

and dried, 0.2 g. It was recrystallized three times from 400 parts of hot water from which it separated on cooling as microscopic crystals with m.p. 263–264° dec. and $[\alpha]^{20}_D -10.3^\circ$ (c 1, *N*-hydrochloric acid).

Anal. Calcd. for $C_{15}H_{22}N_2O_3$: C, 50.27; H, 6.19; N, 7.82. Found: C, 50.24; H, 6.10; N, 7.54.

D-lyxo-*D*-manno-Nonitol (*D*-arabino-*L*-galacto-Nonitol, III) from *D*-lyxo-*D*-manno-Nononic 1,4-Lactone (V).—To a stirred solution of 1 g. of lactone in 30 ml. of water, dropwise over a period of 1.5 hr. After an additional 1.5 hr. of stirring, 10 ml. of acetone was added dropwise to destroy the excess of borohydride. Sodium ions were removed by passage of the solution through a column of Amberlite IR-120 ion-exchange resin and the eluate was concentrated *in vacuo*. The crystalline residue was digested with hot methanol to extract the boric acid; the nearly insoluble nonitol, filtered and dried, weighed 0.80 g. and an additional 0.05 g. was recovered by a similar concentration of the methanolic filtrate (total yield 85%). The *D*-lyxo-*D*-manno-nonitol (III) was recrystallized twice from 50 parts of hot water, from which it separated as needles with m.p. 250–255°.

Anal. Calcd. for $C_9H_{20}O_9$: C, 39.70; H, 7.41. Found: C, 39.72; H, 7.35.

D-lyxo-*D*-manno-Nonitol Nonaacetate (III Nonaacetate).—A 220-mg. portion of the crystalline nonitol (III) derived from the lactone V was acetylated by heating with 150 ml. of acetic anhydride and 1 drop of concentrated sulfuric acid for 1 hr. on the steam bath. When poured onto ice the mixture yielded an oil that crystallized when kept overnight in the refrigerator. The product, filtered and washed with cold water and ethanol, weighed

343 mg.; an additional 55 mg. was obtained by concentration of the filtrate (total yield 76%). The nonaacetate, upon recrystallization from aqueous ethanol, gave prismatic needles of m.p. 149–150° (capillary) and $[\alpha]^{20}_D +27.3^\circ$ (c 2, chloroform). The melting point of a mixture of this nonaacetate with the one of m.p. 146.5–147.5° (hot stage) and $[\alpha]^{20}_D +27.8^\circ$ (c 2, chloroform) obtained from *D*-arabino-*L*-galacto-nononic 1,4-lactone, and a comparison of their infrared spectra showed the identity of the two nonitol nonaacetates. The very strong ester carbonyl absorption band appeared at 1755 cm^{-1} .

Anal. Calcd. for $C_{27}H_{38}O_{13}$: C, 49.85; H, 5.89; CH_3CO , 59.5. Found: C, 49.84; H, 6.03; CH_3CO , 59.4.

Acknowledgment.—The authors wish to thank Dr. William C. Alford and his associates of the Section on Microanalytical Services and Instrumentation, Laboratory of Chemistry, National Institute of Arthritis and Metabolic Diseases, for obtaining the infrared spectra and microanalyses; Professor David Lipkin of the Department of Chemistry, Washington University, St. Louis, Missouri, for furnishing us with additional samples from the collection of the late Professor John C. Sowden; and Professor Clinton E. Ballou of the Department of Biochemistry, University of California, Berkeley, California, for the samples of nononic lactone and phenylhydrazide prepared by Dr. Hagenbach.

Catalytic Carbanionic Addition of Butadiene to Alkyl Aromatic Hydrocarbons

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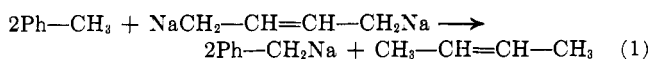
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Conditions and procedures are given for a catalytic 1:1 addition of butadiene to alkyl aromatic hydrocarbons using high-surface potassium or sodium metal on a calcium oxide support. The resulting product is the corresponding terminally substituted 2-pentene. These olefins can be cyclodehydrogenated to a number of specific substituted aromatic hydrocarbons.

The sodium-initiated polymerization of butadiene has been known for a long time.^{1,2} It has also been found that a similar reaction may be run in an autoclave using excess alkylbenzenes and various dienes (*e.g.*, butadiene) yielding a 1:1 adduct,³ and more recently the reaction has been extended to nitrogen-containing aromatics⁴ (*e.g.*, picoline). The work of Ziegler^{5,6} has shown that the mechanism of this reaction involves organosodium intermediates. It was further shown that well-defined organometallic compounds such as 2-phenyl-2-propylpotassium or benzylsodium can add butadiene in a stepwise fashion. More recently Robertson and Marion⁷ found that the sodium-initiated polymerization of butadiene in toluene leads to the formation of telomers of toluene and butadiene. These results were explained by a transmetalation reaction occurring from the growing polybutadiene chain (reaction 3) to toluene, with the formation of benzylsodium, which again is able to initiate a butadiene polymerization. The present work describes conditions under which a catalytic 1:1 addition of butadiene to alkyl aromatic hydrocarbons can

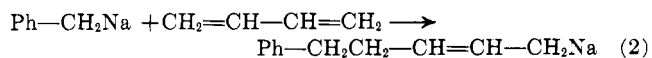
be achieved at high yields. The resulting aromatic olefins are intermediates in the synthesis of specific methyl-substituted naphthalenes *via* a cyclodehydrogenation reaction.

Metalation

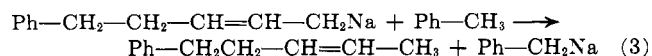


Equations 2 and 3 constitute the catalytic cycle.

Butadiene Addition

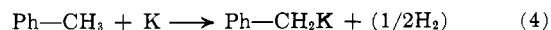


Transmetalation



Discussions and Results

The reaction with potassium metal as catalyst is suggested to involve analogous sequences; only the initial metalation of the alkylaromatic hydrocarbon can occur directly. The uncontrolled addition of butadiene



leads to its polymerization and telomerization, which suggests that reaction 2 is faster than the chain-transfer step 3. Then, an excess of the alkyl aromatic reactant

(1) C. Harries, *Ann.*, **363**, 157 (1911).

(2) F. E. Mathews and E. H. Strange, British Patent 24,790 (1910).

(3) F. Hofmann and A. Michael (to I. G. Farben, A.-G.), German Patent 557,514 (1928).

(4) R. Wegler and G. Pieper, *Ber.*, **83**, 6 (1950).

(5) K. Ziegler, F. Dersch, and H. Wolltham, *Ann.*, **511**, 13 (1934).

(6) K. Ziegler and L. Jacob, *ibid.*, **511**, 45 (1934).

(7) R. E. Robertson and L. Marion, *Can. J. Res.*, **26B**, 657 (1948).

TABLE I
ADDITION OF BUTADIENE TO *o*-XYLENE

Catalyst ^a	Temp., °C.	Flow ^c	Conversion, ^d %	Yield, ^e %
Na	105-110	9	10	50
Na	108-110	25	19	79
Na	115-120	46	25	72
K	108-111	42	31	90
K	115	49	48	59
K	30	16	10	40
K ^b	105	10	9	63

^a CaO support. ^b Na₂O support. ^c Grams of butadiene/hr./l. of *o*-xylene. ^d Based on *o*-xylene reacted. ^e Adduct (1:1) based on butadiene.

in conjunction with a controlled addition of the butadiene should yield a 1:1 addition product exclusively. Furthermore, a limited conversion of the alkyl aromatic substrate will avoid a secondary reaction of the product.⁴ These limiting factors determine the conditions of this catalytic process. Since the catalyst or the catalytic organometallic intermediate is essentially insoluble in the hydrocarbon medium, the use of a supported high-surface catalyst is desirable to increase the number of available catalyst sites. Finely powdered and freshly calcined calcium oxide was found to be a suitable catalyst support. The initiating step of the catalytic cycle is the formation of an organometallic compound; this is illustrated by eq. 4. The metalation of the alkyl aromatic hydrocarbon occurs directly when potassium is used, as shown by Morton,⁸ or, when sodium is used, it involves the intermediate formation of a butadiene-sodium adduct,⁵ which in turn can transmetalate to a benzylic position of the corresponding alkyl aromatic hydrocarbon. The driving force for this transmetalation step, which also takes place within the catalytic cycle,⁴ is the greater acidity of the benzylic hydrogen as compared to the hydrogen in the allylic position.

The product derived from the catalytic addition of butadiene to toluene was identified as 5-phenyl-2-pentene.⁹

Using *o*-xylene as a standard reactant (Table I), it was found that both sodium and potassium can catalytically react to produce a 1:1 adduct with butadiene. Potassium gives a faster and more selective reaction than sodium, and the potassium catalyst allows a somewhat greater conversion of the xylene without excessive formation of oligomers with butadiene. The olefins obtained from the catalytic reaction can be converted to the corresponding cyclodehydrogenation products by contact with an acidic alkylation catalyst.

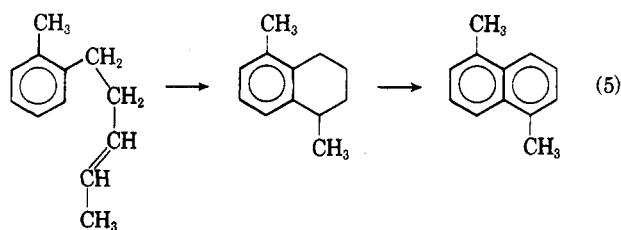


Table II shows the results and products obtained from the catalytic addition reaction of butadiene to various alkyl aromatic hydrocarbons. The conditions are specified in the Experimental section.

(8) A. A. Morton and C. E. Claff, *J. Org. Chem.*, **20**, 440, 981 (1955).

(9) E. Lenicki, H. Pines, and N. C. Sih, *Chem. Ind.* (London), 154 (1964).

Experimental^{10,11}

Catalyst.—Finely powdered calcium oxide was heated in an electric oven to 800° under a flow of dry nitrogen. Approximately 100 g. of the freshly calcined oxide was placed in a 1-l. flask, which was provided with a glass mechanical stirrer and arrangements for a slow nitrogen sweep. The flask was heated to about 150° and 2.5 g. of metal (potassium or sodium) was added. When the metal melted, rapid agitation was applied for 15 min. or until the oxide color changed to that of a uniform gray powder. Freshly prepared batches of catalyst in the weight proportions indicated here were used throughout all the experiments.

5-(*o*-Tolyl)-2-pentene.—To approximately 100 g. of a freshly prepared potassium catalyst was added 341 g. (3.22 moles) of *o*-xylene.¹¹ The contents of the flask were stirred at 108–111° under a nitrogen blanket for 30–60 min., at which time the catalyst slurry was a red-brown color. Then, at the same temperature, butadiene (52 g., 0.96 mole) was bubbled through the liquid phase over a period of 3 hr. The reaction was cooled to room temperature; the catalyst was destroyed with isopropyl alcohol; and the mixture was filtered. The solids were washed with *o*-xylene (two 100-ml. portions) and the washings were combined with the filtrate. The filtrate was washed with water, until neutral, and dried over calcium chloride. Distillation yielded 138 g. (90%) of 5-(*o*-tolyl)-2-pentene, b.p. 93–98° (10 mm.). A gas chromatographic analysis resolved the product into equivalent amounts of its *cis* and *trans* isomers.

1,5-Dimethylnaphthalene.—A solution of 7.5 g. (0.047 mole) of 5-(*o*-tolyl)-2-pentene in 30 ml. of pentane was placed in a 65-mole Hoke bomb. To this solution was added 20 g. (1.0 mole) of anhydrous hydrogen fluoride, and the mixture was shaken for 30 min. at room temperature. The neutralization with bicarbonate yielded 7.4 g. of a crude product. This crude product was refluxed with 2.8 g. of palladium on carbon (10%) for 8 hr. under a nitrogen blanket. The product was a light yellow solid, which after one crystallization yielded 5.2 g. of 1,5-dimethylnaphthalene, m.p. 81–82° (lit.¹² m.p. 81.5°). Its infrared spectrum was identical with that of an authentic sample,¹³ and a mixture melting point gave no depression.

5-Phenyl-2-pentene.—Butadiene (55.6 g., 1.03 moles) was bubbled through a mixture of a potassium catalyst and toluene¹¹ (347 g., 3.8 moles) over a period of 6.5 hr. at a temperature of 91–93°. Distillation, after work-up, gave 120 g. (80%) of 5-phenyl-2-pentene, b.p. 199–201° (lit.¹⁰ 84.5–85.0 at 13–14 mm.). The infrared spectrum gave characteristic peaks at 5.98, 6.06, 7.09, and 10.31 μ . A low-voltage mass spectrum gave mass 146 as the major peak. A mass spectrum of the distillation residues gave mass 200 as a major peak. An n.m.r. spectrum of this olefin showed a singlet at 2.90, and multiplets at τ 4.5–4.7, 7.2–7.5, 7.5–8.0, and 8.3–8.5 with relative areas of 5:2:2:2:3, respectively, assigned to the aromatic, vinyl (C-2,3), α -methylene (C-5), β -methylene (C-4), and methyl protons.

5-(*p*-Tolyl)-2-pentene.—Butadiene (41.7 g., 0.77 mole) was added to a mixture of a potassium catalyst and *p*-xylene¹¹ (290 g., 273 moles) over a period of 4 hr. at 104–111°. Distillation gave 112 g. (91%) of 5-(*p*-tolyl)-2-pentene, b.p. 108–112° (10 mm.). The infrared spectrum gave characteristic peaks at 6.00, 6.08, 7.11, and 11.33 μ , with substitution bands at 8.33, 8.94, 9.60, 9.76, and 12.33 μ .

1,7-Dimethylnaphthalene.—A sample of 5-(*p*-tolyl)-2-pentene was cyclized and dehydrogenated as in the preparation of 1,5-dimethylnaphthalene (above). The product was a viscous oil. The picrate of this material had m.p. 116–118° (lit.¹¹ m.p. 118.5°). The infrared spectrum was identical with that of an authentic sample.¹³

5-Phenyl-2-hexene.—Butadiene (51.4 g., 0.95 mole) was added to a mixture of a potassium catalyst and ethylbenzene¹¹

(10) All melting points are corrected. All boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer spectrophotometer Model 137-B. N.m.r. spectra were determined on a Varian A-60 analytical spectrometer in carbon tetrachloride solutions. All spectra refer to tetramethylsilane as an internal standard. Gas phase analyses were done using an Aerograph gas chromatograph Model A-600 with a hydrogen flame ionization detector (Wilkins Instrument and Research, Inc.) using a 5-ft. silicone column.

(11) All liquid substrates were distilled from sodium and stored over Linde Molecular Sieve type 5-A pellets.

(12) A. S. Bailey, K. C. Bryant, R. A. Hancock, S. H. Morrell, and J. C. Smith, *J. Inst. Petrol.*, **33**, 503 (1947).

(13) Authentic samples kindly supplied by Dr. G. Suld, these laboratories.

TABLE II
ADDITION OF BUTADIENE TO ALKYL AROMATIC HYDROCARBONS^a

Alkyl aromatic	Addition product (1:1)	Yield, ^b %	B.p., °C. (mm.)	Cyclodehydrogenation product	M.p., °C.
Toluene	5-Phenyl-2-pentene	80	199-201 ^c	1-Methylnaphthalene	Liq.
<i>o</i> -Xylene	5-(<i>o</i> -Tolyl)-2-pentene	90	223-225	1,5-Dimethylnaphthalene	81-82
<i>p</i> -Xylene	5-(<i>p</i> -Tolyl)-2-pentene	91	108-112 (10)	1,7-Dimethylnaphthalene	116-118 ^d
Ethylbenzene	5-Phenyl-2-hexene	87	71-74 (1)	1,4-Dimethylnaphthalene	142-143 ^d
Durene	5-(2,4,5-Trimethylphenyl)-2-pentene	35	80-83 (1)
2-Methylnaphthalene	5-(2-Naphthyl)-2-pentene	19	123-137 (3)

^a Potassium (2.5 g.) on CaO (100 g.) support. ^b Based on butadiene used. ^c W. C. Warner and J. R. Shelton [*Ind. Eng. Chem.*, **43**, 1160 (1951)] give b.p. 84.5-85.0° (13 mm.). ^d Picrate. ^e See Experimental.

(185 g., 1.74 moles) over a period of 3 hr. at 108-110°. Distillation gave 132 g. (87%) of 5-phenyl-2-hexene, b.p. 71-74° (1 mm.). A gas chromatographic analysis resolved the product into equivalent amounts of its *cis* and *trans* isomers. An n.m.r. spectrum of this olefin showed a singlet at τ 2.88, multiplets at 4.5-4.8, 7.6-8.0, 8.35, 8.60, a sextet at 7.27 ($J = 6.5$ c.p.s.), and a doublet at 8.79 ($J = 6.5$ c.p.s.), with relative areas of 5:2:2:3:1:3, respectively, assigned to the aromatic, vinyl (C-2,3), β -methylene (C-4), methyl (C-1), α -hydrogen (C-5), and α -methyl protons.

1,4-Dimethylnaphthalene.—A sample of 5-phenyl-2-hexene was cyclized and dehydrogenated¹⁴ as in the preparation of 1,5-dimethylnaphthalene (above). The product was a yellow oil which was purified by elution chromatography over activated alumina. The picrate had m.p. 142-143° (lit.¹² m.p. 143°).

5-(2,4,5-Trimethylphenyl)-2-pentene.—Butadiene (29 g., 0.54 mole) was bubbled through a mixture of a potassium catalyst and 133 g. of durene (m.p. 79.5-80.0°) over a period of 2.5 hr. at a temperature of 155-125°. A liquid product (10 g.) was collected in the cold trap during the reaction, and it was found to be almost entirely butadiene. Distillation, after work-up, yielded 25 g. (35%) of 5-(2,4,5-trimethylphenyl)-2-pentene, b.p. 80-83° at 1 mm. A gas chromatographic analysis of the distillation product showed 5% durene in addition to the *cis* and *trans* isomers. A low-voltage mass spectrum gave mass 188 as the major peak; mass 242 was the major peak in the distillation residue (10.3 g.). The infrared spectrum of the product gave the characteristic olefin peaks at 6.00, 6.07, 7.10, and 10.32 μ , with substitution bands at 8.30, 9.07, 9.76, and 11.45 μ . The n.m.r.

(14) After 4 hr. the dehydrogenation reaction was sampled and it was found to contain 26% (calculated by v.p.c. area method) of 5,8-dimethyl-1,2,3,4-tetrahydronaphthalene. Its structure was determined by a collection of a vapor phase chromatographic cut and comparison of its infrared spectrum with an authentic sample.³ At the end of another 4 hr. this compound was no longer present.

spectrum of this olefin showed a broad singlet at τ 7.88, and multiplets at 3.17-3.3, 4.45-4.7, 7.25-7.66, and 8.3-8.5, with relative areas of 11:2:2:2:3, respectively, assigned to three aromatic methyl plus β -methylene (C-4), aromatic, vinyl (C-2,3), α -methylene (C-5), and methyl (C-1) protons. The areas of the broad singlet and a multiplet at its base [τ 7.66-8.1, assigned to β -methylene (C-4)] were added together because of overlapping.

5-(2-Naphthyl)-2-pentene.—Butadiene (32.3 g., 0.60 mole) was bubbled through a mixture of sodium catalyst and 229 g. (1.61 moles) of 2-methylnaphthalene (m.p. 34.5-35.0°) over a period of 3 hr. at a temperature of 124-130°. During the course of the reaction 16.3 g. of a liquid product consisting of mostly butadiene was collected in a cold trap. Distillation, after work-up, gave 11 g. (19%) of 5-(2-naphthyl)-2-pentene,¹⁵ b.p. 123-137° at 1-3 mm. A low-voltage mass spectrum gave mass 196 as the major peak. A vapor phase chromatograph showed a trace of 2-methylnaphthalene together with the *cis* and *trans* isomers. The infrared spectra gave the characteristic olefin peaks at 6.00, 6.10, 7.11, and 10.31 μ . The n.m.r. spectrum of this olefin showed multiplets at τ 2.2-3.0, 4.4-4.7, 7.1-7.42, 7.42-7.9, and 8.30-8.55, with relative areas of 7:2:2:3, respectively, assigned to aromatic, vinyl (C-2,3), α -methylene (C-5), β -methylene (C-4), and methyl (C-1) protons.

Acknowledgment.—We would like to thank R. L. Urban for running the reactions using hydrogen fluoride, D. S. Baugher for the mass spectral results, H. C. Williams for the n.m.r. spectra, and D. L. Kerr for the infrared spectra and help in the experimental work. The authors wish to thank the Sun Oil Company for permission to publish these results.

(15) A similar experiment using 3.5 g. of potassium supported on 58 g. of sodium oxide gave a 23% of product.

Use of Alkene Chloronium Intermediates in Organic Synthesis. Two New Reactions of Alkene Chloronium Ions

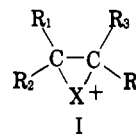
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A number of new chlorinated esters and ethers and one new amide have been prepared utilizing "three-component reactions" involving an olefin, chlorine, and a third material capable of reacting with the intermediate chloronium ion. Two hitherto unreported reactions of alkene chloronium ions were noted and investigated. They were (1) cleavage of the ether linkage, and (2) substitution of the benzene nucleus.

Roberts and Kimball² postulated a positively charged cyclic halonium intermediate (I) to explain the products obtained from a variety of chlorination and bromination reactions of ethylene compounds. Lucas and Gould,³ in a classical paper on chlorohydrin formation



and reactions, gave convincing evidence to support the existence of such an intermediate in these and related

(1) To whom inquiries should be directed at Southern Regional Research Laboratory, P. O. Box 19687, New Orleans, La. 70119.

(2) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937); see also S. Winstein and H. J. Lucas, *ibid.*, **61**, 2845 (1939).

(3) H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).