

to keep the reaction mixture strongly alkaline. The mixture is heated for one hour longer, cooled and extracted with ether. The ether is evaporated and the material is vacuum distilled; yield 138 g., b. p. 105° (16 mm.).

***m*-Methoxyphenethyl Alcohol.**—A Grignard reagent is prepared from 17 g. of magnesium, 120 g. of *m*-bromoanisole and 400 cc. of anhydrous ether. When the magnesium has almost completely dissolved, 35 g. of ethylene oxide (excess) in twice its volume of ether is added through the dropping funnel, cooling the flask in running water. The mixture is refluxed for thirty minutes; 200 cc. of benzene (anhydrous) is added, about three-fourths of the ether is distilled off, and the residue is refluxed for one hour longer (temperature 60°). The mixture is decomposed with diluted sulfuric acid in crushed ice. The ether layer is dried with sodium sulfate, and the ether is evaporated. The residue is vacuum distilled: b. p. 148° (13 mm.); yield 60 g.

Anal. Calcd. for C₉H₁₂O₂: C, 71.05; H, 7.89. Found: C, 70.83; H, 7.96.

***m*-Methoxyphenethyl Chloride.**—*m*-Methoxyphenethyl alcohol (50 g.) is dissolved in 300 cc. of ether; with cooling (in an ice-bath) and stirring 55 g. (excess) of thionyl chloride in an equal volume of ether is added slowly. The mixture is then stirred for one-half hour. The ether is evaporated on a steam-bath and the residue is vacuum distilled: yield 45 g.; b. p. 122° at 18 mm.

Anal. Calcd. for C₉H₁₁OCl: Cl, 20.80. Found: Cl, 20.91.

3,4-Dihydro-5-methyl-3'-methoxydiphenylethane.—*m*-Methoxyphenethylmagnesium chloride is prepared from 45 g. of *m*-methoxyphenethyl chloride and 7 g. of magnesium as described for *m*-methoxybromobenzene. The Grignard reagent is added in the cold to methyl-

cyclohexenone in ether, and allowed to stand overnight. The reaction mixture is worked up as usual: yield 32 g.; b. p. 184° (10 mm.).

Anal. Calcd. for C₁₈H₂₀O: C, 84.21; H, 8.77. Found: C, 83.69; H, 8.96.

1-Methylcyclohexene-1-one-3.—Ethyl acetoacetate (520 g., 4 moles) is mixed with 150 g. (2 moles) of 40% formaldehyde; 10 cc. of piperidine in 50 cc. of alcohol is added drop by drop with mechanical stirring. The flask is allowed to warm to 30° but prevented by running water from going higher. After complete addition (one hour), the material is allowed to stand overnight.

The upper water layer is separated and the lower oily layer is washed with water several times. The oily layer is mixed with 2 liters of 15% sulfuric acid, glass beads added and the mixture is refluxed for fifteen hours. The mixture is cooled, neutralized with ammonium hydroxide and saturated with ammonium sulfate. The methylcyclohexenone is extracted with ether, the ether is dried with anhydrous potassium carbonate and evaporated. The methyl cyclohexenone is distilled at atmospheric pressure, collecting from 195–202°; yield 180 g. Methylcyclohexenone is light sensitive and should be kept in a dark colored bottle. About 10–15% is lost on each distillation due to polymerization.

Summary

Starting with readily available materials, 3,4-dihydro-5-methyl-3'-methoxydiphenylethane has been synthesized. This compound is structurally related to oestrone and attempts are being made to convert it to this sex hormone.

BROOKLYN, N. Y.

RECEIVED FEBRUARY 1, 1939

[CONTRIBUTION FROM JACKSON LABORATORY OF E. I. DU PONT DE NEMOURS AND COMPANY]

Reactions of 3-Hexene. II. Condensations with Aromatic Hydrocarbons and Phenols

BY LOUIS SPIEGLER AND J. M. TINKER

3-Hexene, which behaves normally in common addition reactions, was condensed with hydrocarbons and phenols using a series of catalyzers, such as sulfuric acid, anhydrous hydrogen fluoride, dihydroxyfluoboric acid (H₃BO₂F₂), perchloric acid, zinc chloride, and anhydrous aluminum chloride. Depending upon the molal ratio of the reactants, 1, 2 or 3 secondary hexyl groups could be introduced into the respective aromatic hydrocarbon or phenol. All of the condensation products were non-crystallizable oils. Inability to obtain pure crystalline products probably was due to the formation of mixtures resulting from partial isomerization under the conditions em-

ployed. It is believed, however, that the results obtained are truly indicative of the characteristic reactions of 3-hexene.

Experimental

Table I indicates the methods and reactants used and the yields and products formed from reaction of 3-hexene, or derivatives obtainable from it, with hydrocarbons.

Oxidation of 4-chloro-(1'-ethylbutyl)-benzene (No. 3 in Table I) with sodium dichromate and 50% sulfuric acid at 110–125° yielded *p*-chlorobenzoic acid, m. p. 239–241°. No change in melting point was observed when mixed with pure *p*-chlorobenzoic acid. Similarly oxidation of 1-methyl-4-(1'-ethylbutyl)-benzene (No. 4) with dilute potassium permanganate gave terephthalic acid; dimethyl ester, m. p. 140–142°.

3-(Phenyl)-hexane reacted with chlorine using iodine and anhydrous ferric chloride as catalysts, and depending upon the molal ratio of reactants yielded one of the following: (1) xxx-trichloro-(1'-ethylbutyl)-benzene, b. p. 164-168° (15 mm.), d_{25}^{25} 1.2350, n_D^{20} 1.5413. *Anal.* Calcd. for $C_{12}H_7Cl_3$: Cl, 40.3. Found: Cl, 42.89. (2) xxx-Tetrachloro-(1'-ethylbutyl)-benzene, b. p. 157-162° (5 mm.), d_{25}^{25} 1.2946, n_D^{20} 1.5504. *Anal.* Calcd. for $C_{12}H_5Cl_4$: Cl, 47.3. Found: Cl, 46.9. (3) xxxxx-Pentachloro-(1'-ethylbutyl)-benzene, b. p. 195-197° (15 mm.), d_{25}^{25} 1.3850, n_D^{20} 1.5690. *Anal.* Calcd. for $C_{12}H_3Cl_5$: Cl, 52.9; C, 43.0; H, 4.0. Found: Cl, 52.37; C, 43.11; H, 4.03.

These chlorinated derivatives refluxed for prolonged periods with 20-30% caustic soda solution showed only very faint traces of hydrolysis.

Table II describes the principal products which resulted from the reaction of 3-hexene with phenols. The yields obtained on isolated products were in the order of 45-57%. The molecular weight determinations were made by the Menzies-Wright boiling point and by depression of freezing point methods.

In cases where sulfuric acid,¹ perchloric acid² or anhydrous aluminum chloride³ was used as catalyst, procedures similar to those described in the literature for these catalysts were employed. Typical procedures for the use of hydrogen fluoride,⁴ dihydroxyfluoboric acid⁵ or zinc chloride as catalyst are described below.

Use of Anhydrous Hydrogen Fluoride Catalyst.—Two hundred grams of liquid anhydrous hydrogen fluoride was introduced into a copper vessel fitted with a cover and cooled by means of an external ice pack. Two hundred and thirty-four grams of benzene (3 mols) and one hundred seventy-four grams of 3-hexene (2.07 mols) were then slowly dropped in successively under rapid agitation while maintaining a temperature of 5-10°. The reaction mass was stirred for twenty-four hours at 10°, after which time it was poured into 2000 g. of ice and water. The oil layer was separated, washed with warm water and with dilute ammonia prior to fractional distillation under diminished pressure: yield, 196 g. of 3-(phenyl)-hexane or 58.5%; 31 g. of a fraction containing 1,4-di-(1'-ethylbutyl)-benzene also was obtained.

Use of Dihydroxyfluoboric Acid as Catalyst.—One hundred and ten grams of resorcinol (1 mole), 84 g. of 3-hexene and 5 g. of dihydroxyfluoboric acid were mixed in a flask equipped with mechanical agitation and a water-cooled reflux condenser. The mass was heated gradually to reflux temperature. The thick mass became brownish-red in color and more fluid as the condensation proceeded.

(1) M. A. Brochet, *Bull. soc. chim.*, [3] 687 (1893); *Compt. rend.*, 117, 115 (1893).

(2) Deutsche Hydrierwerke Akt., British Pat. 469,548 (July 23, 1937).

(3) R. Michel, French Patent 35,810 Addition to 628,440 (Aug. 22, 1928) assigned to I. G.; Dow Chemical Co., British Patent 474,414 (Nov. 1, 1937); J. G. Davidson, U. S. Patent 1,953,702 (April 3, 1934) assigned to Carbide and Carbon Chemical Co.; L. F. Martin and G. H. Coleman, U. S. Patent 1,969,984 (Aug. 14, 1934) assigned to Dow Chemical Co.

(4) J. H. Simons and S. Archer, *THIS JOURNAL*, 60, 986 (1938). The use of anhydrous hydrogen fluoride as catalyst for olefin condensations also has been developed recently at Jackson Laboratory.

(5) J. A. Nieuwland and F. J. Sowa, U. S. Patent 2,109,340 (Feb. 22, 1938), assigned to du Pont Co.

| No. | Reactants | Mol. ratio hex. cpd. to aromatic | Catalyst | Principal product | Yield, % | B. p. °C. | Mm. | d_{25}^{25} | n_D^{20} | Formula | Analyses, % | |
|-----|---|----------------------------------|---|--|----------|-----------|-----|---------------|------------|------------------------------------|---------------|-------|
| | | | | | | | | | | | Calcd. | Found |
| 1 | 3-Hexene + benzene | 0.05 | H ₂ SO ₄ | 3-(Phenyl)-hexane ^a | 50 | 65-66 | 2 | 0.850 | 1.4866 | C ₈ H ₁₆ | Calcd. | Found |
| | 3-Hexene + benzene | 0.66 | H ₂ F ₂ | 3-(Phenyl)-hexane | 58.5 | 95-96 | 18 | .8537 | 1.4865 | C ₈ H ₁₆ | 88.9 | 88.67 |
| | 3-Hexene + benzene | 0.66 | H ₂ BO ₂ F ₂ | 3-(Phenyl)-hexane | 24 | 106-107 | 30 | .854 | 1.4863 | C ₈ H ₁₆ | 88.67 | 88.67 |
| | | | | | | 209-212 | ... | .852 | 1.4840 | C ₈ H ₁₆ | 87.8 | 86.5 |
| 2 | 3-Hexene + benzene | 3.00 | H ₂ F ₂ | (a) 1,4-Di-(1'-ethylbutyl)-benzene (b) 3-(Phenyl)-hexane | 41 | 104-106 | 0.3 | .914 | 1.5020 | C ₁₈ H ₂₆ | 87.8 | 86.5 |
| 3 | 3-Hexene + chlorobenzene | 0.66 | H ₂ F ₂ | 4-Chloro-(1'-ethylbutyl)-benzene | 13 | 135-140 | 30 | .9589 | 1.5240 | C ₁₀ H ₁₄ Cl | 87.5 | 87.5 |
| 4 | 3-Hexene + toluene | 0.66 | H ₂ F ₂ | 1-Methyl-4-(1'-ethylbutyl)-benzene | 25 | 162-165 | 135 | .855 | 1.4910 | C ₁₀ H ₁₆ | 88.6 | 88.42 |
| 5 | 3-Hexene + <i>m</i> -xylene | 0.75 | H ₂ F ₂ | Hydrocarb. mixt. unsep. by fract. | 89 | 101-102 | 3 | .862 | 1.493 | C ₁₀ H ₁₆ | 88.6 | 88.42 |
| 6 | <i>s</i> -Dihexyl ether + <i>m</i> -xylene ^b | 0.18 | H ₂ F ₂ | 3-(1',3'-Dimethylphenyl)-hexane | 61 | 101-102 | 3 | .862 | 1.493 | C ₁₀ H ₁₆ | 88.6 | 88.42 |
| 7 | 3-Bromohexane + <i>m</i> -xylene | 1 | AlCl ₃ | 3-(1',3'-Dimethylphenyl)-hexane | 27 | 148-158 | 1 | | | C ₁₀ H ₁₆ | 89.98 | 90.4 |
| 8 | 3-Hexene + naphthalene | 1 | H ₂ F ₂ | (a) 3-(Naphthyl)-hexane (b) Poly- <i>s</i> -hexylnaphthalene | 30 | 200-230 | 1 | | | C ₁₆ H ₂₀ | 89.98 | 90.4 |
| 9 | 3-Hexene + diisopropyl-naphthalene ^c | 1 | H ₂ F ₂ | Mixture of hydrocarbons | 67 | 136-215 | 3 | | | C ₁₆ H ₂₀ | 89.98 | 90.4 |
| 10 | 3-Hexanol + acenaphthene | 1.17 | ZnCl ₂ | 3-Acenaphthyl)-hexane | 31.5 | 170-174 | 4 | .990 | 1.5819 | C ₁₆ H ₂₀ | 238 | 234 |
| 11 | 3-Hexanol + chloroacene naphthene | 1.50 | H ₂ F ₂ | (a) 3-Chloroacenaphthylhexane (b) xx-Di-(1'-ethylbutyl)-chloro-acenaphthene | 21 | 206-220 | 2 | 1.5769 | 1.5769 | C ₁₆ H ₂₀ Cl | 272.5 | 276 |
| | | | | | 7 | 223-241 | 2 | 1.5600 | 1.5600 | C ₁₆ H ₂₀ Cl | 356.5 | 360 |
| 12 | 3-Hexene + anthracene | 0.66 | AlCl ₃ | xx-Di-(1'-ethylbutyl)-anthracene | 20 | 240-256 | 3 | | | C ₂₄ H ₃₀ | Mol. wt., 246 | 311 |

^a B. p. 130° (25 mm.), d_{25}^{25} 0.863. Described by P. A. Levene and R. E. Marker, *J. Biol. Chem.*, 93, 749 (1931). ^b *s*-Dihexyl ether was prepared for this study through condensation of 3-sodium hexanoate and 3-bromohexane. It has been described previously by E. Erlenneyer and J. A. Wanklyn, *Ann.*, 135, 139 (1865). ^c B. p. 166-167 (25 mm.).

TABLE II

| Principal product | Physical properties of product | | | | | Analyses | | | |
|--|--------------------------------|-----|---------------|---------------|--|--------------------|-------------------|-------------|-------|
| | B. p. °C. | Mm. | d_{25}^{25} | n_{25}^{25} | Formula | Mol. wt. Calcd. | Mol. wt. Found | Calcd. | Found |
| Mono- <i>s</i> -hexylphenol | 110 | 3 | 0.956 | 1.5135 | C ₁₂ H ₁₈ O | 178 | 175 | OH no., 316 | 290 |
| Di- <i>s</i> -hexylphenol | 159-175 | 2 | .928 | 1.5028 | C ₁₈ H ₃₀ O | 262 | 284 | | |
| Tri- <i>s</i> -hexylphenol | 170-195 | 7 | .902 | 1.4962 | C ₂₄ H ₄₂ O | 346 | 313 | | |
| Mono- <i>s</i> -hexyl-2-chloro-6-hydroxy-toluene | 145-153 | 5 | | 1.5272 | C ₁₃ H ₁₉ OCl | 226.5 | 231.9 | % Cl, 15.6 | 15.47 |
| Mono- <i>s</i> -hexyl-2-chloro-5-hydroxy-toluene | 155-160 | 5 | | 1.5272 | C ₁₃ H ₁₉ OCl | 226.5 | 236.2 | % Cl, 15.6 | 15.07 |
| Mono- <i>s</i> -hexylcresylic acid | 124-130 | 6 | .948 | 1.5188 | C ₁₃ H ₂₀ O | 192 | 203 | OH no., 293 | 288 |
| Di- <i>s</i> -hexylcresylic acid | 165-195 | 12 | .928 | 1.5066 | C ₁₉ H ₃₂ O | 276 | 247 | | |
| <i>s</i> -Hexylresorcinol | 134 | 1 | | 1.5310 | C ₁₂ H ₁₈ O ₂ | 194 | 210 | OH no., 578 | 537 |
| <i>s</i> -Hexylcatechol | 142-144 | 1 | | 1.5194 | C ₁₂ H ₁₈ O ₂ | 194 | 220.5 | | |
| Mono- <i>s</i> -hexylhydroquinone | 142-151 | 2 | | | C ₁₂ H ₁₈ O ₂ | 194 | 216 | | |
| Di- <i>s</i> -hexylhydroquinone | 182-190 | 3 | | | C ₁₈ H ₃₂ O ₂ | 278 | 270.9 | | |
| <i>s</i> -Hexyl- α -naphthol | 160-168 | 2 | | | C ₁₆ H ₂₀ O | 228 | 223 | OH no., 246 | 178 |
| <i>s</i> -Hexyl- β -naphthol | 180-218 | 3 | | | C ₁₆ H ₂₀ O | 228 | 217.5 | | |

The refluxing temperature gradually rose until the olefin had all reacted. Table III shows the rate of reaction.

TABLE III

| Refluxing temp., °C. | Time elapsed, min. from start |
|-------------------------|-------------------------------|
| 67 | 0 |
| 71 | 15 |
| 74 | 25 |
| 81 | 30 |
| 95 | 35 |
| 100 (no further reflux) | 40 |

The charge was now heated to 140° and held at this temperature for three to four hours. The completed reaction mass was extracted repeatedly with hot water to remove unreacted resorcinol. Prior to vacuum distillation, the water washed oil was distilled with benzene until anhydrous. Vacuum distillation yielded 120 g. of *s*-hexyl-resorcinol (62%), which distilled over at 159 to 165° at 1.6 mm. of mercury pressure. There was also obtained 45 g. (20% yield) of a portion boiling above 200° (1.6 mm.) which probably contained *s*-dihexylresorcinol.

s-Hexylresorcinol obtained as above when purified by solution in aqueous sodium hydroxide (protected from air oxidation while dissolved) boils at 134° (1 mm.).

Use of Zinc Chloride as Catalyst.—One hundred and fifty-four grams of acenaphthene was melted and heated

to 130°. Twenty-seven grams of powdered anhydrous zinc chloride was stirred in, prior to dropwise introduction of 120 g. of 3-hexanol over a period of ten to twelve hours. The temperature was then gradually raised to 180° while distilling out water from the reaction mass. The products volatile with steam containing hexanol were returned to the reactor. When the hexanol was entirely consumed, a total of 13 g. of water and 28 g. of mixed hexenes had been distilled out. The reaction mass after dilution with water was extracted with benzene, and the extract subjected to fractional distillation under diminished pressure. Seventy-five grams of acenaphthylhexane was obtained.

Acknowledgment.—The writers are indebted to Dr. A. S. Carter, Dr. V. Weinmayr, Dr. C. W. Croco, Mr. W. J. Balon and to other members of the Jackson Laboratory Research Staff for their assistance in the above described investigation.

Summary

The condensation of 3-hexene with aromatic hydrocarbons and phenols is described. 1, 2 or more hexyl groups were introduced into the aromatic nuclei to obtain the corresponding secondary hexyl derivatives.

WILMINGTON, DEL.

RECEIVED OCTOBER 3, 1938