

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

***o*-Methoxy-, *p*-Benzyl-, *o*-Fluoro-, and *o*-Cyano-styrenes. Further Examples of the Disproportionation of Phenylmethylcarbinols to Ethylbenzenes¹**

BY C. S. MARVEL AND D. W. HEIN

In connection with the study of a variety of substituted styrenes as substitutes for styrene in GR-S, the syntheses of *o*-methoxy-, *p*-benzyl-, *o*-fluoro-, and *o*-cyano-styrenes have been accomplished by routes not previously described.

***o*-Methoxystyrene**

o-Methoxystyrene has been prepared by a number of methods² which need not be enumerated. We first applied the hot tube cracking process of Mowry, Renoll and Huber³ to 1-(*o*-methoxyphenyl)-ethanol which was prepared both from *o*-methoxybenzaldehyde and methylmagnesium iodide and from *o*-methoxyphenylmagnesium bromide and acetaldehyde. In the first of these processes there was obtained along with the carbinol, a considerable amount of bis-[1-(*o*-methoxyphenyl)-ethyl] ether. This ether cleaved readily over hot alumina to give the desired *o*-methoxystyrene in 75% yields.

The *o*-methoxystyrene produced by catalytic dehydration of 1-(*o*-methoxyphenyl)-ethanol or its ether did not copolymerize well in standard GR-S recipes. Examination of the styrene showed that it contained about 10% of *o*-ethylphenol and a lesser proportion of *o*-ethylanisole. Presumably the *o*-ethylanisole was produced by a disproportionation reaction similar to the one observed in the attempted dehydration of *m*-*N*-methylaminophenylmethylcarbinol.⁴ The *o*-ethylphenol was undoubtedly produced by cleavage of the ether group of *o*-ethylanisole. The other fragment of the disproportionation reaction is undoubtedly the substituted acetophenone since Hunter and Groombridge⁵ have observed the formation of acetophenone during the dehydration of phenylmethylcarbinol over alumina.

Even after the removal of the phenolic impurities the sample of *o*-methoxystyrene prepared from the α -arylcarbinol was not satisfactory for polymerization studies. A very good sample of *o*-methoxystyrene was obtained by the conversion of *o*-methoxyphenylmagnesium bromide to 2-(*o*-methoxyphenyl)-ethanol by the action of ethylene oxide and the dehydration of this alcohol over hot potassium hydroxide. The styrene was obtained in good yield and the polymerization rates were satisfactory but the starting material was somewhat difficult to obtain.

Finally *o*-methoxystyrene was prepared by the method of Walling and Wolfstirn.^{2c} After the *o*-methoxystyrene thus prepared had been washed with alkali it copolymerized satisfactorily. The yields are less satisfactory than in the preceding preparation but *o*-methoxybenzaldehyde is a more readily available starting material than *o*-bromoanisole.

1-(*o*-Methoxyphenyl)-ethanol.—This alcohol was prepared by the reaction of methylmagnesium iodide with *o*-methoxybenzaldehyde by procedures which have been de-

scribed.⁶ We obtained in every run a by-product boiling at 109° at 0.05 mm., m. p. 93.5°, which appears to be the ether formed by dehydration of the carbinol.

Anal.⁷ Calcd. for C₁₂H₂₂O₂: C, 75.44; H, 7.75. Found: C, 75.37; H, 7.58.

This by-product was not described in the earlier reports. In one experiment a yield of crude carbinol amounting to 82% was obtained, but on distillation it was found to contain about 30% of the ether.

From *o*-methoxyphenylmagnesium bromide (from 187 g. of *o*-bromoanisole) and acetaldehyde, a 70% yield of the above alcohol was obtained. No ether was isolated in this run.

2-(*o*-Methoxyphenyl)-ethanol.—To an ether solution of *o*-methoxyphenylmagnesium bromide (from 100 g. of *o*-bromoanisole) was added an ether solution of 44 g. of ethylene oxide and the reaction was carried out in the usual manner. The product amounted to 54.5 g. (67%) and boiled at 79–80° at 0.26 mm. pressure, n_D^{20} 1.5391, d_4^{20} 1.0889.

Anal. Calcd. for C₉H₁₂O₂: C, 71.03; H, 7.95. Found: C, 70.61; H, 7.64.

The phenylurethan was prepared in the usual manner and after recrystallization from ethanol melted at 76°.

Anal. Calcd. for C₁₀H₁₇O₂N: C, 70.83; H, 6.32; N, 5.16. Found: C, 71.05; H, 6.42; N, 5.11.

o-Methoxystyrene.—Dehydration of 150 g. of 1-(*o*-methoxyphenyl)-ethanol over (Alorco) activated alumina at 310° at 30–40 mm. pressure gave 102 g. of product boiling at 73–75° at 10 mm., n_D^{20} 1.5530. This refractive index is lower than most of the values recorded previously for this styrene. In a redistillation it was observed that there was considerable variation in the refractive index at different stages of distillation although the boiling point was unchanged.

By-products in *o*-Methoxystyrene from 1-(*o*-Methoxyphenyl)-ethanol.—A solution of 153 g. of *o*-methoxystyrene made as above in 1 liter of low boiling petroleum ether was repeatedly washed with 500-cc. portions of 2% aqueous sodium hydroxide. The alkaline extracts were combined and acidified with hydrochloric acid and extracted with ether. After evaporation of the ether, the residual oil was distilled under reduced pressure. Redistillation of the main fraction gave about 11 g. of material, b. p. 48° at 0.05 mm., n_D^{20} 1.5367, d_4^{20} 1.0283.

Anal. Calcd. for C₈H₁₀O: C, 78.65; H, 8.25. Found: C, 78.71; H, 7.91.

This material had a strong creosote-like odor, absorbed bromine in carbon tetrachloride, decolorized 1% aqueous potassium permanganate solution and gave a violet blue color with ferric chloride in alcohol. These properties agree with those of *o*-ethylphenol as reported by Behal and Choay.⁸ To confirm the identification the phenol was converted to *o*-ethylphenoxyacetic acid which is reported to melt at 141°.⁹ The product we obtained melted at 134° and a sample made from an authentic specimen of *o*-ethylphenol (n_D^{20} 1.5335) melted at 137–138°. A mixture of the two materials melted at 136–137°.

Careful distillation of the *o*-methoxystyrene which had

(1) The work described in this manuscript was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) (a) Perkin, *Ber.*, **11**, 515 (1878); (b) Klages and Eppelsheim, *ibid.*, **36**, 3584 (1903); (c) Pschorr and Einbeck, *ibid.*, **38**, 2077 (1905); (d) v. Auwers, *Ann.*, **413**, 297 (1916); (e) Shorygin and Shorygina, *J. Gen. Chem. (USSR)*, **9**, 845 (1939); *C. A.*, **34**, 389 (1940); (f) Quelet and Golse, *Compt. rend.*, **223**, 159 (1946); (g) Walling and Wolfstirn, *THIS JOURNAL*, **69**, 853 (1947).

(3) Mowry, Renoll and Huber, *ibid.*, **68**, 1105 (1946).

(4) Marvel and Overberger, *ibid.*, **68**, 185 (1946).

(5) Hunter and Groombridge, British Patent 589,015; *C. A.*, **41**, 6897^d (1947).

(6) Klages and Eppelsheim, *Ber.*, **36**, 3584 (1903); Pschorr and Einbeck, *ibid.*, **38**, 2077 (1905); Stedman and Stedman, *J. Chem. Soc.*, 609 (1929).

(7) All microanalyses reported are by H. S. Clark of the Illinois State Geological Survey.

(8) Behal and Choay, *Bull. soc. chim.*, [3] **11**, 210 (1894).

(9) Steinkopf and Hopner, *J. prakt. Chem.*, [2] **113**, 140, 153 (1926).

been washed with alkali to remove phenol showed that it also was not a homogeneous material. The material was divided into five fractions as follows: (1) 9 g., b. p. 33–35° at 0.6 mm., n_D^{20} 1.5282; (2) 21.6 g., b. p. 32–35° at 0.4–0.55 mm., n_D^{20} 1.5390; (3) 26.7 g., b. p. 33–36° at 0.35 mm., n_D^{20} 1.5500; (4) 47.6 g., b. p. 34° at 0.3 mm., n_D^{20} 1.5582; (5) 20.3 g., b. p. 34° at 0.25 mm., n_D^{20} 1.5592.

Fractions 1 and 2 were combined and redistilled at a reflux ratio of 5 to 1. About 1.5 g. of distillate boiling at 72° and 13 mm. was collected, n_D^{20} 1.5169. The residue was heated in the distillation apparatus under total reflux for two hours to polymerize any *o*-methoxystyrene and then distillation was continued. Seven grams of product boiling at 73° under 14 mm. pressure, n_D^{20} 1.5142 were obtained.

Anal. Calcd. for $C_9H_{10}O$: C, 79.37; H, 8.88. Found: C, 79.58; H, 8.67.

Klages and Eppelsheim^{2b} have reported a boiling point of 70–71° at 11 mm., and n_D^{20} 1.512 for *o*-ethylanisole.

Further confirmation that this product was *o*-ethylanisole was obtained by conversion to a tribromide by bromination with excess bromine in carbon disulfide with a trace of iodine as a catalyst. The product was recrystallized to a constant melting point from 95% alcohol and melted at 108–109°.

An authentic specimen of *o*-ethylanisole was similarly brominated to give a product which melted at 109°. A mixture of the two tribromo derivatives melted at 108–109°.

Anal. Calcd. for $C_9H_9OBr_2$: C, 28.99; H, 2.43; Br, 64.29. Found: C, 28.81; H, 2.28; Br, 64.24.

The dinitro derivative was prepared from the *o*-ethylanisole isolated from the *o*-methoxystyrene and also from authentic *o*-ethylanisole. After recrystallization from 95% alcohol the sample from the *o*-ethylanisole isolated from the styrene preparation melted at 67°, the authentic specimen at 67.5° and the mixture of the two at 67°.

Anal. Calcd. for $C_9H_9O_2N_2$: C, 47.79; H, 4.46; N, 12.39. Found: C, 47.98; H, 4.58; N, 12.37.

***o*-Methoxystyrene from 2-(*o*-Methoxyphenyl)-ethanol.**—In a 500-cc. round-bottomed flask fitted with a dropping funnel and a distilling tube with receiver, was placed 150 g. of U.S.P. potassium hydroxide pellets. A very small amount of picric acid was introduced to act as a polymerization inhibitor. The apparatus was pumped out to about 12 mm. pressure, the reaction flask heated to 225° and after the water had distilled out of the potassium hydroxide, 54.5 g. of 2-(*o*-methoxyphenyl)-ethanol was added dropwise at the rate of 15–20 drops per minute. To the distillate was added 100 cc. of low boiling petroleum ether, the water separated and the solvent distilled. The residue was distilled to yield 33.3 g. (69.4%) of quite pure *o*-methoxystyrene boiling at 35° under 0.20 mm. pressure, n_D^{20} 1.5595.

***o*-Methoxystyrene from *trans*-*o*-Methoxycinnamic Acid.**—The procedure was that of Walling and Wolfstirn^{2c} except that it was found necessary to wash the substituted styrene with sodium hydroxide solution to remove traces of phenolic compounds and unchanged acid. The major portion of this product boiled at 36–37° under 0.2 mm., n_D^{20} 1.5600.

p-Benzylstyrene

The synthesis of *p*-benzylstyrene from diphenylmethane was effected by the usual methods of acetylation, reduction and dehydration. The general procedure of Mowry, Renoll and Huber³ for the preparation of alkylacetophenones was followed for the acetylation of diphenylmethane and as a by-product some bis-(*p*-acetylphenyl)-methane was obtained. This was converted to the new bis-(*p*-vinylphenyl)-methane which was characterized.

The *p*-benzylstyrene which resulted from the dehydration of 1-(*p*-benzylphenyl)-ethanol was found to contain small amounts of *p*-benzylethylbenzene. This is further evidence that the disproportionation of phenylmethylcarbinols over alumina^{4,5} is a general reaction.

***p*-Benzylacetophenone.**—When the general procedure of Mowry, Renoll and Huber³ was followed, 425 g. of diphenylmethane gave 413 g. of *p*-benzylacetophenone, m. p. 39° (lit.¹⁰, 39°), and 60 g. of higher boiling residue.

Bis-(*p*-acetylphenyl)-methane.—Three hundred and five grams of high boiling residues from the above preparation was distilled at 180° and 0.05 mm. and the distillate was recrystallized from 95% alcohol. The yield of diketone was 210 g., m. p. 90–92°. Duval¹⁰ reported a melting point of 93°.

1-(*p*-Benzylphenyl)-ethanol.—A solution of 170 g. of *p*-benzylacetophenone in enough absolute alcohol to make 510 cc. of solution was treated with Raney nickel catalyst at the boiling point for two hours; the nickel was removed by filtration; fresh catalyst was added and reduction with hydrogen was carried out at 75° and 1600 p.s.i. The catalyst was removed by centrifuging, the alcohol was distilled and the product purified by distillation. The yield was 147.5 g., b. p. 125–130° at 0.1 mm., m. p. 43–45°. A small sample was redistilled and it boiled at 114° at 0.06 mm. and melted at 46°.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 84.69; H, 7.88.

***p*-Benzylstyrene.**—Dehydration of 150 g. of 1-(*p*-benzylphenyl)-ethanol over (Alorco) activated alumina at 310° at 30–40 mm. pressure gave 114 g. (83.3%) of *p*-benzylstyrene, b. p. 76–78° at 0.06 mm., n_D^{20} 1.5949; d_4^{20} 1.0011.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.88; H, 7.28.

One cubic centimeter of the above styrene was treated with bromine in glacial acetic acid until the color of bromine persisted. It was then warmed on a steam cone a few minutes and diluted with water. The solid which separated on cooling was recrystallized from methanol. The product melted at 92–93°.

Anal. Calcd. for $C_{15}H_{14}Br_2$: C, 50.87; H, 3.99. Found: C, 51.17; H, 3.96.

A sample of 58 g. of the crude *p*-benzylstyrene was heated under total reflux for two hours and distilled to give 30 g. of product b. p. 83–90° at 0.2 mm., n_D^{20} 1.5806. This product was treated with bromine in glacial acetic acid until no more bromine was absorbed and then diluted with water. The oil was collected in ether and the solvent evaporated. The residue was crystallized from alcohol to remove most of the *p*-benzylstyrene dibromide. The alcoholic mother liquors were then distilled under reduced pressure to yield 2 g. of a product which boiled at 89–96° at 0.08 mm. pressure, n_D^{20} 1.5622. Another distillation gave a purer product, n_D^{20} 1.5620.

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.57; H, 8.19.

Walker¹¹ reported that *p*-benzylethylbenzene boils at 294–295° at 754 mm. but gave no refractive index. A small sample of *p*-benzylstyrene was reduced over Raney nickel catalyst to give *p*-benzylethylbenzene which boiled at 85° at 0.2 mm., n_D^{20} 1.5616.

Bis-[*p*-(1-hydroxyethyl)-phenyl]-methane.—A solution of 210 g. of bis-(*p*-acetylphenyl)-methane in 1500 cc. of alcohol was first treated with Raney nickel catalyst and then reduced with hydrogen over fresh catalyst at 75° and 1600 p.s.i. The catalyst was removed by filtration, the solution evaporated and a crude residue of 200 g. was obtained. Most of this material was used directly for dehydration. Five grams of the crude product was purified by twice recrystallizing from a 1:2 mixture of low boiling petroleum ether and benzene to yield a product, m. p. 85–86°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.87. Found: C, 79.85; H, 7.81.

The diphenylurethan prepared by the usual procedure was washed with carbon tetrachloride and low boiling

(10) Duval, *Compt. rend.*, **146**, 341 (1908); *Bull. soc. chim.*, [4] **7**, 796 (1910).

(11) Walker, *Ber.*, **5**, 686 (1872).

petroleum ether and then recrystallized from 95% alcohol. The product melted at 149–150°.

Anal. Calcd. for $C_{21}H_{20}O_4N_2$: C, 75.28; H, 6.11; N, 5.67. Found: C, 75.37; H, 6.27; N, 5.73.

Bis-(*p*-vinylphenyl)-methane.—The crude dicarbinol (134 g.) obtained above, dehydrated as described under *p*-benzylstyrene at 310° and 12 mm., gave 89 g. of crude product. Attempts to distil part of the product produced polymer in the distilling flask even when an inhibitor such as picric acid was added. By dissolving the product in ethyl alcohol at room temperature and cooling in a Dry Ice-bath and filtering at low temperature, pure hydrocarbon melting at 32° was obtained.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.62; H, 7.32. Found: C, 92.80; H, 7.18.

The tetrabromide was made by adding bromine in glacial acetic acid to glacial acetic acid solution of 2 g. of the hydrocarbon. The product was precipitated with water and recrystallized from a mixture of 20 cc. of methanol and 10 cc. of benzene; m. p. 146°.

Anal. Calcd. for $C_{17}H_{16}Br_4$: C, 37.81; H, 2.99. Found: C, 38.09; H, 2.97.

o-Fluorostyrene

o-Fluorostyrene has been prepared by Brooks.¹² We have applied the general styrene synthesis of Walling and Wolfstirn²⁸ to *o*-fluorobenzaldehyde and found the method very satisfactory.

o-Fluorotoluene.—When the general procedure described for the preparation of fluorobenzene¹³ was used, 574 g. of *o*-toluidine hydrochloride gave 207 g. of *o*-fluorotoluene.

o-Fluorobenzaldehyde.—When the general procedure described for the preparation of *p*-bromobenzaldehyde¹⁴ was followed, 127.6 g. of *o*-fluorotoluene gave 100 g. (71.3%) of *o*-fluorobenzaldehyde. Brooks¹² used chlorination in place of bromination in this preparation and obtained a 48% yield.

o-Fluorocinnamic Acid.—When the general procedure of Walling and Wolfstirn²⁸ was used, 100 g. of *o*-fluorobenzaldehyde gave 101 g. of the corresponding cinnamic acid, m. p. 177–178°. Kinder,¹⁵ who prepared this acid by a different route reports it as melting at 175°.

o-Fluorostyrene.—The general procedure of Walling and Wolfstirn²⁸ was used for the decarboxylation and from 95 g. of the cinnamic acid 45.6 g. (65.6%) of *o*-fluorostyrene, boiling at 46° at 32 mm., n_D^{20} 1.5201, was obtained. Brooks¹² reports n_D^{20} 1.5197.

o-Cyanostyrene

o-Cyanostyrene was prepared from *o*-tolunitrile by oxidation to *o*-cyanobenzaldehyde, followed by condensation with malonic acid and subsequent decarboxylation of the substituted cinnamic acid. The polymerization of this substituted styrene has not been studied.

o-Cyanobenzaldehyde Diacetate.—The procedure described for the conversion of *p*-nitrotoluene to *p*-nitrobenzaldehyde diacetate¹⁶ was used. From 84.2 g. of *o*-tolunitrile there was obtained 58.2 g. (34.6%) of the *o*-cyanobenzaldehyde diacetate, m. p. 94–95° after recrystallization from 95% alcohol.

Anal. Calcd. for $C_{12}H_{11}O_4N$: C, 61.79; H, 4.76. Found: C, 61.95; H, 4.69.

o-Cyanobenzaldehyde.—Hydrolysis of the above diacetate was carried out as described for the corresponding *p*-nitro compound.¹⁶ From 58.2 g. of diacetate there was obtained 26.7 g. (81.6%) of *o*-cyanobenzaldehyde which melted at 103–104° after recrystallization from alcohol.

(12) Brooks, *THIS JOURNAL*, **66**, 1295 (1944).

(13) Flood, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 295.

(14) Coleman and Honeywell, *ibid.*, p. 89.

(15) Kinder, *Ann.*, **464**, 278 (1928).

(16) Lieberman and Connor, "Organic Syntheses" Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943 p. 441

Blicke and Pobelski¹⁷ prepared this aldehyde from the corresponding benzal dibromide and reported the melting point at 108–109°.

o-Cyanocinnamic Acid.—The *o*-cyanobenzaldehyde, m. p. 103–104°, was converted to the cinnamic acid by the procedure of Walling and Wolfstirn²⁸ except the reaction mixture was heated for five hours. From 48.5 g. of aldehyde there was obtained 39.5 g. (61.7%) of *o*-cyanocinnamic acid, m. p. 253–254°. This agrees with the melting point (255°) reported in the Bayer Company patent.¹⁸

Anal. Calcd. for $C_{10}H_7O_2N$: C, 69.36; H, 4.07; N, 8.09. Found: C, 69.42; H, 3.80; N, 8.07.

o-Cyanostyrene.—The general method of Walling and Wolfstirn²⁸ was modified for the decarboxylation of *o*-cyanocinnamic acid by using more quinoline and distilling more slowly than they recommend. Twenty-three grams of the cinnamic acid, 5 g. of copper bronze powder and 275 g. of quinoline were used. About five-sixths of the material distilled in ninety minutes. Redistillation gave 5 g. (28.9%) of product, b. p. 53° at 0.15 mm., n_D^{20} 1.5756.

Anal. Calcd. for C_9H_7N : C, 83.69; H, 5.46. Found: C, 84.55; H, 5.61.

o-Cyanostyrene has been described as boiling at 96–100° at 9 mm., d_4^{20} 1.012.¹⁹

o-Cyanostyrene Dibromide.—Addition of excess bromine to a glacial acetic acid solution of *o*-cyanostyrene followed by dilution with water gave a solid dibromide.

After recrystallization from alcohol it melted at 86–86.5°.

Anal. Calcd. for $C_9H_7NBr_2$: C, 37.40; H, 2.44; Br, 55.31. Found: C, 37.65; H, 2.51; Br, 55.15.

Polymers of the New Styrene Derivatives.—Two cubic centimeters of monomer was placed in a quartz tube and placed under a 500-watt ultraviolet lamp until a solid polymer had formed. The time varied from two to four days for different monomers. The polymer was dissolved in 50 cc. of benzene and precipitated by dropping the solution into 500 cc. of vigorously stirred methanol. The powder thus obtained was dried in a vacuum desiccator at 0.03 mm. pressure.

Poly-*p*-benzylstyrene softened in a melting point tube at 105° and shrunk to a soft mass at 110°. It was slightly soluble in benzene, $[\eta]$ 0.91.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 91.84; H, 7.51.

Poly-bis-(*p*-vinylphenylmethane) did not soften visibly below 250°. It was insoluble in benzene, chloroform, nitromethane, carbon disulfide and other common solvents.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 91.65; H, 7.74.

Poly-*o*-methoxystyrene softened at 125° and turned to a soft mass at 130°. It was very soluble in benzene, $[\eta]$ 0.57.

Anal. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.45; H, 7.40.

Poly-*o*-fluorostyrene softened at 105° and shrunk to a soft mass at 110°. It was very soluble in benzene, $[\eta]$ 0.36.

Anal. Calcd. for C_8H_7F : C, 78.86; H, 5.78. Found: C, 77.88; H, 6.07.

The copolymerization of these styrenes with butadiene will be described later.

Summary

p-Benzylstyrene and bis-(*p*-vinylphenyl)-methane and their polymers are described for the first

(17) Blicke and Pobelski, *THIS JOURNAL*, **58**, 559 (1936).

(18) Bayer and Company, German Patent 116,123; *Chem. Zentr.*, **72**, I, 69 (1901); see also Drory, *Ber.*, **24**, 2574 (1891); Werner and Piquet, *ibid.*, **37**, 4310 (1904).

(19) Wingfoot Corporation, British Patent 571,829 (1945); *C. A.*, **41**, 3323 (1947).

time. New procedures for preparing *o*-fluorostyrene, *o*-methoxystyrene and *o*-cyanostyrene are described.

Two more examples of the disproportionation of phenylmethylcarbinols to ethylbenzenes under

the influence of activated alumina have been observed in the dehydration of *p*-benzylphenylmethylcarbinol and *o*-methoxyphenylmethylcarbinol.

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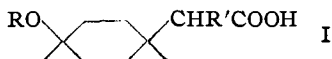
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The Hydrogenation of Phenolic Acids

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The catalytic reduction of phenolic acids has been investigated in the hope of obtaining a reasonably simple method for the preparation of acids of the type (I).



Previous attempts to prepare the methoxy acid (I, R = CH₃, R' = H) by catalytic reduction of the corresponding aromatic acid with platinum catalyst have been unsuccessful.¹ In numerous other investigations the catalytic reduction of phenolic acids has been reported to give low yields of hydroxycyclohexane acids due to side reactions. Low pressure hydrogenation, particularly in acid medium, causes considerable hydrogenolysis of the carbon-oxygen linkage with resultant loss of the hydroxyl group^{2,3,4} whereas high pressure hydrogenation with nickel catalyst leads largely to decarboxylation⁵ regardless of whether the acids or their sodium salts are reduced.⁴ The hydrogenolysis reaction in the low pressure hydrogenation with platinum can be repressed by reducing in the presence of alkali. Good yields of 4-hydroxycyclohexanecarboxylic acid have thus far been reported only for the hydrogenation of *p*-hydroxybenzoic acid in ethyl acetate over palladium-oxstrontium carbonate under high pressure.⁴

It has been shown in the present investigation that phenolic acids can be reduced smoothly to the hexahydro compounds by high pressure hydrogenation of their esters in alcoholic solution with W-2 Raney nickel catalyst⁶ in the presence of approximately 0.3 mole % of the sodium salts of these compounds. The reduction products are pure substances which consist of mixtures of *cis*- and *trans*-isomers and which are formed in nearly quantitative yield. A direct separation of the

isomers is rather difficult. A partial separation can be effected by adsorption of the esters on alumina. The *trans*-isomer is more strongly adsorbed.

The best method for the preparation of the pure *cis*- and *trans*-isomers consists in the reduction of the keto acids by specific reduction methods. Sodium and alcohol or sodium amalgam gives fairly pure *trans*-alcohols while the catalytic reduction with Raney nickel at room temperature yields predominantly *cis*-isomers.³

Experimental^{7,8}

The phenolic acids used in this investigation were commercial products with the exception of α -(*p*-hydroxyphenyl)-butyric acid which was prepared according to Wilds and Biggerstaff.^{9,10}

The ethyl esters of the phenolic acids were prepared by esterification of the acids with ethyl alcohol and sulfuric acid or by the method of Thielepape.¹¹ They were distilled under reduced pressure prior to reduction.

Hydrogenation of the Phenolic Esters.—The phenolic esters (0.2–1.0 mole) were dissolved in 100 cc. of absolute ethyl alcohol containing 0.3 mole % (on the basis of phenolic ester) of sodium ethoxide. Raney nickel (3–6 g.) was added and the mixture was immediately hydrogenated at between 160–220° (240–270 atm.) until the pressure remained constant. The catalyst was filtered off, the solvent was removed and the residue was distilled under reduced pressure. The constants of the products are given in Table I.

Preparation of the Keto Acids.—The hydroxycyclohexane esters described above were hydrolyzed by refluxing for two hours with four volumes of 10–20% aqueous sodium hydroxide solution and one volume of ethyl alcohol. The resultant solution was acidified with hydrochloric acid and extracted continuously with benzene. Most of the water and benzene were removed by distillation from a water-bath, the last traces under reduced pressure. The residual acids were used for the preparation of the keto acids without further purification. The mixtures of the isomeric acids were oxidized with chromic anhydride in aqueous acetic acid below 15°. Ethyl 4-hydroxycyclohexanecarboxylate was oxidized without previous hydrolysis. The resulting keto ester was purified through its bisulfite addition compound and was hydrolyzed on regeneration. The experimental data are given in Table II.

The keto acids were isolated by dilution of the reaction mixture with water and continuous extraction of the resultant solution with ether. The ether was removed by

- (1) Ruggli, Leupin and Businger, *Helv. Chim. Acta*, **24**, 339 (1941).
- (2) Balas and Kosik, *Časopis Českoslov. Lékárnictva*, **7**, 105 (1927); Balas and Srol, *Coll. Českoslov. Chem. Commun.*, **1**, 658 (1929); Edson, *J. Soc. Chem. Ind.*, **63**, 138T (1934); Long and Burger, *J. Org. Chem.*, **6**, 852 (1941); Price, Enos and Kaplan, *THIS JOURNAL*, **69**, 2261 (1947).
- (3) Hardegger, Plattner and Blank, *Helv. Chim. Acta*, **27**, 793 (1944).
- (4) Levin and Pendergrass, *THIS JOURNAL*, **69**, 2436 (1947).
- (5) Ipatiew and Razuvajew, *Ber.*, **58B**, 306 (1926); Mitsui, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **A18**, 329 (1935); Martin and Robinson, *J. Chem. Soc.*, 491 (1943).
- (6) Adkins and Pavlic, *THIS JOURNAL*, **69**, 3040 (1947).

- (7) All temperatures uncorrected.
- (8) Analyses by Karl Zilch.
- (9) Wilds and Biggerstaff, *THIS JOURNAL*, **67**, 789 (1945).
- (10) The authors are indebted to Dr. V. H. Wallingford of the Mallinckrodt Chemical Works for a generous supply of diethyl ethylphenylmalonate from which this acid was prepared.
- (11) Thielepape, *Ber.*, **66**, 1454 (1933).