the experimental facts. One of the tests of the hypothesis was made by comparing the rate of decomposition of trinitrobenzoic acid in ethyl alcohol in the presence of several aromatic amines with the basic strength of the amine. It was found that there was a quantitative relation between the number of trinitrobenzoate ions formed with amines of different strengths and the rate of decomposition. One exception to this generalization was observed, however, in the case of di-

methylaniline, for which the rate of decomposition was much smaller than would be expected for the number of ions formed in the presence of a base of the strength of dimethylaniline. For the trinitrobenzoates dimethylaniline was the only tertiary amine investigated.

The present research with trichloroacetates in ethyl alcohol was undertaken to provide more quantitative data for testing the "decomposing-ion" hypothesis for the trichloroacetates, and to find out whether the behavior observed for dimethylaniline and the trinitrobenzoates was general for all tertiary amines. This paper reports the decomposition of trichloroacetic acid and its sodium salt in ethyl alcohol in the presence of primary, secondary and tertiary amines at 60 and 70°.

Experimental

The experimental measurement of the decomposition velocity was carried out in the same manner as previously,[2] with the difference that potentiometric titration was unnecessary and the titrations were made using thymol blue as indicator. It had been previously shown that hydrolysis of the chloroform formed was inappreciable in alcohol solution, and no corrections for chloride formation

(1) Verhoek, THIS JOURNAL, 56, 571 (1934).

(2) Verhoek, *ibid.*, 61, 186 (1939).

(3) Trivich and Verhoek, *ibid.*, 65, 1919 (1943).