Anal. Calcd. for $C_{19}H_{17}N$: C, 88.0; H, 6.6. Found: C, 88.2; H, 6.9.

This carbazole gave with tetrachlorophthalic anhydride an orange addition-product, crystallizing from acetic acid in fine orange needles; with picric acid, a picrate was formed, which crystallized from ethanol in fine brown red needles, m.p. 162°.

3-Butyl-7H-benzo[c]carbazole (VII; R = n-C_4H_9). Similarly prepared from 4 g. of 6-butyl-2-naphthol, this carbazole (3.5 g., 64%) crystallized from cyclohexane in lustrous colorless leaflets, m.p. 127°; the crystals were solvated, and the solvent was given off above 115°.

Anal. Calcd. for $C_{20}H_{19}N$: C, 87.9; H, 7.0. Found: C, 88.1; H, 7.0.

The corresponding picrate crystallized from ethanol in brown red needles, m.p. 168–169°; the addition-compound with tetrachlorophthalic anhydride crystallized from acetic acid in shiny orange prisms, m.p. 165–166°.

3-Propyl-12-chloro-7,12-dihydrobenzo[a]phenarsazine (IX; R = n-C_3H_7). 6-Propyl-2-(phenylamino)naphthalene (VIII; R = n-C_3H_7), previously described as a viscous oil,[9] was now obtained as a solid, m.p. 75°. A solution of 2.6 g. of this diarylamine in 5 ml. of *o*-dichlorobenzene was gently heated with 1.1 g. of arsenic trichloride until a vigorous reaction set up, then refluxed for 3 min.; cyclohexane was then added, and the solid obtained in 85% yield was filtered off and recrystallized from toluene, giving shiny deep yellow leaflets, m.p. 217–218°.

Anal. Calcd. for $C_{19}H_{17}AsClN$: C, 61.7; H, 3.8. Found: C, 61.4; H, 3.6.

3-Methyl-10-phenyl-12-chloro-7,12-dihydrobenzo[a]phenarsazine. 6-Methyl-2-(p-xenylamino)naphthalene was prepared by heating for 24 hr. a mixture of 3 g. of 6-methyl-2-naphthol, 4 g. of *p*-aminobiphenyl, and 0.1 g. of iodine;[10] the reaction product was taken up in benzene, the benzene solution washed with aqueous sodium hydroxide, then with water, dried over sodium sulfate, the solvent removed, and the residue recrystallized from ethanol, giving shiny colorless needles, m.p. 170°. The yield was 1.6 g. (27.5%).

Anal. Calcd. for $C_{23}H_{19}N$: C, 89.3; H, 6.2. Found: C, 89.2; H, 6.2.

Condensation of this amine (3.1 g.) with arsenic trichloride (1.1 g.) in *o*-dichlorobenzene was almost instantaneous, and gave a 90% yield of the phenarsazine, which crystallized from *o*-dichlorobenzene in shiny deep yellow prisms, melting with decomposition at 268°, and giving a deep blue coloration in sulfuric acid.

Anal. Calcd. for $C_{23}H_{17}AsClN$: C, 66.1; H, 3.4. Found: C, 65.8; H, 3.1.

3-Propyl-7H-benzo[c]phenothiazine (X). A mixture of 2.6 g. of 6-propyl-2-(phenylamino)naphthalene and 0.64 g. of sulfur was heated with 0.02 g. of iodine until a vigorous reaction set up, then kept at 150–160° for 2 min.; the reaction product gave on recrystallization from cyclohexane, 2.1 g. (72%) of pale yellow needles, m.p. 143–144°, giving a deep blue coloration in sulfuric acid.

Anal. Calcd. for $C_{19}H_{17}NS$: C, 78.3; H, 5.9. Found: C, 78.2; H, 6.2.

6-Butyl-2-(phenylamino)naphthalene (VIII; R = n-C_4H_9). This amine, prepared in the usual way from 3 g. of 6-butyl-2-naphthol, 2 g. of aniline, and 0.05 g. of iodine, boiled at 277–279°/20 mm., and crystallized from petroleum ether in shiny needles, m.p. 60°. Yield: 2 g. (48%).

Anal. Calcd. for $C_{20}H_{21}N$: C, 87.2; H, 7.7. Found: C, 87.1; H, 8.0.

PARIS V^{e}, FRANCE

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[9] N. P. Buu-Hoï, R. Royer, B. Eckert, and P. Jacquignon, *J. Chem. Soc.*, 4867 (1952).

[10] See N. P. Buu-Hoï, *J. Chem. Soc.*, 4346 (1952).

[CONTRIBUTION FROM THE MELLON INSTITUTE]

Preparation of Vinylphenols and Isopropenylphenols

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Directions for the preparation of five alkenylphenols are reported.

Five alkenylphenols were prepared for evaluation as monomers—*o*-vinylphenol, *m*-vinylphenol, *p*-vinylphenol, *m*-isopropenylphenol, and *p*-isopropenylphenol. Of these alkenylphenols, *o*-vinylphenol and *p*-vinylphenol are the most accessible. Five preparative methods were employed: (*a*) decarboxylation of *o*-coumaric acid for *o*-vinylphenol; (*b*) dehydrogenation of *m*- and *p*-ethylphenols for *m*- and *p*-vinylphenols, dehydrogenation of *m*- and *p*-isopropylphenols for *m*- and *p*-isopropenylphenols; (*c*) hydrogenation of *p*-acetoxyacetophenone followed by dehydration-hydrolysis for *p*-vinylphenol; (*d*) cracking of 2,2-bis(*p*-hydroxyphenyl)propane and 2,2-bis(*p*-acetoxyphenyl) propane for *p*-isopropenylphenol; (*e*) depolymerization of poly-*p*-isopropenylphenol for *p*-isopropenylphenol.

o-Vinylphenol has usually been prepared by the decarboxylation of *o*-coumaric acid.[1-7] It has also been prepared from salicylaldehyde *via* the Grignard reaction[8] and by the pyrolysis of 2,4-dimethyl-1,3-benzodioxane.[9] Our starting material was *o*-coumaric acid. We confirmed the findings of

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[1] K. Fries and G. Fickewirth, *Ber.*, 41, 367 (1908).

[2] K. Auwers, *Ann.*, **413**, 253 (1917).

[3] H. Kunz-Krause, *Arch. Pharm.*, **236**, 542 (1898); *Chem. Zentr.*, II, 973 (1898).

[4] H. Kunz-Krause and P. Manicke, *Arch. Pharm.*, **267**, 555 (1929).

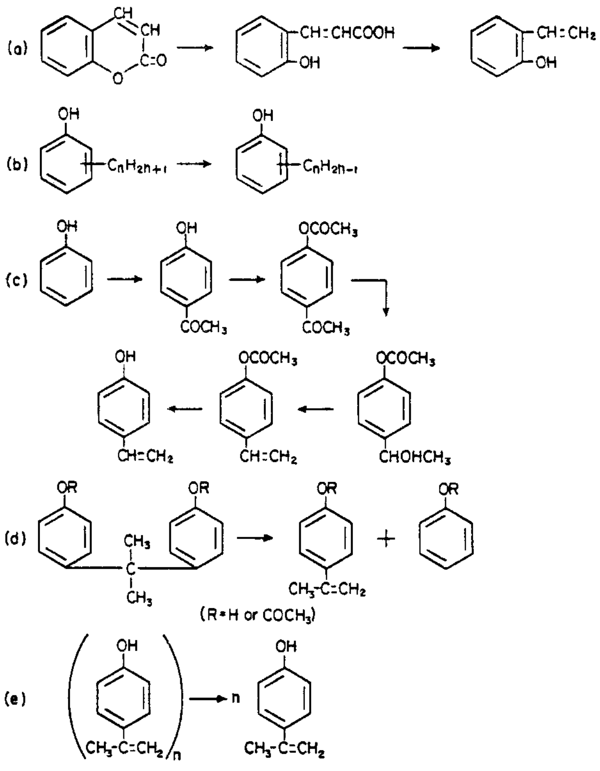
[5] C. S. Marvel and N. S. Rao, *J. Poly. Sci.*, **4**, 703 (1949).

[6] A. R. Bader, *J. Am. Chem. Soc.*, **77**, 4155 (1955).

[7] W. J. Dale and H. E. Hennis, Atlantic City A.C.S. Meeting, 1956.

[8] P. Hoering and F. Baum, Ger. patent **208,886** (1907).

[9] E. Adler, H. Euler, and G. Gie, *Arkiv. Kemi, Mineral., Geol.*, **16A**, No. 12, 1 (1943).



Bader[6] and Williams, Borden, and Laakso[10] that *o*-vinylphenol is not obtainable by following the directions of Smith and Niederl[11] (reaction of phenol with ethylene oxide or ethylene chlorohydrin) nor those of Niederl, Smith, and McGreal[12] (reaction of vinyl acetate with phenol). Other fruitless attempts included the alkenylation of phenol with vinyl chloride and the rearrangement of vinyl phenyl ether.

The yield of *o*-vinylphenol by the thermal decarboxylation of *o*-coumaric acid was 61%. Numerous attempts to improve the yield by catalysis failed. For example: (*a*) mixtures of *o*-coumaric acid in pyridine and quinoline were passed over copperized pumice at 200 to 300° at 15 mm. and 740 mm.; (*b*) quinoline solutions of *o*-coumaric acid containing soluble metal naphthenates (copper, cobalt, and manganese) were passed through a tube at 238°; (*c*) quinaldine and 2,4,6-collidine solutions of *o*-coumaric acid were distilled at atmospheric pressure in the presence of copper powder.

o-Vinylphenol is relatively stable on storage. Its purity fell from 100 to 76% in 257 hr. under laboratory conditions of temperature and illumination, and from 100 to 89% in 2015 hr. at −5° in the dark.

m-Vinylphenol has been prepared from *m*-aminostyrene *via* diazotization by Komppa,[13] Dahlig,[14] and Matsui;[15] by cracking several *m*-alkyl-substituted phenols according to the patent literature;[16] and recently by Dale and Hennis[7] from *m*-hydroxybenzaldehyde *via* the Grignard reaction.

We prepared *m*-vinylphenol by the dehydrogenation of *m*-ethylphenol. With chromia-alumina catalyst the maximum yields of *m*-vinylphenol were 42% per pass and 68% ultimate, obtained at 600°. With 1707 dehydrogenation catalyst[17] the maximum yields were 11% per pass and 48% ultimate, obtained at 525°. The dehydrogenation yield is satisfactory but it is difficult to separate *m*-vinylphenol from the catalyzate by distillation because of loss due to polymerization. Acetylation of the dehydrogenation catalyzate prior to distillation did not eliminate this difficulty.

p-Vinylphenol has been obtained by Schmid and Karrer[18] in small amount from poppy straw and in trace yield by the decarboxylation of *p*-hydroxycinnamic acid. Recently it was made by Dale and Hennis[7] *via* the decarboxylation of the benzoate of *p*-hydroxycinnamic acid. Schmid and Karrer showed the alleged preparation of *p*-vinylphenol *via* diazotization by Miller and Kinkelin[19] to be inoperative.

We prepared *p*-vinylphenol from phenol in 53% yield by a five-step process: (1) acetylation of phenol to *p*-hydroxyacetophenone, (*2*) acetylation of the latter to *p*-acetoxyacetophenone, (*3*) hydrogenation of the ketone to *p*-acetoxyphenylmethylcarbinol, (*4*) dehydration of the carbinol to *p*-acetoxystyrene, (*5*) saponification of *p*-acetoxystyrene to *p*-vinylphenol.

p-Acetoxystyrene, the immediate precursor of *p*-vinylphenol, has good storage stability. Storage for 4 months under laboratory conditions lowered its freezing point from 7.19 to 6.99° which corresponds to a fall in purity from 97.8 to 97.2 mole %. The conversion of *p*-acetoxystyrene to *p*-vinylphenol is quantitative and the conditions of hydrolysis are so gentle that the sensitive *p*-vinylphenol requires no purification.

We also prepared *p*-vinylphenol by the dehydrogenation of *p*-ethylphenol over chromia-alumina catalyst at 600°. Only one experiment was made; the yield of *p*-vinylphenol was 15%.

m-Isopropenylphenol has been prepared by Auwers[2] from ethyl *m*-hydroxybenzoate *via* the Grignard reaction. We prepared it by the dehydrogenation of *m*-isopropylphenol. With 1707 catalyst

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(10) J. L. R. Williams, D. G. Borden, and T. M. Laakso, *J. Org. Chem.*, **21**, 1461 (1956).

(11) R. A. Smith and J. B. Niederl, *J. Am. Chem. Soc.*, **53**, 806 (1931).

(12) J. B. Niederl, R. A. Smith, and M. E. McGreal, *J. Am. Chem. Soc.*, **53**, 3390 (1931).

(13) G. Komppa, *Ber.*, **26**, Ref., 677 (1893).

(14) W. Dahlig, *Prace Placówek Nauk-Badawczych. Ministerstwa Przemystu Chem.*, **1**, 29 (1952).

(15) E. Matsui, *J. Soc. Chem. Ind. Japan*, **46**, Suppl. binding, 125 (1943).

(16) J. E. S. Whitney and E. M. Evans, Brit. patent **669,074** (1952).

(17) K. Kearby, U. S. patent **2,395,875** (1946).

(18) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **28**, 722 (1945).

(19) W. Miller and F. Kinkelin, *Ber.*, **22**, 1705 (1889).

TABLE I

DEHYDROGENATION OF ALKYLPHENOLS
(12-HR. RUNS)

Alkylphenol	*m*-Ethylphenol		*p*-Ethylphenol	*m*-Isopropylphenol	*p*-Isopropylphenol	
Conditions						
Catalyst[a]	1707	Cr_2O_3-Al_2O_3	Cr_2O_3-Al_2O_3	1707	1707	Cr_2O_3-Al_2O_3
Water rate, ml./hr.	52	48	48	52	52	48
Alkylphenol rate, ml./hr.	36	32	32	40	40	36
Temperature, °C.	525	600	600	525	525	600
Products, wt. % of charge						
Light ends[b]	1	2	—	1	3	7
Recovered alkylphenol	77	39	—	75	62	25
Alkenylphenol (purity, %)[c]	11 (95)	43 (95)	15 (95)	17 (95)	28 (90)	52 (80)
Residue[d]	11	16	—	7	7	16
Alkenylphenol yield, wt. %						
Per pass	11	42	15	16	25	43
Ultimate	48	68	—	69	64	56

[a] 100 ml. of $^1/_8 \times {}^1/_8$-inch pellets. [b] Includes gaseous products and material distilling below starting alkylphenol. [c] Purity determined by analytical hydrogenation. [d] Includes high boiling liquid products and carbonaceous deposit on catalyst.

the maximum yields were 17% per pass and 69% ultimate, obtained at 525°. Auwers' product was a liquid; we were able to obtain crystalline *m*-isopropenylphenol.

p-Isopropenylphenol has not previously been reported in the scientific literature. We prepared it by the dehydrogenation of *p*-isopropylphenol. With chromia-alumina catalyst the maximum yields were 43% per pass and 56% ultimate, obtained at 600°. With 1707 catalyst the maximum yields were 25% per pass and 64% ultimate, obtained at 525°. We also prepared *p*-isopropenylphenol by both thermal and catalytic cracking of 2,2-bis(*p*-hydroxyphenyl)propane[20] and its diacetate.

p-Isopropenylphenol polymerizes slowly on storage. At −5° in the dark its purity fell from 100 to 87% in 3000 hr., whereas under laboratory conditions of temperature and illumination it fell from 100 to 25% in 3000 hr. *p*-Isopropenylphenol polymer can be depolymerized thermally.

EXPERIMENTAL

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

Catalysts. The chromia-alumina (15% Cr_2O_3-85% Al_2O_3), activated alumina, nickel-kieselguhr (65% Ni-35% SiO_2), and copper chromite catalysts were purchased from the Harshaw Chemical Co. "Solid phosphoric acid" was the Universal Oil Products catalyst No. 2. Super Filtrol was obtained from the Filtrol Corp., and the 1707 catalyst[17] (72.4% MgO—18.4% Fe_2O_3—4.6% CuO—4.6% K_2O) from the Standard Oil Development Co. of New Jersey.

Alkylphenols. m-Ethylphenol (b.p. 112–114°/20 mm., m.p. −3.4°) and *p*-ethylphenol (b.p. 112–114°/20 mm., m.p. 47.0°) were purchased from the Reilly Tar and Chemical Co. *m*-Isopropylphenol (b.p. 121–122°/20 mm., m.p. 25.6°) and *p*-isopropylphenol (b.p. 121–122°/20 mm., m.p. 62.6°) were obtained from Koppers Co., Inc.

Dehydrogenation apparatus and procedure. The apparatus and procedure employed have been described.[21] The separate alkylphenols were dehydrogenated (Table I) at atmospheric pressure in the presence of about 10 moles of diluent steam per mole of alkylphenol, water and alkylphenol being delivered separately by micro bellows pumps to the preheater section of the vertical reactor whence the gasified mixture passed down through the catalyst bed. The catalyzates were collected in an ice-cooled receiver. The *m*-ethyl-, *m*-isopropyl-, and *p*-isopropylphenol catalyzates were distilled at 20 mm. through a 27-plate column at 5/1 reflux ratio. Fractions were collected as follows: *m*-ethylphenol, b.p. 100–116°; *m*-vinylphenol, b.p. 116–123°; *m*-isopropylphenol, b.p. 118–125°; *m*-isopropenylphenol, b.p. 125–160°; *p*-isopropylphenol, b.p. 118–125°; *p*-isopropenylphenol, b.p. 125–160°. The *p*-ethylphenol catalyzate was not distilled; *p*-vinylphenol was isolated from it by crystallization. The other alkenylphenols were purified by redistillation and/or crystallization.

Analysis and proof of structure of alkenylphenols. Approximate purities (±3%) were determined by analytical hydrogenation of 1.5-g. samples of alkenylphenols in 100 ml. of methanol in the presence of 0.08 g. of Adams' platinum catalyst at room temperature and pressure. Proof of structure of the alkenylphenols was accomplished by mixture melting point comparisons of hydrogenated derivatives with authentic specimens.

o-Coumaric acid. To a solution of 143 g. (6.2 g.-atoms) of sodium in 2180 ml. of ethanol was added 450 g. (3.1 moles) of coumarin and the solution was refluxed for 3 hr. The solution was diluted with 2 l. of water and distilled to remove 2 l. of distillate. The residue was diluted with 2 l. of water and 800 ml. of distillate was removed. The residual liquid was stirred at 85° with 25 g. of activated carbon for 0.5 hr. and filtered. To the cooled filtrate (40°) was added 1 l. of benzene and the stirred mixture was acidified with 620 ml. (7.3 moles) of concentrated hydrochloric acid, stirring being continued for 0.5 hr. The mixture was filtered and the filter cake was washed with two 500-ml. portions of water followed by two 150-ml. portions of benzene. The weight of the air-dried *o*-coumaric acid was 425 g. [84% yield, 93–95% pure by electrometric titration, m.p. 205–206° (dec.);

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(20) Schering-Kahlbaum, Fr. patent **657,122** (1928); U. S. Patent **1,798,813** (1931).

(21) J. E. Nickels, G. A. Webb, W. J. Heintzelman, and B. B. Corson, *Ind. Eng. Chem.*, **41**, 563 (1949).

lit. m.p. 190°,[22a] 207–208° [22b]]. This preparative method is a modification of that of Reychler.[23]

A sample of *o*-coumaric acid, air-dried after 3 crystallizations from water, analyzed 99.4% pure by electrometric titration. Air-dried *o*-coumaric acid, therefore, does not contain water of crystallization, contrary to the report of Kuntz-Krause and Manicke.[4]

o-Vinylphenol by thermal decarboxylation of o-coumaric acid. o-Coumaric acid prepared by the preceding directions gave a low yield of *o*-vinylphenol, presumably because of its fluffiness and the resultant low heat transfer rate. The yield was improved by using a dense variety of acid obtained by slow evaporation of an acetone solution or by reprecipitation from its sodium salt with concentrated hydrochloric acid.

Dense *o*-coumaric acid (100 g., 0.61 mole) in a 500-ml. flask connected *via* an air condenser to a 500-ml. ice-cooled receiver containing 250 g. of 25% aqueous sodium hydroxide (1.6 moles) was heated in an oil bath to 260°/15 mm. until distillate no longer came over (1 hr.). In the decarboxylation flask there remained 14 g. of polymeric residue and 10 g. of *o*-coumaric acid sublimate. The pyrolyzate, diluted with 750 ml. of cold water, was extracted with ether to remove 3 g. of viscous oil. The stirred alkaline solution was acidified at 0–5° with gaseous carbon dioxide to *p*H 8 and extracted with ether. The extract was concentrated under reduced pressure and the residue evacuated at 35°/2 mm. for 1 hr. to yield 46.5 g. of *o*-vinylphenol (61% per pass, 68% ultimate).

o-Vinylphenol by catalytic decarboxylation of o-coumaric acid. (*a*) Copperized pumice containing 6% of copper was prepared as follows: 4–8 mesh pumice was soaked in hot saturated copper sulfate solution and the impregnated pumice was drained, dried at 110°, and reduced in a stream of hydrogen for 6 hr. at 300°. A quinoline (200 g.) solution of *o*-coumaric acid (50 g.) was passed (150 ml./hr.) down through a 50-ml. bed of copperized pumice under nitrogen at 250°. The catalyzate, diluted with an equal volume of ether, was acidified with cold 6*N* hydrochloric acid. The ether layer was extracted with cold 5% aqueous sodium hydroxide and the extract acidified with carbon dioxide to yield 16 g. (44%) of *o*-vinylphenol. When Pyrex beads were substituted for copperized pumice the yield of *o*-vinylphenol was the same.

(*b*) A solution containing 50 g. of *o*-coumaric acid, 200 g. of quinoline, and 5 g. of copper naphthenate was passed (160 ml./hr.) down a glass spiral path (125-cm. long) at 238° under nitrogen. The yield of *o*-vinylphenol was 18.5 g. (51%). Experiments in which copper naphthenate was replaced by cobalt and manganese naphthenates gave similar yields of *o*-vinylphenol.

(*c*) A mixture of 78 g. of *o*-coumaric acid, 102 g. of quinaldine, and 14 g. of copper powder was heated to 250°; the yield of *o*-vinylphenol was 20 g. (36%). When 2,4,6-collidine was substituted for quinaldine the yield of *o*-vinylphenol was 27 g. (47%).

Recovery of o-vinylphenol by selective springing. A 100-g. composite of crudes containing about 30% of *o*-vinylphenol was extracted with 10% aqueous sodium hydroxide and the extract was washed with ether. The stirred alkaline solution was acidified with carbon dioxide at 0–5° and extracted with ether. Concentration of the ether extract yielded 20 g. of *o*-vinylphenol (yellow oil which solidified, m.p. 23–24°). Reaction of this solid with monochloroacetic acid yielded *o*-vinylphenoxyacetic acid; melting point and mixture melting point with an authentic specimen 136.5–137.5° (lit. m.p. 137° [1]).

Purification of o-vinylphenol by equilibrium melting. A 510-g. sample of *o*-vinylphenol (m.p. about 24°) was frozen, then allowed to melt and drain at 28° to the extent of 50%. The residual solid was held at 28°/1 mm. for 4 hr., then flash-distilled through a continuous unit at 165°/15 mm. The constants of the distillate were: f.p. 26.0° (lit. m.p. 29° [1,2]), n_D^{20} 1.5850 (lit. n_D^{20} 1.584[2], $n_D^{27.5}$ 1.5783[5]), d_4^{20} 1.0607 (lit. d_4^{20} 1.060,[2] $d_4^{25.5}$ 1.0293[5]).

o-Vinylphenyl N-phenylcarbamate. White needles from carbon tetrachloride, m.p. 150–151°.

Anal. Calcd. for $C_{15}H_{13}NO_2$: N, 5.85. Found: N, 5.91.

The identity of this urethane was established by hydrogenation to *o*-ethylphenyl *N*-phenylcarbamate; melting point and mixture melting point with an authentic specimen 144–145° (lit. m.p. 141° [24]).

o-Vinylphenyl N-(α-naphthyl)carbamate. White fluffy powder from carbon tetrachloride, m.p. 146–147°.

Anal. Calcd. for $C_{19}H_{15}NO_2$: N, 4.84. Found: N, 4.80.

m-Vinylphenol by dehydrogenation of m-ethylphenol. Redistillation of the crude *m*-vinylphenol fraction gave a heart cut boiling at 120°/20 mm. (lit. b.p. 114–116°/16–17 mm.[13]); n_D^{25} 1.5770, d_4^{25} 1.0459, m.p. 0.5 to 1.0°. Hydrogenation of *m*-vinylphenol yielded *m*-ethylphenol which was identified by converting it to *m*-ethylphenyl *N*-phenylcarbamate; melting point and mixture melting point with an authentic specimen 140.0–141.5° (lit. m.p. 138.8° [25]).

m-Vinylphenyl benzoate (white leaflets from ethanol, m.p. 63–64°, lit. m.p. 62.5–63.5° [13]) was identified by hydrogenation to *m*-ethylphenyl benzoate; melting point and mixture melting point with an authentic specimen 50–52° (lit. m.p. 52°,[25,26] 50° [27]).

m-Vinylphenyl p-nitrobenzoate. Ivory needles from methanol, m.p. 84–85°.

Anal. Calcd. for $C_{15}H_{11}NO_4$: N, 5.20. Found: N, 5.23.

Separation of m-vinyl- and m-ethylphenols as acetates. Dehydrogenation catalyzate (395 g., 3.3 moles) containing 45% of *m*-vinylphenol was mixed with 800 g. of 25% aqueous sodium hydroxide (5.0 moles) and 7.5 kg. of cracked ice, and to the mixture was quickly added 420 g. (4.1 moles) of acetic anhydride. The mixture was stirred for 5 min. and extracted with ether; the extract was washed with cold 10% sodium hydroxide followed by water. The dried extract was concentrated at 50 mm. to yield 491 g. (96%) of mixed acetates. Distillation at 20 mm. through a 27-plate column at 5/1 reflux ratio gave: (*a*) 16 g., b.p. 94–111°, phenyl acetate; (*b*) 204 g., b.p. 111–117°, *m*-ethylphenyl acetate; (*c*) 42 g., b.p. 117–121°, 12% *m*-vinylphenyl acetate–88% *m*-ethylphenyl acetate; (*d*) 74 g., b.p. 121–130°, 87% *m*-vinylphenyl acetate; (*e*) 106 g., brown residue. Redistillation of the *m*-ethylphenyl acetate fraction (*b*) gave 184 g. of distillate with the following constants: b.p. 117°/20 mm. (lit. b.p. 222–223° [26]), n_D^{25} 1.4981, d_4^{25} 1.0232, f.p. −38.69°, purity 97.0 ± 1.0 mole %.

The 74 g. (0.45 mole) of 87% *m*-vinylphenyl acetate (fraction *d*) was stirred with 180 ml. of 25% aqueous sodium hydroxide (1.2 moles) until the mixture was homogeneous (15 min.). The solution was washed with ether, acidified at 0–5° with carbon dioxide and extracted with ether. The extract was washed with water, dried, and concentrated to give 53 g. (0.44 mole) of 87% *m*-vinylphenol.

p-Vinylphenol from phenol via 5-step synthesis. p-Hydroxyacetophenone. Boron trifluoride was passed into a 0–5° stirred mixture of 470 g. (5.0 moles) of phenol and 600 g. (10 moles) of acetic acid until the gas was no longer absorbed (12 hr.); 1020 g. (15 moles) of boron trifluoride was absorbed. The solution was stirred for 5 hr. at 80°, allowed to stand for 16 hr. at 30°, then poured into a mixture of cracked ice and water. After stirring for 1 hr. at 0–5° the mixture was filtered and the red solid was dissolved in 2 l. of aqueous

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(22) (a) H. Bleibtreu, *Ann.*, **59**, 177 (1846); (b) F. Tiemann and H. Herzfeld, *Ber.*, **10**, 283 (1877).

(23) A. Reychler, *Bull. soc. chim. France* (4), **3**, 551 (1908).

(24) G. Vavon and V. M. Mitchovitch, *Bull. soc. chim. France* (4), **45**, 961 (1929).

(25) O. Kruber and A. Schmitt, *Ber.*, **64**, 2270 (1931).

(26) A. Behal and E. Choay, *Bull soc. chim. France* (3), **11**, 206 (1894).

(27) J. Kenner and F. S. Statham, *J. Chem. Soc.*, 299 (1935).

caustic containing 280 g. (7.0 moles) of sodium hydroxide. The solution was stirred at 30° with 10 g. of activated carbon for 0.5 hr. and filtered. The filtrate was cooled to −5°, acidified with concentrated hydrochloric acid and filtered. The light tan solid was air-dried; 640 g., 85% yield,[28] m.p. 105–108°, lit. m.p. 107°,[29a,b] 109°,[29c] 110°.[29d]

p-Acetoxyacetophenone. To a stirred solution of 98 g. (0.72 mole) of *p*-hydroxyacetophenone in 780 ml. of 7.5% aqueous sodium hydroxide (1.45 moles) was added 110 g. (1.08 moles) of freshly distilled acetic anhydride during 5 min. at 5–10°. The mixture was stirred for 1 hr. at 5–10° and filtered. The solid was crystallized from 55–45 water-ethanol to yield 119 g. (93%) of *p*-acetoxyacetophenone, m.p. 52–53°. This product is satisfactory for the next step. A portion of it was recrystallized from methanol to give material with f.p. 52.05°; purity 97.3 ± 0.9 mole % (lit. m.p. 54° [30]).

p-Acetoxyphenylmethylcarbinol. *p*-Acetoxyacetophenone (300 g., 1.7 moles) diluted with 700 ml. of methanol was hydrogenated at 30°/110 p.s.i. in the presence of 10 g. of 10% palladiumized carbon (9 hr., hydrogen consumption 1.6 moles). The catalyzate was filtered and the filtrate concentrated under reduced pressure to yield 295 g. (95%) of *p*-acetoxyphenylmethylcarbinol.

Anal. Calcd. for $C_{10}H_{12}O_3$: hydroxyl, 9.44; sapon. equiv., 180. Found: hydroxyl, 9.00; sapon. equiv., 173.

p-Acetoxyphenylmethylcarbinol can be distilled through a 10-cm. Vigreux column at 1 mm. without decomposition (b.p. 115–125°). However, extensive dehydration-polymerization took place in an attempt to distill it through a 27-plate column at 10 mm.

In two experiments the previous use of the autoclave in copper chromite–catalyzed hydrogenations seemed to poison palladium for the hydrogenation of *p*-acetoxyacetophenone. This trouble was remedied by filtering off the poisoned palladium catalyst and replacing it with fresh catalyst. With nickel-kieselguhr as hydrogenation catalyst it was difficult to prevent over-hydrogenation to *p*-acetoxyethylbenzene. With Raney nickel it was possible to halt the reaction at the carbinol stage, but the ester group was cleaved to give *p*-hydroxyphenylmethylcarbinol.

p-Acetoxystyrene. Three dehydration methods were tried for the conversion of *p*-acetoxyphenylmethylcarbinol to *p*-acetoxystyrene.

(*a*) *Liquid phase dehydration in the presence of potassium acid sulfate.* A mixture of 280 g. (1.56 moles) of *p*-acetoxyphenylmethylcarbinol, 3 g. of fused potassium acid sulfate, and 3 g. of *t*-butylcatechol (TBC) was heated at 190–200°/20 mm. for 1.8 hr. and the distillate (b.p. 105–121°) collected in an ice-cooled receiver containing 1 g. of TBC. A 51-g. residue (18% of the charge) remained in the flask. The distillate was dissolved in ether (water yield 22 ml., 79%) and the solution washed with 5% sodium carbonate followed by saturated calcium chloride solution and dried over anhydrous calcium chloride. The ether was evaporated and the residue distilled through a 10-cm. Vigreux column to yield 179 g. (71%) of *p*-acetoxystyrene; b.p. 73–75°/0.6 mm. (lit. b.p. 100–105°/4 mm.[31] and 83–86°/1 mm.[32]), f.p. 6.94°, purity 97.5 ± 0.5 mole %.

(*b*) *Vapor phase dehydration over potassium acid sulfate-impregnated pumice.* A solution of 150 g. (0.88 mole) of *p*-acetoxyphenylmethylcarbinol, 1.5 g. of TBC, and 385 g. of toluene was passed at a rate of 60 ml./hr. at 225°/20 mm. through a 100-ml. bed of 4–8 mesh pumice impregnated with 3% of potassium acid sulfate. The catalyzate passed into a flask at 150° whence it was continuously flash-distilled into an ice-cooled receiver containing 1 g. of TBC (water yield 8.4 ml., 56%). The distillate was redistilled to yield 58 g. (43%) of *p*-acetoxystyrene (f.p. 7.19°, purity 97.7 ± 0.8 mole %) plus 34.6 g. of residue.

(*c*) *Vapor phase dehydration of p-acetoxyphenylmethylcarbinol over activated alumina.* A 700-g. mixture of *p*-acetoxyphenylmethylcarbinol, acetic acid, and acetic anhydride in a mole ratio of 1:3.3:1 was passed at a rate of 170 ml./hr. through a 100-ml. bed of activated alumina at 350°/25 mm. and the catalyzate collected in an ice-cooled receiver containing 7 g. of TBC. The purpose of the acetic acid–acetic anhydride was to repress cleavage of the acetoxy group. Acetic acid and acetic anhydride were distilled from the catalyzate at 85°/30 mm. and the concentrate was distilled through a 10-cm. Vigreux column. The yields of *p*-acetoxystyrene were 56% per pass and 78% ultimate. The product was 80 ± 5 mole % pure; its infrared spectrum indicated the main impurity to be *p*-vinylphenol. A 100-g. batch of product was cooled at −5° for 15 hr. with seeding. The mother liquor was drained from the solid. The solid was melted and the process repeated four times to yield 27 g. (27%) of *p*-acetoxystyrene; n_D^{25} 1.5360, d_4^{25} 1.056,[33] f.p. 7.64°, purity 98.9 ± 0.4 mole %.

p-Acetoxystyrene is dimorphic, the freezing points of the α- and β-modifications being 8.2 ± 0.1° and 7.4 ± 0.2°, respectively. Several samples of *p*-acetoxystyrene froze initially in the β-form which quickly changed to the α-form upon addition of α-seed.

p-Vinylphenol. A mixture of 16.2 g. (0.10 mole) of *p*-acetoxystyrene, 13.8 g. (0.25 mole) of potassium hydroxide, and 140 ml. of water was stirred at 0–5° until homogeneous (1 hr.). Gaseous carbon dioxide was passed into the stirred cold solution to *p*H 8 to produce 12 g. (100% yield) of *p*-vinylphenol, m.p. 68–69° (lit. m.p. 73.5° [18]). *p*-Vinylphenol was identified by hydrogenating it to *p*-ethylphenol and converting the latter to *p*-ethylphenyl *N*-phenylcarbamate; melting point and mixture melting point with an authentic specimen 119–120° (lit. m.p. 120° [25]).

p-Vinylphenyl benzoate. Crystallized from methanol, white needles, m.p. 75.5–76.5°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39; double bond, 1.00. Found: C, 80.45; H, 5.50; double bond, 0.98.

p-Vinylphenyl benzoate was hydrogenated to *p*-ethylphenyl benzoate; melting point and mixture melting point with authentic *p*-ethylphenyl benzoate 58–59° (lit. m.p. 59–60° [25]).

p-Vinylphenyl p-nitrobenzoate. Yellow needles from methanol, m.p. 109.5–110.5°.

Anal. Calcd. for $C_{15}H_{11}NO_4$: N, 5.20. Found: N, 4.99.

p-Vinylphenyl 3,5-dinitrobenzoate. White needles from methanol, m.p. 132.5–133.0°.

Anal. Calcd. for $C_{15}H_{10}N_2O_6$: N, 8.92. Found: N, 9.18.

p-Vinylphenol by dehydrogenation of p-ethylphenol. The chromia-alumina catalyst was badly carbonized; oxidation of the used catalyst showed the presence of 19 g. of carbon. Half of the catalyzate was heated under a 27-plate column at 20 mm. There resulted 5 g. of distillate (b.p. 70–100°) and a viscous residue, neither of which was investigated. The other half of the catalyzate was extracted with a 50–50 mixture of ether–petroleum ether. The extract was cooled at −5° for 18 hr. and filtered. The solid was recrystallized from *n*-hexane to yield 29.5 g. of *p*-vinylphenol, m.p. 68–69°; its mixture melting point with authentic *p*-vinylphenol was not depressed. The solubility of *p*-vinylphenol in 10 ml. of

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n-hexane is 0.04 g. at 13°, 0.11 g. at 25°, 0.31 g. at 31°, and 0.49 g. at 39°.

m-Isopropenylphenol by dehydrogenation of m-isopropylphenol. The *m*-isopropenylphenol fraction was crystallized from Skellysolve B to yield white crystals (m.p. 39.5–40.5°) which liquefied on standing at room temperature for 8 days; the resulting liquid was insoluble in Skellysolve B. The crystalline *m*-isopropenylphenol was converted to *m*-isopropenylphenoxyacetic acid (white needles from water, m.p. 98.5–99.5°, lit. m.p. 98°[2]).

m-Isopropylphenoxyacetic acid. White flakes from *n*-hexane, m.p. 65.5–66.0°; its mixture melting point with hydrogenated *m*-isopropenylphenoxyacetic acid was not depressed.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.27; H, 7.35.

m-Isopropylphenyl N-phenylcarbamate. White needles from Skellysolve B, m.p. 116.5–117.5°, prepared from *m*-isopropylphenol plus phenyl isocyanate.

Anal. Calcd. for $C_{16}H_{17}NO_2$: N, 5.49. Found: N, 5.58.

Its mixture melting point with product obtained by the reaction of hydrogenated *m*-isopropenylphenol with phenyl isocyanate was not depressed.

m-Isopropenylphenyl p-nitrobenzoate. Ivory needles from ethanol, m.p. 90.5–91.5°.

Anal. Calcd. for $C_{16}H_{13}NO_4$: N, 4.95. Found: N, 4.96.

p-Isopropenylphenol by dehydrogenation of p-isopropylphenol. Redistillation of the crude *p*-isopropenylphenol fraction gave a heart cut boiling at 136–137°/20 mm. The latter was crystallized from cyclohexane to yield white crystals, m.p. 83–84°.

Anal. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51; double bond, 1.00. Found: C, 80.26; H, 7.60; double bond, 1.00.

The hydrogenation of *p*-isopropenylphenol produced *p*-isopropylphenol; melting point and mixture melting point with an authentic specimen 62–64° (lit. m.p. 61°,[34a] 60.5–61.5°).[34b]

2,2-bis(p-Hydroxyphenyl)propane. A mixture of 2205 g. (23.4 moles) of phenol, 458 g. (7.9 moles) of acetone and 366 ml. of concentrated hydrochloric acid was allowed to stand for 6 days at room temperature, then filtered. The water-washed solid was air-dried for 7 days to yield 1400 g. (55%) of a solid (m.p. 103–121°) containing approximately equimolal amounts of bisphenol and phenol. Crystallization from benzene or 50% aqueous acetic acid yielded bisphenol, m.p. 157–159° (lit. m.p. 151–152°,[35] 155°[36]); m.p. of dibenzoate 161–162° (lit. m.p. 153.5°,[35] 161°[36]). Phenol can also be removed from the complex by steam distillation or vacuum distillation. For example, 473 g. of air-dried complex was heated under a 23-plate column until the vapor temperature was 100°; 146 g. of distillate (phenol) was obtained and a flask residue of 326 g. (bisphenol, m.p. 157–159° after crystallization from benzene). This corresponds to a phenol/bisphenol mole ratio of 1.08/1.00.

p-Isopropenylphenol by cracking of 2,2-bis(p-hydroxyphenyl)propane. Molten bisphenol (90 g.) was passed through a 20-ml. bed of "solid phosphoric acid" at 250° during 28 min. The catalyzate was dissolved in benzene and the solution was washed with aqueous sodium bicarbonate, dried azeotropically and concentrated. The concentrate was distilled at 20 mm. to yield 41 g. of phenol, 29 g. of *p*-isopropenylphenol (48%, b.p. 125–145°) plus 14 g. of residue.

2,2-Bis(p-acetoxyphenyl)propane. A mixture of 114 g. (0.5 mole) of 2,2-bis(*p*-hydroxyphenyl)propane, 204 g. (2.0 moles) of acetic anhydride, and 50 g. of anhydrous sodium acetate was refluxed for 2 hr. The cooled reaction mixture was stirred with 400 ml. of water and filtered. The product was crystallized from methanol to yield 147 g. (94%) of 2,2-bis(*p*-acetoxyphenyl)propane, heavy white crystals, m.p. 79.5–81.5° (lit. m.p. 78°[37]).

p-Isopropenylphenol by cracking of 2,2-bis(p-acetoxyphenyl)-propane. (*a*) 2,2-Bis(*p*-acetoxyphenyl)propane (100 g.) was heated to 370° to yield 85 g. of distillate which was stirred for 2 hr. at 25° with dilute sodium hydroxide. The mixture was extracted with ether and the extract concentrated to give 18.5 g. of recovered 2,2-bis(*p*-acetoxyphenyl)propane, m.p. and mixture m.p. 80–82°. The aqueous layer was acidified to *p*H 8 at 0–5° with carbon dioxide and extracted with ether. The extract was concentrated and the residue distilled through a 27-plate column to yield 18 g. of *p*-isopropenylphenol (37%), b.p. 125–145°, m.p. 83–84°.

(*b*) A mixture of 100 g. of 2,2-bis(*p*-acetoxyphenyl)propane and 4.5 g. of Super Filtrol was heated to 370° to give 72 g. of distillate which was worked up as in method (*a*). The yield of *p*-isopropenylphenol was 15 g.

p-Isopropenylphenol by depolymerization of poly-p-isopropenylphenol. Sixty grams of 90% *p*-isopropenylphenol changed to a yellow, taffy-like material during a 6-month storage in the laboratory. This material was heated under a 27-plate column at 20 mm. to give: (*a*) 10 g., b.p. 105–125°, not identified; (*b*) 45 g., b.p. 125–145°, m.p. 83–84°, *p*-isopropenylphenol; (*c*) 5 g. of residue.

The *p*-isopropenylphenol obtained from depolymerization and cracking was identified by mixture melting point with an authentic specimen.

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