[CONTRIBUTION FROM MELLON INSTITUTE]

Preparation of Vinyltetramethylbenzenes

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Directions for the preparation of three vinyltetramethylbenzenes are reported.

Three vinyltetramethylbenzenes were prepared for evaluation as monomers—vinyldurene (IV), divinyldurene (VIII), and vinylprehnitene (XI). The general preparative method involved acetylation of the hydrocarbon, hydrogenation of the ketone, and dehydration of the carbinol.

The best procedure for the acetylation of durene to acetodurene was a modification of the Perrier method[1] in which durene was added to the preformed aluminum chloride–acetyl chloride complex in carbon tetrachloride. Diacetoisodurene was coproduct when acetic anhydride was added to a mixture of durene and a large excess of aluminum chloride in carbon disulfide.

Claus and Foecking[2] claim to have reduced acetodurene to durylmethylcarbinol by means of zinc dust. Their evidence was the carbon-hydrogen composition of the product, but this does not distinguish between ketone and carbinol. They report the melting point of the carbinol to be 72° which is the same as that of the ketone. No mixture melting point comparison was reported. We repeated the work of Claus and Foecking and found the product made by their method to be unchanged acetodurene. The reduction of acetodurene with lithium aluminum hydride gives a product melting at 51–52°. That our product is durylmethylcarbinol was confirmed by the preparation of its *p*-nitrobenzoate and α-*N*-naphthylcarbamate derivatives.

An attempt to distil durylmethylcarbinol resulted in dehydration. A small amount of vinyldurene was obtained as distillate but the major product was the nondistilled residue from which two products (m.p. 152–153° and 103–104°) were obtained by fractional crystallization. We believe these compounds to be the *meso* and *dl* modifications of α,α'-diduryldiethyl ether (V). Both show infrared absorption at 9.2μ characteristic of the aliphatic ether linkage and their carbon-hydrogen analyses and molecular weights agree with the ether formula.

Fuson and co-workers[3] have shown that hindered ketones such as acetomesitylene, acetodurene, and acetoisodurene form stable trihalo derivatives upon treatment with alkaline hypohalite. Likewise diacetodurene (VI) forms bis(trichloroaceto)durene by the action of sodium hypochlorite and this product is unchanged by refluxing with 2*N* sodium hydroxide for twenty-four hours.

Diacetodurene is easily reduced to the corresponding diol (VII) by means of lithium aluminum hydride. Aluminum isopropoxide–isopropyl alcohol, however, was unable to accomplish this reduction.

Acetodurene was isomerized[4] to acetoprehnitene (IX) by means of aluminum chloride. The reaction of acetoprehnitene with semicarbazide hydrochloride gave two products. One of these was the semicarbazone (m.p. 211–212°) reported by Baddeley and Pendleton;[4] the other melted at 182–183°. The carbon hydrogen ratios, molecular weights, and infrared spectra suggest that these compounds are the *syn* and *anti* forms of acetoprehnitene semicarbazone.

The carbinols were dehydrated to the corresponding vinyl compounds by distillation in the presence of potassium acid sulfate.

EXPERIMENTAL

The freezing points are corrected; the latter were determined by extrapolation of freezing curves, temperatures being measured by certified platinum resistance thermometer and G-2 Mueller bridge. Purities were estimated from the shapes of the freezing curves. Boiling points and melting points are uncorrected.

Acetylation of durene (*A*). To a stirred slurry (5°) of 587 g. (4.4 moles) of aluminum chloride in 1200 ml. of carbon tetrachloride was added 314 g. (4.0 moles) of acetyl chloride during 1 hr. After stirring for 1 hr., a solution of 536 g. (4.0 moles) of durene in 1200 ml. of carbon tetrachloride was added at 0–10° during 1 hr.; the mixture was stirred at 0–10° for 2 hr., at 20–30° for 2 hr., then poured into a mixture of 480 ml. of concentrated hydrochloric acid and 1400 g. of crushed ice. The carbon tetrachloride layer was washed with 5% sodium carbonate followed by water, dried, and concentrated. Distillation of the residue yielded 565 g. (80%) of crude acetodurene (b.p. 129–140°/9 mm., m.p. 69–72°). Redistillation of a 1120-g. batch of acetodurene through a 53-plate column at 5/1 reflux ratio yielded 978 g. (69%) of acetodurene (b.p. 128–132°/9 mm., f.p. 71.74°, purity 96.5 ± 0.5 mole %). Part of this material was crystallized from petroleum ether (b.p. 30–60°) to give an 88% recovery of acetodurene; f.p. 72.92°, purity 99.2 ± 0.2 mole % (lit. b.p. 129–131°/10 mm., m.p. 73°[5]).

Acetylation of durene (*B*). To a stirred slurry (25°) of 800 ml. of carbon disulfide, 168 g. (1.25 moles) of durene, and

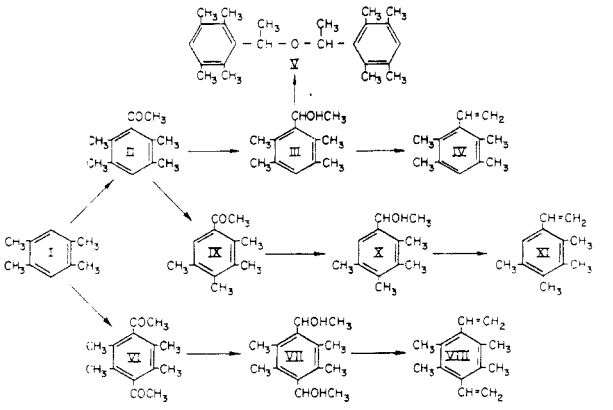
(1) G. Perrier, *Ber.*, **33**, 815 (1900); W. J. Heintzelman and B. B. Corson, *J. Org. Chem.*, **22**, 25 (1957).

(2) A. Claus and C. Foecking, *Ber.*, **20**, 3097 (1887).

(3) A. R. Gray, J. T. Walker, and R. C. Fuson, *J. Am. Chem. Soc.*, **53**, 3494 (1931).

(4) G. Baddeley and A. G. Pendleton, *J. Chem. Soc.*, 807 (1952).

(5) L. I. Smith and C. Guss, *J. Am. Chem. Soc.*, **59**, 804 (1937).



587 g. (4.4 moles) of anhydrous aluminum chloride was added 245 g. (2.4 moles) of acetic anhydride during 1 hr. The mixture was stirred and refluxed for 3 hr., then cooled and poured into a mixture of 230 ml. of concentrated hydrochloric acid and 700 g. of crushed ice. The carbon disulfide layer was washed successively with water, 5% sodium carbonate, and water, dried and concentrated. The concentrate was distilled to yield 123 g. (56%) of crude acetodurene (b.p. 125–131°/10 mm.) and a residue. The latter was crystallized from ether to yield 31 g. (14%) of diacetoisodurene, m.p. 121–122° (lit. m.p. 121°[5]).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.21; H, 8.50.

Durylmethylcarbinol. Acetodurene (200 g., 1.14 moles) in 1200 ml. of dry ether was added during 1.5 hr. to a stirred solution of 43.2 g. (1.14 moles) of lithium aluminum hydride in 1200 ml. of dry ether. After stirring and refluxing for 3 hr. the mixture was cooled to 20°, diluted with 400 ml. of cold water, and poured into 3 l. of 10% sulfuric acid. The ether layer was washed with 5% sodium carbonate followed by water, dried, and concentrated under reduced pressure to yield 195 g. (96%) of durylmethylcarbinol, m.p. 50–52°. Recrystallization from petroleum ether raised the m.p. to 51–52°.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.81; H, 10.40.

α-Durylethyl-p-nitrobenzoate. Colorless needles from methanol, m.p. 109–110°.

Anal. Calcd. for $C_{19}H_{21}NO_4$: C, 69.70; H, 6.47; N, 4.28. Found: C, 70.01; H, 6.61; N, 4.40.

α-Durylethyl-α-naphthylcarbamate. Colorless crystals from methanol, m.p. 151–152°.

Anal. Calcd. for $C_{23}H_{25}NO_2$: N, 4.03. Found: N, 4.30.

α,α'-Diduryl diethyl ether. An attempt to distill 290 g. of durylmethylcarbinol gave 50 g. of distillate (b.p. 108–110°/11 mm.) which solidified and 196 g. of residue. The distillate was crystallized from petroleum ether to give vinyldurene; melting point and mixture melting point with an authentic sample 34–35°. The distillation residue was separated by fractional crystallization (first from methanol, finally from methyl ethyl ketone) into two components, (A), m.p. 152–153° (37 g.) and (B) m.p. 103–104° (12 g.). Both of these compounds showed infrared absorption at 9.2 μ indicative of an aliphatic ether.

Anal. Calcd. for $C_{24}H_{34}O$: C, 85.15; H, 10.12; mol. wt., 338. Found (I): C, 85.11; H, 10.21; mol. wt, 334. Found: (B); C, 85.06; H, 10.17; mol. wt., 340.

Vinyldurene. A mixture of 185 g. (1.04 moles) of durylmethylcarbinol, 6 g. of fused potassium acid sulfate, and 5 g. of *t*-butylcatechol was heated from 190 to 250° at 20 mm. for 1 hr. during which 145 g. of distillate (b.p. 110–150°) was collected. The product was distilled through a 20-cm. Vigreux column to yield 133 g. of crude vinyldurene which was redistilled through a 53-plate column at 5/1 reflux ratio to yield 102 g. (62%) of vinyldurene; b.p. 104°/7.5 mm., f.p. 34.10°, purity 99.85 ± 0.05 mole %. Infrared scanning revealed bands corresponding to a terminal vinyl group at 10.1 and 10.9 μ.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.02; H, 10.10.

α,β-Dibromoethyldurene. To an ice cooled solution of 11.6 g. (0.073 mole) of vinyldurene in 115 ml. of dry ether was added 11.5 g. (0.073 mole) of bromine during 0.5 hr. and the mixture was stirred for 2 hr. Ether was evaporated under reduced pressure to yield 21.3 g. (92%) of dibromide. Crystallization from petroleum ether gave colorless crystals, m.p. 93.5–94.5°.

Anal. Calcd. for $C_{12}H_{16}Br_2$: Br, 49.94. Found: Br, 50.00.

Diacetodurene.[6] To a stirred slurry (25°) of 4500 ml. of carbon disulfide and 900 g. (6.72 moles) of aluminum chloride was added 375 g. (4.77 moles) of acetyl chloride during 0.5 hr.; after stirring for 1 hr., 150 g. (1.11 moles) of durene was added and the mixture was stirred and refluxed for 1 hr. Carbon disulfide was stripped off and the residue poured into a mixture of 300 ml. of concentrated hydrochloric acid and 4500 g. of crushed ice. The aqueous suspension was digested on the steam bath for 3 hr., cooled, and filtered. The solid was washed with water and crystallized from methanol to yield 89 g. (37%) of diacetodurene, m.p. 182.5–183.0° (lit. m.p. 178°[5]).

Bis(trichloroaceto)durene. To a stirred solution of 0.1 mole of potassium hypochlorite in 130 ml. of water at 55° was added 3.3 g. (0.015 mole) of diacetodurene. The mixture was stirred at 55° for 5 hr. followed by 14 hr. at 25°. Excess hypochlorite was destroyed by bisulfite and the mixture was filtered. The precipitate was washed with water, air-dried, and crystallized from ethanol to yield 2.4 g. (36%) of bis(trichloroaceto)durene, m.p. 222–223°.

Anal. Calcd. for $C_{14}H_{12}Cl_6O_2$: C, 39.56; H, 2.85; Cl, 50.05. Found: C, 39.65; H, 3.19; Cl, 50.16.

An attempt to hydrolyze the hexachloro compound by refluxing with 2*N* sodium hydroxide for 24 hr. resulted in a 90% recovery of starting material. No evidence of an acidic product was obtained.

Reaction of diacetodurene with lithium aluminum hydride. A flask containing 19.0 g. (0.50 mole) of lithium aluminum hydride in 2 l. of dry ether was attached to a Soxhlet apparatus containing 54.5 g. (0.25 mole) of diacetodurene. The ether was refluxed for 14 hr. The flask was cooled in ice, 100 ml. of cold water was added, and the mixture was poured into 10% sulfuric acid. Filtration gave a solid which was washed successively with 10% sulfuric acid, 5% sodium carbonate, and water. The ether layer was separated from the filtrate, washed with 5% sodium carbonate followed by water, and dried. The ether was evaporated under reduced pressure to give additional solid which was combined with that obtained by filtration. The yield of bis(α-hydroxyethyldurene) was 47.6 g. (86%), m.p. 220–223°. Recrystallization from chloroform raised the melting point to 222–223°.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.78; H, 10.06.

Duryl-di-α-ethyl-di-α-naphthylcarbamate. Colorless crystals, first from chloroform, finally from toluene, m.p. 221.0–222.5° (dec.).

Anal. Calcd. for $C_{36}H_{36}N_2O_4$: N, 5.00. Found: N, 4.98.

Divinyldurene. A mixture of 42 g. (0.19 mole) of crude bis(α-hydroxyethyl)durene, 3 g. of fused potassium acid sulfate, and 2 g. of *t*-butylcatechol was heated from 200 to 250° at 3 mm. during 0.5 hr. and the distillate (b.p. 120–160°/3 mm.) was redistilled to yield 23 g. (65%) of crude divinyldurene (b.p. 114–124°/3 mm.). Redistillation through a 15-cm. Vigreux column gave a fraction (b.p. 114–115°/3 mm.) which after two recrystallizations from methanol melted at 67–68°.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.12; H, 10.10.

(6) F. Baum and V. Meyer, *Ber.*, **28**, 3212 (1895); V. Meyer, *Ber.*, **29**, 846 (1896).

Bis(α,β-dibromoethyl)durene. To a stirred ice cooled solution of 9.3 g. (0.05 mole) of divinyldurene in 150 ml. of dry ether was added 16.0 g. (0.10 mole) of bromine during 0.5 hr. After stirring overnight at room temperature the ether was evaporated under reduced pressure to yield 23 g. (91%) of residue. Crystallization, first from cyclohexane, finally from methyl ethyl ketone, gave bis(α,β-dibromoethyl)-durene, m.p. 166–167°.

Anal. Calcd. for $C_{14}H_{18}Br_4$: Br, 63.18. Found: Br, 63.62.

Isomerization of acetodurene to acetoprehnitene. A mixture of 323 g. (1.84 moles) of acetodurene, 645 g. (4.84 moles) of aluminum chloride and 43 g. of sodium chloride was stirred at 90° for 2 hr. The product was poured into a mixture of 500 ml. of concentrated hydrochloric acid and 2 kg. of crushed ice. The organic layer was washed successively with water, 5% sodium carbonate, and water, then dried. The ether was stripped off and the residue distilled to give 290 g. of crude acetoprehnitene (b.p. 125–150°/10 mm.) which was redistilled through a 53-plate column at 5/1 reflux ratio to yield 228 g. of acetoprehnitene; b.p. 141–142°/10 mm., f.p. 11.52°, purity 98.5 ± 0.6 mole % (lit. b.p. 122–124°/8 mm.[4]).

Acetylation of prehnitene. To a stirred mixture (−5°) of 114 g. (0.85 mole) of aluminum chloride and 230 ml. of carbon tetrachloride was added 61 g. (0.78 mole) of acetyl chloride during 30 min. After stirring for 1 hr. a solution of 104 g. (0.78 mole) of prehnitene (f.p. −11.42°; purity 98.6 ± 0.5 mole %) in 230 ml. of carbon tetrachloride was added at a rate such that the temperature did not exceed 0°. The mixture was stirred for 2 hr. at 0° followed by 2 hr. at room temperature, then poured into a mixture of 100 ml. of concentrated hydrochloric acid and 300 g. of crushed ice. The organic layer was washed successively with water, 5% sodium carbonate and water, then dried. Carbon tetrachloride was stripped off and the residue distilled through a 10-cm. Vigreux column. The distillate was redistilled through a 53-plate column at 5/1 reflux ratio to yield 87 g. (64%) of acetoprehnitene; b.p. 137–138°/9 mm., f.p. 10.56°, purity 97.0 ± 1.0 mole %.

Acetoprehnitene semicarbazone. A mixture of 49.2 g. (0.279 mole) of acetoprehnitene (f.p. 11.36°, purity 99.1 ± 0.3 mole %), 41.7 g., 0.374 mole) of semicarbazide hydrochloride, 56.1 g. (0.685 mole) of anhydrous sodium acetate, 208 ml. of ethanol, and 164 ml. of water was refluxed for 3 hr., cooled at 5° for 12 hr., and filtered to yield 16.1 g. (24%) of acetoprehnitene semicarbazone (A), m.p. 211–212° (from ethanol); lit. m.p. 209°.[4] The filtrate was concentrated to 50% of its original volume, cooled to 5°, and filtered to yield 10.7 g. (16%) of an isomeric acetoprehnitene semicarbazone (B), m.p. 182–183° (from carbon tetrachloride).

Anal. Calcd. for $C_{13}H_{19}N_3O$: C, 66.92; H, 8.21; N, 18.01; mol. wt., 233. Found (A): C, 67.01; H, 8.11; N, 17.93; mol. wt., 240. Found (B): C, 67.06; H, 7.99; N, 17.81; mol. wt., 225.

Reaction of acetoprehnitene with lithium aluminum hydride. A solution of 72.3 g. (0.41 mole) of acetoprehnitene in 400 ml. of dry ether was added during 30 min. to a stirred solution of 15.6 g. (0.41 mole) of lithium aluminum hydride in 510 ml. of dry ether. The mixture was stirred and refluxed for 3 hr., cooled to 5°, and 100 ml. of wet ether was added followed by 200 ml. of water. The mixture was poured into 1 l. of 10% sulfuric acid. The ether layer was washed with 5% sodium carbonate followed by water, dried, and concentrated under reduced pressure to yield 66 g. (91%) of prehnitylmethylcarbinol, m.p. 53–55°. Crystallization from petroleum ether raised the m.p. to 54–55°.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.20; H, 10.56.

α-Prehnitylethyl-α-naphthylcarbamate. Colorless solid, crystallized first from cyclohexane, finally from methanol, m.p. 146–147°.

Anal. Calcd. for $C_{23}H_{25}NO_2$: N, 4.28. Found: N, 4.03.

Vinylprehnitene. A mixture of 390 g. (2.19 moles) of prehnitylmethylcarbinol, 10 g. of fused potassium acid sulfate, and 10 g. of *t*-butylcatechol was heated from 190 to 220° at 20 mm for 1 hr. during which 315 g. of distillate was collected. The product was distilled through a 53-plate column at 2/1 reflux ratio to yield 218 g. (62%) of vinylprehnitene; b.p. 117–118°/10 mm., f.p. −9.88°, purity 94.5 ± 2.0 mole %.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.37; H, 9.66.

α,β-Dibromoethylprehnitene. To an ice cooled solution of 17.4 g. (0.11 mole) of vinylprehnitene in 173 ml. of dry ether was added 17.3 g. (0.11 mole) of bromine during 0.5 hr. and the mixture was stirred for 2 hr. Ether was evaporated under reduced pressure to yield 32.8 g. (86%) of dibromide. Crystallization from petroleum ether gave colorless crystals, m.p. 76.5–77.5°.

Anal. Calcd. for $C_{12}H_{16}Br_2$: Br, 49.94. Found: Br, 50.00.

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