THE ALKENYLATION OF AROMATICS WITH BUTADIENE: A SYNTHESIS OF 1-PHENYL-2-BUTENE
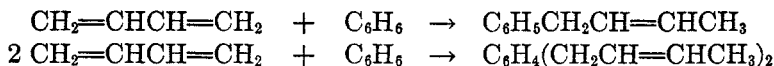
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Aromatic hydrocarbons can be alkylated with butadiene in the presence of catalysts such as clay, sulfuric acid, or liquid hydrogen fluoride; the products from benzene are diphenylbutane derivatives (10). In the presence of silico-phosphoric acid or zinc chloride, mixtures of diphenylbutane and phenylbutenes result (11).

During a study of the properties of the low-molecular-weight alkanesulfonic acids, it was found that such acids promote the alkenylation of aromatic hydrocarbons. Butadiene reacts readily with aromatic hydrocarbons at temperatures of 0–150° when 5% or more of an alkanesulfonic acid is used as catalyst. In the range 0–40° the products are exclusively butenyl and polybutenyl compounds. The reaction with benzene proceeds according to the equations:

$$CH_2{=}CHCH{=}CH_2 \; + \; C_6H_6 \; \rightarrow \; C_6H_5CH_2CH{=}CHCH_3$$
$$2\;CH_2{=}CHCH{=}CH_2 \; + \; C_6H_6 \; \rightarrow \; C_6H_4(CH_2CH{=}CHCH_3)_2$$

Above about 40°, the butenyl groups react further and the product includes a mixture of diarylbutanes, arylbutenes, and more complex products. The mono-alkenylated product produced below 40° appears to be a single isomer.

Since the reaction showed promise of being a general method of preparing specific arylalkenes, a study was made of the structure and purity of this phenyl-butene. No attempt has been made to identify the polybutenyl aromatic fractions.

STRUCTURE OF PHENYLBUTENE

A sample of phenylbutene was prepared by the reaction of butadiene and benzene, and subsequent fractionation, as described in the experimental section. Care was taken to secure the entire phenylbutene cut without discarding any possible isomers as forerun or tail cuts.

Preliminary investigation showed that the phenylbutene contained one double bond and that hydrogenation yielded *n*-butylbenzene (Table I). The butenyl group is therefore unbranched and primary, and the possible phenyl butenes are then those listed in Table II. The physical and chemical properties of the dibromide and the isomerization of the phenylbutene to 1-phenyl-1-butene, indicate that the material is largely 1-phenyl-2-butene.

A further evaluation of the structure was made to determine the purity of this 1-phenyl-2-butene. Ozonolysis gave phenylacetaldehyde and acetalde-hyde, and no formaldehyde or propionaldehyde was found. Infrared examination indicated the 1-phenyl-2-butene contained not more than 5% 1-phenyl-3-butene, but gave no information as to 1-phenyl-1-butene.

The 1-phenyl-2-butene can exist in either *cis*- or *trans*-form. Infrared absorption indicates that the present sample is the *trans*-structure. The conditions of formation (acid catalysis) also make this probable (16).

DISCUSSION

The reaction of butadiene and benzene yields 1-phenyl-2-butene. In addition, butadiene also reacts readily with other aromatic hydrocarbons, as given in detail in the experimental section. In the case of *p*-xylene, an apparently pure monobutenyl-*p*-xylene was obtained whose structure was not determined

TABLE I
PROPERTIES OF BUTYLBENZENES

COMPOUND	B.P., °C. AT 760 mm.	REFRACTIVE INDEX n_D^{20}
Hydrogenated phenylbutene..................	182–183.3	1.4906
n-Butylbenzene[a].............................	183.4	1.4900
Isobutylbenzene[a]............................	172.7	1.4865
sec-Butylbenzene[a]	173.3	1.4902

[a] A.P.I. Project 44.

TABLE II
PROPERTIES OF 1-PHENYLBUTENES

CONSTANT	1-PHENYL-1-BUTENE	1-PHENYL-2-BUTENE	1-PHENYL-3-BUTENE	PRESENT SAMPLE
B.P., °C., 760 mm.	187–189 (13)	176 (13)	178[c] (5)	176
B.P., °C., 12 mm.	78 (3) 82 (1) 73–74.5, 76–78 (14)[a] 78 (17)[c]	70 (17)	72 (17)	70
REFRACTIVE INDEX, n_4^{20}	1.5387 (17)	1.5101 (17)	1.5059 (17)	1.5115
DENSITY, d_4^{20}	0.9106 (17)	0.8831 (17)	0.8831 (17)	0.88
M.P. of DIBROMIDE	(a) 70° (3, 14)[b] (b) liquid (14)[b]	liquid (13)	liquid (17)	liquid

[a] *cis*- and *trans*-isomers boil at 74° and 77° respectively.

[b] The two forms are diastereomers.

[c] Calculated from vapor pressure curve.

but which probably has the same 2-butenyl group as demonstrated for benzene. Phenol, naphthalene, and methylnaphthalene also give butenyl derivatives presumably of structure analogous to butenylbenzene, but these compounds are mixtures of position isomers. Many of these appear to be separable, for example, by distillation. The synthesis is operable over a range of 0–100°, but when it is desired to obtain the purest butenyl aryls, it is best to conduct the butenylation at 10–30°, which range was used for the described preparations. The low-temperature alkenylation appears to be a general method for introducing a 2-butenyl group into an aromatic nucleus.

EXPERIMENTAL

Experimental work included the synthesis and purification of a number of arylbutenes, and determination of structure and purity by chemical and physical means.

Synthesis of arylbutenes. Reagent grade chemicals were used in the following preparations. The 1,3-butadiene was Phillips Pure Grade (99 Mole-%). The alkanesulfonic acid used as catalyst comprised two grades; technical mixed 95% acid (C_1–C_3) of molecular weight 110, supplied by Indoil Chemical Co.; and distilled ethanesulfonic acid (free of sulfuric acid) prepared by the vacuum-distillation of Indoil Chemical Co. 95% ethanesulfonic acid. The distilled ethanesulfonic acid was slightly more reactive than the technical mixed acid. In a few cases it was found desirable to wash the aromatic hydrocarbons with a little sulfonic acid prior to use, to remove traces of peroxides, water, etc. Data on purification of the acid (15) are also available. Results of the following preparations are summarized in Table III.

1-Phenyl-2-butene. A water-cooled, three-necked flask was provided with stirrer, gas-inlet tube, reflux condenser, and thermometer. The flask was charged with benzene (3023 g., 39.8 moles) and 396 g. of technical mixed 95% alkanesulfonic acid. Butadiene was passed into the mixture at such a rate that the temperature did not rise above 30°. After three hours, when 746 g. (13.8 moles) of butadiene had been absorbed, the gas flow was shut off and the mixture was allowed to react for an additional hour. The product was stirred with 500 ml. of water, the acid phase was separated, and the oil phase was then washed with dilute ammonia. The product was distilled rapidly at reduced pressure without a column. This preliminary distillation was made to remove traces of alkanesulfonic acids and esters so that the final fractionation could be carried out without having polymerization occur in the pot. The water-white distillate was refractionated through a 28-section one-inch Stedman column, and yielded 415 g. (23% yield) of phenylbutene, 225 g. (17% yield) of dibutenyl-benzene, and a residue of 440 g. (40% yield) of higher-boiling material, chiefly tributenyl-benzene. The phenylbutene cut was selected to include all possible isomers in the C_{10} range and boiled at 47.9–48.5° (4.0 mm.); 96% of the material boiled in the range 48.2–48.5° (4.0 mm.); it had n_D^{20} 1.5115; and the specific dispersion was 178.

1-(2,5-Dimethylphenyl)-2-butene. p-Xylene (28.8 moles) was alkenylated with butadiene (16.1 moles) as in the synthesis of phenylbutene. The monobutenyl cut included 8.8 moles (54% yield).

Butenylphenol. A mixture of phenol (896 g., 9.5 moles) and 95% mixed alkanesulfonic acid (102 g.) was warmed to fusion point (35°). Pure butadiene was passed in; as the melting point of the batch dropped, the reactor was cooled with a water-bath to 20–25°. Butadiene (143 g., 2.64 moles) was added within a period of two hours after which the mixture was allowed to react an additional 15 minutes. Water was added to quench the reaction, and the water-washed oil was distilled to yield 200 g. (50% yield) of crude monobutenyl-phenol. Fractionation of the crude distillate gave a small forerun of non-phenolic material (probably chromanes), 16% *ortho* (?)-butenylphenol, b.p. 93° (4.3 mm.), 10% of an intermediate fraction, 53% of *para*(?)-butenylphenol, b.p. 108° (4.1 mm.), and a residue of polybutenylphenol. The crude reaction mixture contained a substantial amount of chromanes (about 15%).

β-Methylnaphthyl-2-butene. β-Methylnaphthalene[1] was easily alkylated by the above methods, using distilled ethanesulfonic acid as catalyst. From 6.1 moles of β-methylnaphthalene and 2.9 moles of butadiene, a 31% yield (0.93 mole) of the monobutenyl β-methyl-naphthalene was obtained, b.p. 88–105° (0.20 mm.). Several positional isomers were present as is shown by the boiling range.

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[1] Commercial β-methylnaphthalene contained about 2% of amines which otherwise inhibited the alkylation. It was necessary to prewash the hydrocarbon with alkanesulfonic acid.

STRUCTURE DETERMINATION

Bromination. Phenylbutene (88 g., 0.67 mole) was dissolved in 100 ml. of chloroform and 0.70 mole of bromine was added. Distillation gave 180 g. (93% yield) of liquid dibromophenylbutane, b.p. 96° (0.60 mm.), n_D^{20} 1.5748, d_4^{23} 1.582, which did not crystallize on long standing. The dibromide was refluxed with 20% alcoholic potassium hydroxide and distilled to give a small yield (10%) of a hydrocarbon, b.p. 66° (4.8 mm.), n_D^{20} 1.5680, specific dispersion 270, d_4^{23} 0.94. This presumed acetylene gave a negative test with Nef's reagent (12) for a terminal acetylene group.

Hydrogenation. Phenylbutene (100 ml.) was hydrogenated with 6 g. of Raney nickel in alcohol for three hours at 20° and 40 p.s.i.g. On fractionation the product boiled in the range 113.5–115.5° (100 mm.), 181.5–182.8° (750 mm.); n_D^{20} 1.4906.

Isomerization. Several attempts to isomerize the supposed 1-phenyl-2-butene with ethanolic potassium hydroxide according to the method of Fichter (3) were unsuccessful. The isomerization was accomplished by refluxing 87 ml. of phenylbutene with 500 ml. of *n*-butanol and 100 g. of potassium hydroxide for ten hours. Fractionation gave several cuts totalling 62 ml. of hydrocarbon, b.p. 69–74° (6 mm.), n_D^{20} 1.5204–1.5385. A 9-ml. cut, n_D^{20} 1.5360, was brominated in chloroform with excess reagent. The product on evaporation gave a large crop of white crystals, which, after recrystallization from isopentane,

TABLE III

PROPERTIES OF ARYLBUTENES

COMPOUND	YIELD,[a] %	B.P., °C.	mm.	n_D^{20}
1-Phenyl-2-butene..................	23	48.5	4.0	1.5115
1-(2,5-Dimethylphenyl)-2-butene.....	54	72	2.6	1.5157
		26	0.10	
ortho(?)-Butenylphenol...............	8	93	4.3	
para(?)-Butenylphenol...............	26	108	4.1	
Butenyl-β-methylnaphthalene........	31	88–105	0.20	

[a] Based on butadiene.

melted at 69–69.5°. An approximately equal weight of uncrystallizable oil was recovered from the chloroform.

Ozonolysis. A baffled glass-reactor provided with a high-speed metal rotor was charged with 15 ml. of phenylbutene and 46 ml. of water. The reactor was cooled in ice, and had a suitable gas inlet and outlet; the outlet exhausted into ice-water. A controlled stream of ozone in excess oxygen was passed into the reactor for 4.2 hours, at which time traces of ozone began to come through the reactor. The product was removed, and was allowed to stand overnight. The dense colorless oil originally present crystallized to a mass of large, thin-bladed crystals. A sample crystal showed m.p. 90–100°; its identity was not determined (unstable to storage, non-acidic, not phenylacetaldehyde trimer). The entire mixture of crystals and water was steam-distilled according to the method of Harries (13) and yielded 6 ml. of a colorless, fragrant oil; 0.5 g. of resin; and a residual aqueous phase which was evaporated to 0.5 g. of solid acidic material having the odor of phenylacetic acid. Microdistillation of the 6 ml. of oily distillate was unsuccessful because of continual polymerization. A sample gave a negative benzaldehyde test with phenylhydrazine (6) but yielded a copious amount of a 2,4-dinitrophenylhydrazone, m.p. 121°. Literature values for the 2,4-dinitrophenylhydrazones of phenylacetaldehyde, benzaldehyde, and phenylpropionaldehyde are 121° (2), 237° (7), and 149° (7), respectively.

The volatile aldehydes from the ozonolysis were retained in the aqueous phase from the

steam-distillation and in a water trap. The gallic acid test (8) and the resorcinol test (8) were negative for formaldehyde. The Simons nitroprusside test (9) for acetaldehyde was strongly positive. Attempts to obtain semicarbazones or *p*-nitrophenylhydrazones from this distillate failed, probably because of the great dilution of the aldehydes (about 1:400, in water). The entire aqueous phase was therefore shaken with 30 ml. of ethyl mercaptan at 20° and was saturated with hydrogen chloride with cooling. An oil phase separated which on distillation gave 6 ml. of oil, b.p. 46–50° (2.2 mm.); estimated b.p. at 760 mm., 195°. Acetaldehyde diethylmercaptal is known to boil at 186° (760 mm.) (4). Only a trace of non-volatile bottoms was left from the distillation. The mercaptal was oxidized with acetic acid-hydrogen peroxide to the disulfone, m.p. 74°. Refluxing the disulfone with 20% aqueous potassium hydroxide and methyl iodide for four hours replaced the active hydrogen with a methyl group and gave acetone diethylmercaptal disulfone, m.p. 124.5°. The melting points reported for the acetaldehyde diethylmercaptal disulfone and its derivative, acetone diethylmercaptal disulfone, are 75° and 125° respectively (4). The melting points for the other possible aldehyde derivatives are: formaldehyde diethylmercaptal disulfone, m.p. 104°; propionaldehyde diethylmercaptal disulfone, m.p. 74°; and its methylated derivative, methyl ethyl ketone diethylmercaptal disulfone, m.p. 74° (4). (The volatile aldehyde was therefore acetaldehyde.)
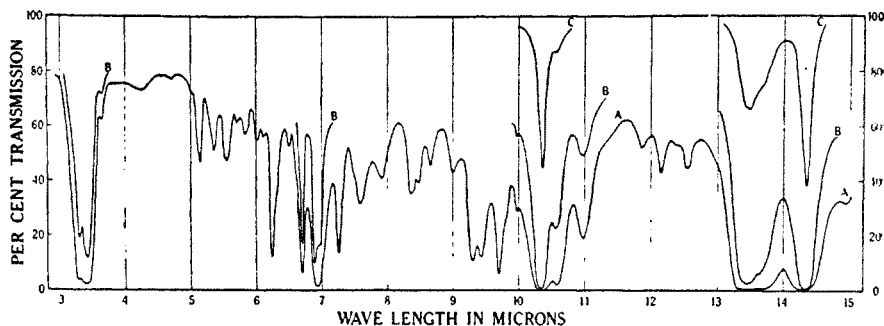

FIGURE 1. INFRARED SPECTRUM OF 1-PHENYL-2-BUTENE. A. 0.097-mm. cell; B. 0.028-mm. cell; C. 10% (Vol.) solution in carbon disulfide, 0.028-mm. cell.

Infrared analysis. A freshly distilled sample of phenylbutene was examined by infrared absorption with the results given in Figure 1. Strong bands at 13.4 μ and at 10.3 μ showed the presence of a phenylmethylene linkage and a —CH=CH— (probably *trans*) structure respectively. With the presence of large amounts of 1-phenyl-2-butene established, attention was directed to examining the spectrum for evidences of the possible impurities, 1-phenyl-3-butene and 1-phenyl-1-butene. No absorption was noted at 13.15 μ, a band characteristic of branching adjacent to the ring. A terminal double bond (position 3) would absorb at 11.0 μ but this band is masked by an aromatic band. A band at 10.0–10.05 μ which is also due to terminal double bonds, is partially masked by the strong 10.3 μ band; as no absorption was observed at 10.05 μ, it was concluded that the amount of any terminal-bond material is in the range of 0–5%, the uncertainty being due to the masking effect of the 10.3 μ band. No evidence was obtained as to the presence of 1-phenyl-1-butene.

DISCUSSION OF CHEMICAL AND PHYSICAL EVIDENCE OF PURITY

Bromination of the phenylbutene showed that it contained one double bond and that no paraffins (from hydrogen transfer) were present. The dibromide was dehydrohalogenated to give an unsaturated hydrocarbon, which was found not to be a primary acetylene. Since the dibromide of 1-phenyl-3-butene is known

to give a terminal acetylene (4, 12), the double bond cannot be in position 3. It is known that 1-phenyl-2-butene can be isomerized to 1-phenyl-1-butene by hot alcoholic alkali (3, 13). Long treatment of the present sample with alkali gave a fair yield of a high-refractive index phenylbutene, which was isolated by fractionation and brominated to give a solid dibromide, m.p. 69–69.5°. The isomerized olefin was therefore 1-phenyl-1-butene (14), and the initial material was 1-phenyl-2-butene.

Ozonolysis gave a mixture of phenylacetaldehyde and acetaldehyde, which are the expected products from the phenylbutene with the double bond in the 2 position. If 1-phenyl-1-butene or 1-phenyl-3-butene had been present, benzaldehyde and propionaldehyde, or phenylpropionaldehyde and formaldehyde, should have been formed. It was not possible to examine the phenylacetaldehyde for the presence of small amounts of benzaldehyde or phenylpropionaldehyde, as attempts to isolate these by precise fractional distillation led to polymerization of the phenylacetaldehyde. The total volatile aldehydes were therefore closely investigated for the presence of formaldehyde and propionaldehyde. Color tests indicated that neither was present. The entire aqueous solution of volatile aldehydes was treated with excess ethylmercaptan, and the distillation range of the recovered acetaldehyde diethylmercaptal showed that only one mercaptal was present, which was positively identified as the sulfone and, by alkylation, as the known acetone diethylmercaptal sulfone. The ozonolysis therefore gave no evidence for the presence of material other than 1-phenyl-2-butene.

Infrared examination indicates the substantial absence of 1-phenyl-3-butene, the presence of (trans)-1-phenyl-2-butene, and has no information on the presence of 1-phenyl-1-butene.

The combined physical and chemical evidence indicates the product is 1-phenyl-2-butene.

SUMMARY

Alkanesulfonic acids are effective catalysts for the alkenylation of the aromatic nucleus by butadiene. In the case of benzene, the monoalkenylated product is 1-phenyl-2-butene.

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