2-Bromo-1-phenoxy-1-propene.—2-Bromo-1-phenoxy-1-propene was prepared by the reaction between potassium phenoxide and *trans*-1,2-dibromo-1-propene. A mixture of the *cis* and *trans* isomers of 1,2-dibromo-1-propene (from Columbia Organic Chemicals) was distilled through a three-foot, glass-helix packed column at 28 mm. The fraction boiling at 38.0–39.5° was collected as the *trans* isomer, lit.[5] b.p. 40.9° (28 mm.).

One hundred twenty grams (0.91 mole) of potassium phenoxide in 350 ml. of methanol and 214 g. (1.15 moles) of *trans*-1,2-dibromo-1-propene were placed in a glass container in a 2-liter stainless steel pressure reactor. The reactor and its contents were heated to 95° over a period of six hours. This temperature was maintained for 24 hours, after which time the reactor was allowed to cool to room temperature overnight.

The reactor was opened cautiously because of the possibility of the formation of flammable 1-bromo-1-propyne[6] from the dehydrobromination of the *trans*-1,2-dibromo-1-propene. Apparently an appreciable quantity was formed. The reaction mixture was steam distilled. A colorless oil was separated and the water layer was continuously extracted with ether for 24 hours. The organic layers were combined, washed with 20% potassium hydroxide solution to remove the phenol, with water, and then placed over magnesium sulfate.

Fractional distillation under nitrogen gave 107 g. of *trans*-1,2-dibromo-1-propene and 9.0 g. of 2-bromo-1-phenoxy-1-propene boiling at 72.5–73.0° (1 mm.). This represents a 50% conversion with a 7.5% yield. A center cut of this product had the following physical constants: b.p. 72.5–73.0° (1 mm.), $n^{20}D$ 1.5556, $n^{25}D$ 1.5540, $n^{30}D$ 1.5521; d^{20}_4 1.3871, d^{25}_4 1.3821, d^{30}_4 1.3771; MR_D obsd. 49.10, MR_D calcd. 49.35.

Anal. Calcd. for C_9H_9OBr: Br, 38.97. Found: Br, 38.83, 38.91.

Phenoxypropadiene.—Phenoxypropadiene was prepared by the dehydrobromination of 2-bromo-1-phenoxy-1-propene using powdered potassium hydroxide. Forty grams (0.71 mole) of powdered potassium hydroxide was placed in a 125-ml. Claisen flask and heated to 50° in an oil-bath. Eighteen grams (0.085 mole) of 2-bromo-1-phenoxy-1-propene was added to the hot alkali, the pressure lowered to 17 mm., the flask heated rapidly. A vigorous reaction occurred at 90° and the product distilled over rapidly. The product was collected in a receiver immersed in Dry Ice. The crude phenoxypropadiene was dried in ether over sodium sulfate. Fractional distillation under nitrogen gave 5.5 g. (50% yield) of phenoxypropadiene boiling at 45.5–46.5° (2 mm.). The physical constants are in Table I.

Anal. Calcd. for C_9H_8O: C, 81.79; H, 6.11. Found: C, 81.39; H, 5.91.

Infrared Spectra.—The infrared spectra of 2-bromo-1-phenoxy-1-propene, methylphenoxyacetylene and phenoxypropadiene were obtained through the courtesy of William F. Hamner and the Monsanto Chemical Co., Texas City, Texas. A Baird Associates double-beam recording infrared spectrophotometer equipped with sodium chloride optics was used. The cell thickness was 0.025 mm. The infrared spectra of methylphenoxyacetylene and phenoxypropadiene are given in Fig. 1.

The following are the principal wave lengths in microns for 2-bromo-1-phenoxy-1-propene (w = weak, vw = very weak, m = medium, s = strong, vs = very strong): 3.31 m, 3.51 w, 5.20 vw, 6.12 m, 6.28 s, 6.73 s, 6.92 w, 7.28 m, 7.92 w, 8.24 vs, 8.61 s, 8.78 m, 9.32 m, 9.61 s, 9.80 w, 10.1 vw, 10.39 w, 10.95 s, 11.20 m, 12.05 w, 12.78 w, 13.27 s, 14.56 m.

Austin 12, Texas

(5) H. A. Smith and L. E. Line, This Journal, **72**, 5434 (1950).

(6) L. F. Hatch and L. E. Kidwell, *ibid.*, **76**, 289 (1954).

[Contribution from the Chemical Laboratories of the University of Maryland]

The Chemistry of 1,3,5-Hexatriene

By G. F. Woods, N. C. Bolgiano and D. E. Duggan

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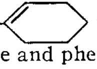
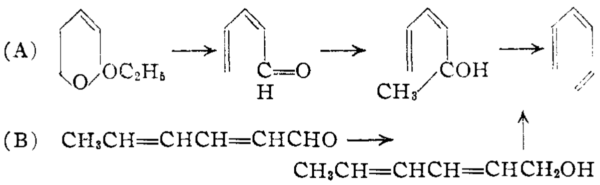
1,3,5-Hexatriene has been obtained by the catalytic dehydration of 2,4-hexadien-1-ol which was prepared by reduction of 2,4-hexadienal with lithium aluminum hydride. Nitrohexatriene was prepared by the nitration of hexatriene. 1,2,3-Benzenetricarboxylic acid was readily synthesized from the Diels–Alder adduct of maleic anhydride and hexatriene. When 1-phenyl-1,3,5-hexatriene was passed over alumina at 350°, it underwent cyclization to yield a phenylcyclohexadiene. This type of cyclization occurs with —CH=CH— which yielded phenanthrene after dehydrogenation; in like manner 2,4-hexadienal and sorbic acid yielded benzene and phenol, respectively.

Earlier syntheses of 1,3,5-hexatriene[1] have involved difficultly available substances. 2,4-Hexadienal,[2] a more convenient starting material, was reduced to the conjugate unsaturated alcohol with lithium aluminum hydride and catalytic dehydration of the alcohol with alumina afforded 1,3,5-hexatriene in excellent yield. The properties of the intermediate, 2,4-hexadien-1-ol, correspond closely with those reported by Reichstein and co-workers.[3] The wide variations reported for the physica constants of 1,3,5-hexatriene[1] could be attributed to either geometrical isomerism or to the identity or purity of the sample. We favor the latter explanation since the same hexatriene is obtained from both 2,4-hexadien-1-ol and 1,3-hexadien-5-ol as



The fact that the same hexatriene is obtained by both A and B indicates that one geometrical isomer is favored; but it is not argued that the *cis* configuration is maintained in A since dehydration over alumina could cause isomerization.

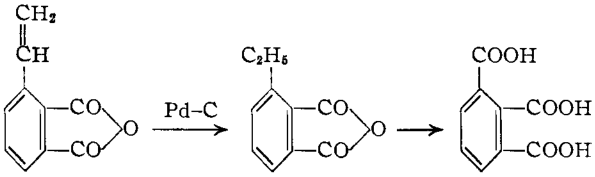
To compare the stability of hexatriene, samples of which have been stored at room temperature with no special precautions and with no discernible polymerization, with that of benzene, nitration of the former was studied. The sulfuric acid–nitric acid method is too drastic, but a 5–10% yield of a nitrohexatriene can be obtained by nitration with acetic acid–nitric acid.

(1) G. F. Woods and L. H. Schwartzman, This Journal, **70**, 3394 (1948).

(2) Kindly provided by Carbide and Carbon Chemicals Co., New York, N. Y.

(3) T. Reichstein, C. Ammann and G. Trivelli, *Helv. Chim. Acta*, **15**, 264 (1932).

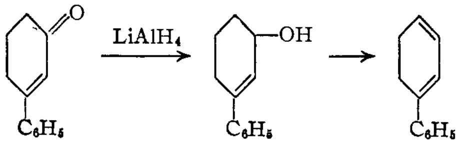
1,2,3-Benzenetricarboxylic acid was synthesized *via* the Diels–Alder adduct of hexatriene with maleic anhydride[1,4] as



I II III

The properties of II and III compare favorably with those reported by Parker and Goldblatt.[5]

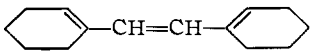
The reaction of phenylmagnesium bromide with 2,4-hexadienal yielded 1-phenyl-2,4-hexadien-1-ol and this substance was isomerized to 1-phenyl-1,3-hexadien-5-ol.[6] Catalytic dehydration of either alcohol with alumina below 300° yielded 1-phenyl-1,3,5-hexatriene (m.p. 55°) which was catalytically hydrogenated to 1-phenylhexane; dehydration of either alcohol above 300° and below 350° yielded a mixture of changing composition; dehydration at 350° yielded an isomeric substance ($C_{12}H_{12}$), m.p. 83–85°. The 85° isomer also was obtained by the passage of 1-phenyl-1,3,5-hexatriene over alumina at 350°. This substance was at first mistakenly assumed to be a geometrical isomer of 1-phenyl-1,3,5-hexatriene. However, its hydrogen uptake under catalytic conditions was erratic and always less than one-half of the calculated three-mole uptake; isolation of the products yielded biphenyl and phenylcyclohexane. This behavior is indicative of a phenylcyclohexadiene undergoing disproportionation under the conditions of catalytic hydrogenation. Apparently at higher temperatures the hexatrienyl portion of phenylhexatriene undergoes cyclization to a cyclohexadiene. This was proved by the following synthesis of the same phenylcyclohexadiene, m.p. 85°.



IV V VI

The structure of V was confirmed by its reduction to 3-phenylcyclohexanol[7] which was oxidized to 3-phenylcyclohexanone; the latter and its derivatives were compared with the corresponding substances obtained by the catalytic reduction of the ethylenic link of 3-phenyl-2-cyclohexanone (IV). The phenylcyclohexadiene obtained by dehydration of V over alumina at 350° is assumed to be VI but isomerization of the unsaturation could occur under these conditions. In an attempt to prepare 2-phenyl-1,3-cyclohexadiene, 2-cyclohexenone was treated with phenylmagnesium bromide. The expected alcohol, 1-phenyl-2-cyclohexen-1-ol, was not obtained; instead an allylic rearrangement took place to give V.

This ring closure of phenylhexatriene is not unique. It was found that the triene



underwent cyclization with aromatization when heated at 350° in the presence of palladinized charcoal to yield phenanthrene; 2,4-hexadienal and sorbic acid cyclize to benzene and phenol, respectively, upon passage over alumina at 350–400°.

Experimental

2,4-Hexadien-1-ol.—To a mixture of lithium aluminum hydride (17 g., 0.5 mole) and 500 ml. of ether in an ice–salt-bath was added with stirring 60 g. of freshly distilled 2,4-hexadienal,[2] a pale yellow liquid (b.p. 55–57° (15 mm.), n^{25}D 1.5288) in 300 ml. of ether. The aldehyde solution was added at such a rate that the temperature of the mixture was maintained below 0°, generally at −5°; approximately 1 hour was required. The solution was stirred for an additional 15 minutes, then decomposed with 5% sulfuric acid and the ether layer removed. The aqueous layer was twice extracted with ether. The combined extract was washed with sodium carbonate solution and dried with magnesium sulfate. After removal of the solvent, the product was distilled under nitrogen to yield 55 g. (85%) of 2,4-hexadien-1-ol, b.p. 48–50° (5 mm.), n^{30}D 1.4980; recrystallized from petroleum ether (60–80°) it melted at 29°.

Anal. Calcd. for $C_6H_{10}O$: C, 73.49; H, 10.20. Found: C, 73.55; H, 10.19.

The 3,5-dinitrobenzoate of 2,4-hexadien-1-ol was prepared in the usual manner and recrystallized from petroleum ether (60–80°), m.p. 85°.

Anal. Calcd. for $C_{13}H_{12}O_6N_2$: C, 53.41; H, 4.14. Found: C, 53.37; H, 4.20.

The melting points of the alcohol and the derivative check well with those reported by Reichstein and coworkers.[3]

1,3,5-Hexatriene.—One mole (98 g.) of 2,4-hexadien-1-ol was distilled under reduced pressure in a nitrogen atmosphere through a column packed with 8–12 mesh activated alumina and heated to 300–320°; the receiver was cooled with Dry Ice. The product was melted and most of the water removed with an eye-dropper. Distillation of the dried (calcium oxide) material yielded 55 g. (68%) of 1,3,5-hexatriene, b.p. 79–80°, n^{25}D 1.5025. Passage of this substance through a small column packed with 80–200 mesh alumina removed a small amount of colorless material which gave a very dark brown adsorption band. The hexatriene thus obtained is identical with that previously prepared by the dehydration of 3,5-hexadien-2-ol.[1]

Nitration of 1,3,5-Hexatriene.—When small amounts of hexatriene were added to a sulfuric–nitric acid mixture a white polymer appeared almost instantaneously over the surface of the nitrating medium; shortly afterward carbonization was observed.

To a solution of hexatriene (5 g.), acetic acid (60 ml.) and acetic anhydride (30 ml.) was added dropwise with stirring 4.1 g. of nitric acid, prepared from potassium nitrate and sulfuric acid. The temperature was maintained below 40°. After the solution had stood at room temperature for 12–15 hours, it was added dropwise into a pot from which steam distillation was in progress. The pale yellow distillate was extracted with ether; sodium chloride was used for salting out. The extract was washed with sodium bicarbonate and dried with magnesium sulfate. The ether was removed and the residue distilled at reduced pressure in a nitrogen atmosphere to yield yellow nitrohexatriene, yield 1 g., b.p. 60–70° (6 mm.), n^{25}D 1.5534. This unstable material polymerizes rapidly. The ultraviolet absorption spectrum of nitrohexatriene in ethanol has no fine structure (ϵ_{max} (305 mμ) 8 × 10^3) and is very similar to that of nitrobenzene but is shifted considerably toward the red.

Anal. Calcd. for $C_6H_7NO_2$: C, 57.60; H, 5.60. Found: C, 56.51; H, 5.84.

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(4) E. H. Farmer and F. L. Warren, *J. Chem. Soc.*, 908 (1929).

(5) E. D. Parker and L. A. Goldblatt, THIS JOURNAL, **72**, 2151 (1950).

(6) H. C. Barany, E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2094 (1951), had prepared these alcohols by the same method and obtained 1-phenyl-1,3,5-hexatriene by the dehydration of 1-phenyl-2,4-hexadien-1-ol with potassium acid sulfate.

(7) R. L. Frank and R. W. Meikle, THIS JOURNAL, **72**, 4184 (1950); A. J. Boyd, P. H. Clifford and M. E. Probert, *J. Chem. Soc.*, **117**, 1383 (1920).

If the nitration medium is poured into water, extracted with ether and worked up in the usual manner, attempted distillation leads to a violent explosion.

Hydrogenation with Adams catalyst of 1 g. of this material in 100 ml. of ethanol–water absorbed 1312 ml. of hydrogen; calculated for the reduction of 3 ethylenic links and one nitro group: 1180 ml.

1,2,3-Benzenetricarboxylic Acid.—The Diels–Alder product, 3-vinyl-1,2,3,6-tetrahydrophthalic anhydride[1] obtained in 60% yield, was hydrolyzed in dilute base and the mixture acidified to yield the corresponding vinyltetrahydrophthalic acid which was recrystallized from water, m.p. 158–159°.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.40; H, 6.07.

3-Vinyl-1,2,3,6-tetrahydrophthalic anhydride was heated at 300° with 10% palladinized carbon until hydrogen evolution ceased; distillation yielded 3-ethylphthalic (35% yield) anhydride which was recrystallized from petroleum ether (100–120°), m.p. 96–98°, reported[5] m.p. 101–102°.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.18; H, 4.59. Found: C, 68.49; H, 4.45.

3-Ethylphthalic acid was obtained by treatment of the anhydride with dilute sodium hydroxide followed by acidification with hydrochloric acid. It was recrystallized from water–hydrochloric acid; m.p. 171–172°, reported[5] m.p. 172°.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 62.15; H, 5.13.

3-Ethylphthalic anhydride (5.1 g. in 200 ml. of water containing 3 g. of potassium hydroxide) was oxidized with 24 g. of potassium permanganate which was added gradually over eight hours with stirring, the temperature was held below 45° for the first 12 hours and then raised to 80° for a short period. After the aqueous medium had been worked up in the usual manner it was continuously extracted with ether. Evaporation of the ether yielded 4.4 g. (62%) of 1,2,3-benzenecarboxylic acid which, after recrystallization from dioxane-benzene, melted at 190°, the trimethyl ester melted at 98–100°, reported[8] m.p. 98–100°.

Anal. Calcd. for $C_{12}H_{12}O_6$: C, 57.14; H, 4.80. Found: C, 57.53; H, 4.67.

1-Phenyl-1,3,5-hexatriene.—Hexadienal reacted with phenylmagnesium bromide to yield 1-phenyl-2,4-hexadien-1-ol (A), part of which was then isomerized to 1-phenyl-1,3-hexadien-5-ol (B).[6] Alcohol A is noticeably unstable in air and rapidly degenerates from a crystalline structure into a yellow viscous mass with the development of strong aldehyde odor. Distillation of the yellow material under reduced pressure afforded 5-phenyl-2,4-pentadienal, semicarbazone m.p. 220° dec., reported m.p. 218–219°.[9]

Anal. Calcd. for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09. Found: C, 66.85; H, 6.16.

The 2,4-dinitrophenylhydrazone, m.p. 194–196°, also was prepared.

Anal. Calcd. for $C_{17}H_{14}N_4O_4$: C, 60.35; H, 4.17. Found: C, 59.69; H, 4.24.

Silver oxide oxidation of the aldehyde gave 5-phenyl-2,4-pentadienoic acid, m.p. 164–165°, reported[9] m.p. 164–164.6°. This behavior of A in air apparently parallels that of 1-phenyl-2,4-pentadien-1-ol which decomposes to cinnamaldehyde under similar conditions.[10]

To ascertain their structure, the two alcohols A and B were hydrogenated and the saturated alcohols oxidized to caprophenone and 1-phenyl-5-hexanone, respectively. The former ketone and its semicarbazone were identical with authentic samples; the latter gave a semicarbazone and a positive iodoform test. Catalytic dehydration over alumina of either alcohol, A or B, at 275° yielded 1-phenyl-1,3,5-hexatriene corresponding exactly with that reported.[6] Passage of either alcohol or of the phenylhexatriene over the alumina bed at 350° provided phenylcyclohexadiene, probably 1-phenyl-1,3-cyclohexadiene, the ultraviolet absorption spectrum of which $\epsilon_{\max}$ (248 mμ) 9 × 10^3 (ethanol) is very similar in shape to that of biphenyl. The yield of phenylcyclohexadiene from A and B was 30 to 50% and from phenylhexatriene 60%. After several recrystallizations (with difficulty) from petroleum ether (30–40°), phenylcyclohexadiene, m.p. 85°, was obtained.

Anal. Calcd. for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 92.40; H, 7.79.

The results of hydrogenation of phenylcyclohexadiene were erratic, but on the hydrogenation of a large quantity in ethanol with 10% palladinized charcoal, biphenyl and phenylcyclohexane were isolated by careful fractional distillation. Biphenyl was identified by its mixed melting point with an authentic sample and phenylcyclohexane by its refractive index.

3-Phenyl-2-cyclohexen-1-ol.—3-Phenyl-2-cyclohexenone[11] (26 g.) was reduced with lithium aluminum hydride at a temperature below 0°. The product was worked up in the usual manner to yield 19 g. of 3-phenyl-2-cyclohexen-1-ol (V), m.p. 60–61° after recrystallization from petroleum ether (100–120°).

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.76; H, 8.10. Found: C, 82.93; H, 8.20.

V also was obtained by the reaction of phenylmagnesium bromide with 2-cyclohexenone. The Grignard addition complex was poured onto ammonium chloride–ice and the biphenyl removed by steam distillation.

3-Phenyl-2-cyclohexenol (V) was catalytically hydrogenated with palladinized charcoal in ethanol to give 3-phenylcyclohexanol which was recrystallized from petroleum ether (30–40°), m.p. 78–80°.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 82.01; H, 8.94.

Only one melting point[7] is given in the literature for 3-phenylcyclohexanol and no second form is mentioned. 3-Phenylcyclohexanol was oxidized with potassium dichromate to 3-phenylcyclohexanone, which formed both a semicarbazone and a 2,4-dinitrophenylhydrazone, m.p. 167–169° and m.p. 169–171°, respectively; these derivatives were identical with authentic samples.[10]

Dehydration of 3-phenyl-2-cyclohexenol over alumina provided a phenylcyclohexadiene, m.p. 85° after recrystallization from petroleum ether (30–40°), which was identical with the $C_{12}H_{12}$ compound obtained from either of the phenylhexadienols or phenylhexatriene by dehydration at 350°.

Phenanthrene.—Di-(1-hydroxycyclohexyl)-acetylene[12] was hydrogenated with Raney nickel until a molar equivalent of hydrogen had been absorbed. The ethanolic solution was concentrated and the resulting 1,2-di-(1-hydroxycyclohexyl)-ethylene was recrystallized from absolute ethanol, m.p. 147–148°, reported[13] m.p. 150–151°.

Anal. Calcd. for $C_{14}H_{24}O_2$: C, 72.95; H, 10.78. Found: C, 75.14; H, 10.73.

Vapor of this material (30 g., 0.13 mole) was passed at reduced pressure over alumina at 325–350°. The dried product was distilled under nitrogen to yield 15 g. (60%) of 1,2-di-(1-cyclohexenyl)-ethylene, b.p. 105° (0.2 mm.), reported[14] b.p. 110–115° (1 mm.).

Anal. Calcd. for $C_{14}H_{20}$: C, 89.30; H, 10.70. Found: C, 89.39; H, 10.66.

Five grams of 1,2-di-(1-cyclohexenyl)-ethylene and 0.1 g. of 10% palladinized charcoal in a 200-ml. flask was heated under reflux conditions until the evolution of hydrogen ceased. Distillation of the product gave a viscous oil which solidified in the receiver and was recrystallized from ethanol, m.p. 97–99°, admixture with an authentic sample of phenanthrene (m.p. 97–101°) gave no depression of m.p.

Anal. Calcd. for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.63; H, 5.83.

Conversion of 2,4-Hexadienal to Benzene; Sorbic Acid to Phenol.—2,4-Hexadienal was dehydrated over alumina at 350–400° and the product washed with cold concentrated sulfuric acid and distilled. Benzene was identified as the *o*-benzoylbenzoic acid derivative (m.p. 127°) which was identical with an authentic sample.

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[8] K. Alder, K. Heimbach and R. Kuhle, *Ber.*, **86**, 1364 (1953).

[9] E. T. Clapperton and W. S. MacGregor, This Journal, **72**, 2501 (1950)

[10] G. F. Woods and H. Sanders *ibid.*, **69**, 2926 (1947).

[11] G. F. Woods and I. W. Tucker, *ibid.*, **70**, 2176 (1948).

[12] *Organic Syntheses*, **32**, 70 (1952).

[13] J. D. Chanley, This Journal, **71**, 829 (1949).

[14] G. N. Burkhardt and N. C. Hindley, *J. Chem. Soc.*, 987 (1938).

Sorbic acid prepared by the silver oxide oxidation of 2,4-hexadienal was dehydrated over alumina at 440–450° to give phenol which was identified as the tribromo derivative (m.p. 93–94°) prepared in the usual manner; with admixture an authentic sample gave no depression of m.p.

COLLEGE PARK, MD.

[CONTRIBUTION FROM RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Effect of Acid Strength on Alkylation of Arenes with Olefins. I. *m*-Xylene with Ethylene

BY D. A. MCCAULAY AND A. P. LIEN

RECEIVED OCTOBER 4, 1954

m-Xylene, when alkylated with equimolar amounts of ethylene, gives product distributions that depend upon the acid strength of the catalyst. Hydrogen fluoride alone—a typical alkylation catalyst—forms predominantly polyethylxylenes. Hydrogen fluoride plus excess boron trifluoride—a much stronger acid—produces predominantly 1,3,5-ethylxylene along with relatively small amounts of polyethylxylenes. This difference is explained by the hypothesis that the stronger acid isomerizes the first-formed 1,3,4-ethylxylene into the 1,3,5-isomer. The latter, because it is much more basic than the other ethylxylenes, preferentially forms a positively charged σ-complex with the strong acid. This cation repels the incoming positively charged ethyl group, which must then react with uncomplexed *m*-xylene. Alkylation with strong acids can thus produce high yields of single isomers.

The rate of alkylation of arenes with olefins generally increases with the number of alkyl substituents in the ring.[1,2] In alkylation processes, therefore, high ratios of arene to olefin are used whenever high yields of a monoalkylated product are desired. Recent work on the disproportionation of alkylbenzenes[3] suggested that high yields of monoalkylate might be obtained by another method: the interaction of near-stoichiometric amounts of olefin and arene in the presence of an extremely strong acid catalyst.

Alkylation by this method requires an acid catalyst strong enough to form a σ-complex[4] with the alkylated arene. The σ-complex—a salt resulting from the addition of a proton to the arene, which acts as a base—bears a positive charge and so is not further alkylated by the electrophilic alkylating agent. Alkylated arenes are more basic than unalkylated arenes[5] and form more stable σ-complexes. Hence, the alkylated product is tied up preferentially, while the unalkylated aromatic is left free to react with incoming olefin.

This concept was tested by the conversion of *m*-xylene and ethylene to 1,3,5-ethylxylene in the presence of a strong acid: anhydrous hydrogen fluoride plus excess boron trifluoride. For comparison, the same reactants in the same mole ratios reacted in the presence of a weaker, but typical, alkylation catalyst: hydrogen fluoride alone.

Experimental

m-Xylene from Eastman Kodak Co. (White Label grade) was used without further purification. Ethylene, 98% pure, was obtained from Union Carbide and Carbon Corp. Commercial grades of hydrogen fluoride, 99.6% pure, and boron trifluoride, about 99% pure, were obtained from the Harshaw Chemical Co.

All experiments were carried out in a 1570-ml. carbon-steel autoclave fitted with a 1725-r.p.m. stirrer.[6] The *m*-xylene, hydrogen fluoride and boron trifluoride were charged to the autoclave. Ethylene was added at a uniform rate to the stirred mixture at a controlled temperature. Because no pressure built up during the addition step, the rate of alkylation must have been practically instantaneous. After reaction, the entire reactor contents were withdrawn into crushed ice. The hydrocarbon product was separated into successive carbon-number fractions by distillation through a column of thirty theoretical plates. The individual fractions were identified by their physical properties and by spectrometric analysis.

Results and Discussion

Detailed results are summarized in Table I. All four runs were made with about 2.5 moles each of *m*-xylene and ethylene and with 22 moles of hydrogen fluoride. In the first run, no boron trifluoride was used; in the other three about 3.5 moles was added.

TABLE I

ALKYLATION OF *m*-XYLENE WITH ETHYLENE

9 moles hydrogen fluoride per mole *m*-xylene

Experiment	1	2	3	4
BF_3, moles/mole xylene	0	1.6	1.2	1.3
Temperature, °C.	15	15	62	16
Olefin, addition time, min.	15	15	60	3960
Ethylene, moles/mole xylene	1.0	1.1	1.1	1.2
Product distribution, mole %				
Xylenes	62	27	5	1
1,3,5-Ethylxylene	1	32	83	81
1,3,4-Ethylxylene	15	12	0	0
1,2,3-Ethylxylene	4	2	0	0
Diethylxylenes	6	22	11	16
Triethylxylenes	2	5	1	2
Tetraethylxylenes	10	0	0	0
(k_2/k_1)[a]	2.8	0.60	0.042	0.043

[a] k_1 = rate of ethylation of *m*-xylene. k_2 = rate of ethylation of ethylxylene.

In experiment 1, with hydrogen fluoride alone, only about 38% of the xylene reacted. The product distribution shows that 75% of the ethylene formed polyethylated xylenes. The 1,3,4- and the 1,2,3-isomers comprise most of the ethylxylene fraction. Evidently the positions in the ring that are *ortho* or *para* to the methyl groups react at a much faster rate than the unactivated meta position.

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(2) H. C. Brown and K. L. Nelson, paper presented before the Division of Organic Chemistry, 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 15–19, 1953.

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