[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

The Use of Liquid Phase Oxidation for the Preparation of Nuclearly Substituted Styrenes. III. *p*-Vinylbenzyl Acetate

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This paper is a continuation of previous work on the preparation of nuclearly substituted styrenes from the corresponding ethylbenzenes by oxidation, hydrogenation and dehydration.[1,2] Ethylbenzene was chloromethylated by Blanc's procedure[3] to give 71% of *p*-ethylbenzyl chloride. Blanc reported 65%. It was necessary to control the reaction temperature very closely at 66–69° to avoid markedly lower yields.

Treatment of *p*-ethylbenzyl chloride with sodium acetate in glacial acetic acid and with sodium ethylate in ethyl alcohol yielded *p*-ethylbenzyl acetate and *p*-ethylbenzyl ethyl ether, respectively. The yields were over 90%. Oxidation of the latter compound with air in the presence of chromium oxide attacked the carbon atom carrying the alkoxy group to give principally *p*-ethylbenzoic acid and ethyl *p*-ethylbenzoate.

In the presence of chromium oxide and calcium carbonate *p*-ethylbenzyl acetate was oxidized to *p*-acetylbenzylacetate in 23% conversion and 55% yield. This ketone was smoothly reduced to the corresponding carbinol with hydrogen in the presence of copper chromite. Some transesterification probably took place during the hydrogenation, since the product boiled over a fairly wide range. With aqueous potassium hydroxide this crude product yielded the glycol, *p*-(α-hydroxyethyl)-benzyl alcohol, and with acetic anhydride it yielded the diacetate, *p*-(α-acetoxyethyl)-benzyl acetate.

When *p*-(α-acetoxyethyl)-benzyl acetate was passed over a silica gel catalyst in the presence of steam at 475–500°, a 72% yield of *p*-vinylbenzyl acetate was obtained. Treatment of this compound with alcoholic potassium hydroxide yielded *p*-vinylbenzyl alcohol.

Experimental

***p*-Ethylbenzyl Chloride.**—In a 1-liter, three-necked flask equipped with a stirrer, thermometer, gas inlet and reflux condenser were placed 800 cc. of ethylbenzene, 60 g. of paraformaldehyde and 40 g. of fused and pulverized zinc chloride. While this mixture was stirred as vigorously as possible and the internal temperature was held strictly at 66–69°, a vigorous stream of hydrogen chloride was introduced until the mixture was saturated. At this point the flow was moderated, so that hydrogen chloride evolved slowly from the top of the condenser. The total reaction time was one hour. The hydrogen chloride flow was then stopped and the reaction mixture cooled to 25°. After pouring into a 1-liter separatory funnel, the layers were separated and the ethylbenzene transferred to another 1 liter separatory funnel to free it from any zinc chloride adhering to the sides of the original funnel. The ethylbenzene solution was washed six times with water and then dried over sodium sulfate. Distillation yielded, besides recovered ethylbenzene, 222 g. (71% based on formaldehyde) of *p*-ethylbenzyl chloride, b. p. 94–100° (11 mm.), (106–110° (15 mm.)),[4] n^{25}_{D} 1.5293.

***p*-Ethylbenzyl Ethyl Ether.**—To a solution of 5 g. of sodium in 200 cc. of absolute ethyl alcohol was added 31 g. of *p*-ethylbenzyl chloride and the mixture was refluxed for four hours. Upon cooling, it was diluted with water, acidified with acetic acid and the product extracted with benzene. Distillation of the benzene extracts yielded 31 g. (95%) of *p*-ethylbenzyl ethyl ether, b. p. 103–113° (14 mm.), n^{25}_{D} 1.4921. An analytical sample boiled at 106–107° (14 mm.), n^{25}_{D} 1.4918, d^{25}_{25} 0.923.

Anal.[5] Calcd. for $C_{11}H_{16}O$; C, 80.5; H, 9.76. Found: C, 80.7; H, 9.51.

Oxidation of *p*-Ethylbenzyl Ethyl Ether.—A stirred autoclave of about 1-liter capacity equipped with a stirrer, thermocouple well and reflux condenser with water trap was charged with 400 g. of *p*-ethylbenzyl ethyl ether and 4 g. of chromium oxide. While the mixture was stirred at 140°, air at 100 lb. per sq. in. was blown through the bomb for six hours at a rate of 2 cu. ft. per hr. Upon cooling, the bomb was opened and washed out with benzene. The combined reaction mixture and washings were filtered free of catalyst and then washed with sufficient aqueous sodium carbonate followed by water to remove all the acid products of the oxidation. When this extract was acidified, the precipitated *p*-ethylbenzoic acid was filtered, washed with water and dried. The yield was 80.1 g. (22%). It was purified by treating its solution in ammonium hydroxide with Norite and crystallizing the reprecipitated acid from 50% alcohol and then from water, m. p. 107.5–109.0° (113.5°).[6]

After being dried over potassium carbonate, the benzene solution was fractionated through a short Vigreux column. Two fractions were collected: at 96–98° (12 mm.) (107 g., n^{25}_{D} 1.5025) and at 98–104° (12 mm.) (21 g., n^{25}_{D} 1.4996) which represented a 32% recovery of crude *p*-ethylbenzyl ethyl ether. There was then obtained 27 g. (6%) of ethyl *p*-ethylbenzoate, b. p. 113–115° (12 mm.), n^{25}_{D} 1.5050, and 36 g. of high boiling oil, b. p. 116–156° (12 mm.), n^{25}_{D} 1.5099. An analytical sample of the ethyl *p*-ethylbenzoate boiled at 116° (13 mm.) (127.0–127.5° (16 mm.)),[1] n^{25}_{D} 1.5054 (n^{25}_{D} 1.5065),[1] d^{25}_{25} 1.011 (d^{25}_{25} 1.010).[1]

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.2; H, 7.87. Found: C, 74.9; H, 8.12.

Five grams of this material was refluxed for one and one-half hours with 40 cc. of 25% sodium hydroxide. The 2 cc. of distillate had n^{25}_{D} 1.3564 (n^{25}_{D} 1.3595 for ethyl alcohol)[7] and its 3,5-dinitrobenzoate melted at 88–92° (93° for ethyl 3,5-dinitrobenzoate).[8] The acid in the residue was obtained by acidification with dilute phosphoric acid. After crystallization from alcohol and then from water, it was found to be *p*-ethylbenzoic acid, m. p. 109–110° (113.5°).[6]

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[1] Emerson, Heyd, Lucas, Chapin, Owens and Shortridge, THIS JOURNAL, **68**, 674 (1946).

[2] Emerson, Heyd, Lucas, Cook, Owens and Shortridge, *ibid.*, **68**, 1665 (1946).

[3] Blanc, *Bull. soc. chim.*, [4] **33**, 313 (1923).

[4] Jones, *J. Chem. Soc.*, 1414 (1938).

[5] All of the analyses are microanalyses performed by the Oakwold Laboratories, Alexandria, Virginia.

[6] Kindler, *Ann.*, **452**, 90 (1927).

[7] Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1934, Vol. II, p. 16.

[8] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1940, p. 185.

p-**Ethylbenzyl Acetate.**—A mixture of 110 g. of fused sodium acetate, 800 cc. of glacial acetic acid and 223 g. of *p*-ethylbenzyl chloride was refluxed for thirty minutes. Upon cooling, the precipitated sodium chloride was removed by filtration, washed with 200 cc. of glacial acetic acid, and these washings together with 25 g. of fused sodium acetate were added to the filtrate. This was then refluxed for an additional two and one-half hours before dilution with water and removal of the product by benzene extraction. Distillation of this extract yielded 238 g. (93%) of *p*-ethylbenzyl acetate, b. p. 117–127° (14 mm.), n^{25}_{D} 1.5018. An analytical sample of the compound boiled at 130–132° (15 mm.), n^{25}_{D} 1.5042, d^{25}_{25} 1.028.

Anal. Calcd. for $C_{11}H_{14}O_2$; C, 74.3; H, 7.86. Found: C, 73.9; H, 7.91.

p-**Acetylbenzyl Acetate.**—A vigorous stream of air was introduced through an alundum disperser into a mixture of 485 g. of *p*-ethylbenzyl acetate, 5 g. of chromium oxide and 20 g. of calcium carbonate held at 130–140° for twenty-eight hours. Upon cooling, the catalyst was removed by filtration, and the filtered product was then refluxed for two hours with 10 g. of sodium acetate and 100 cc. of acetic anhydride. After dilution with water, the product was extracted with benzene and distilled to give 287 g. (59% recovery) of *p*-ethylbenzyl acetate, b. p. 119–129° (12 mm.), n^{25}_{D} 1.5011, and 118 g. (23% conversion and 55% yield) of *p*-acetylbenzyl acetate, b. p. 155–185° (12 mm.), n^{25}_{D} 1.5225. An analytical sample boiled at 161–163° (11 mm.), n^{25}_{D} 1.5225, d^{25}_{25} 1.126.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.8; H, 6.25. Found: C, 68.9; H, 6.66.

Its 2,4-dinitrophenylhydrazone melted at 182–183° after one crystallization from ethyl acetate.

Anal. Calcd. for $C_{17}H_{16}O_6N_4$: N, 15.1. Found: N, 15.0.

Its semicarbazone was crystallized twice from 50% alcohol and twice from 95% alcohol, m. p. 166–167°.

Anal. Calcd. for $C_{12}H_{15}O_3N_3$: C, 57.8; H, 6.02; N, 16.9. Found: C, 58.0; H, 6.05; N, 16.9.

p-(α-**Hydroxyethyl)-benzyl Acetate.**—A mixture of 215 g. of *p*-acetylbenzyl acetate and 25 g. of copper chromite was shaken for six hours in standard equipment with hydrogen at an initial pressure of 2000 pounds. Reduction was effected at 135–155°. Upon cooling, the charge was removed from the bomb, filtered and the precipitate washed with benzene. Distillation of the filtrate yielded 184 g. (85%) of crude *p*-(α-hydroxyethyl)-benzyl acetate, b. p. 135–160° (3 mm.).

p-(α-**Hydroxyethyl)-benzyl Alcohol.**—A mixture of 48 g. of crude *p*-(α-hydroxyethyl)-benzyl acetate, 56 g. of potassium hydroxide and 500 cc. of water was boiled under reflux overnight. After cooling, the solution was saturated with potassium carbonate and the organic layer separated. It was distilled to give 10 g. (27%) of *p*-(α-hydroxyethyl)-benzyl alcohol, b. p. 170° (7 mm.), n^{25}_{D} 1.5493, d^{25}_{25} 1.122.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.1; H, 7.90. Found: C, 71.0; H, 7.92.

p-(α-**Acetoxyethyl)-benzyl Acetate.**—A mixture of 48 g. of crude *p*-(α-hydroxyethyl)-benzyl acetate, 24 g. of sodium acetate and 480 cc. of acetic anhydride was heated at 100° for three hours and then allowed to stand overnight. The acetic anhydride was then distilled until the volume of the residue was reduced to 200 cc. before dilution with 1.0 liter of water. After it had stood one hour, it was extracted three times with benzene. The combined extracts were washed three times with water. Distillation yielded 44 g. (75%) of *p*-(α-acetoxyethyl)-benzyl acetate, b. p. 144–153° (3 mm.), n^{25}_{D} 1.4998, d^{25}_{25} 1.114.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.1; H, 6.78; sap. equiv., 118. Found: C, 66.0; H, 6.73; sap. equiv., 125, 123.

p-**Vinylbenzyl Acetate.**—A quartz tube similar to that described previously[9] was packed with a silica gel catalyst. While the tube was kept at 475–500° and steam was introduced at a pressure of 25–30 mm., 139.5 g. of *p*-(α-acetoxyethyl)-benzyl acetate was introduced over a one hundred-minute period. The tube was steamed for another ten minutes, cooled and washed with benzene. The combined distillate and washings were twice extracted with benzene. The combined extracts were distilled from sulfur and hydroquinone to give 57 g. (55%) of *p*-vinylbenzyl acetate, b. p. 128–158° (15 mm.), n^{25}_{D} 1.5348, and 33 g. of *p*-acetylbenzyl acetate, b. p. 158–178° (15 mm.), n^{25}_{D} 1.5201. The latter compound was apparently present in the crude *p*-(α-acetoxyethyl)-benzyl acetate which was obtained from a different reduction than that described above. Correction therefor raises the yield of *p*-vinylbenzyl acetate to 72%. An analytical sample boiled at 136–139° (15 mm.), n^{25}_{D} 1.5350, d^{25}_{25} 1.051.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.0; H, 6.82. Found: C, 75.1; H, 6.96.

p-**Vinylbenzyl Alcohol.**—A solution of 3.5 g. of *p*-vinylbenzyl acetate, 3.5 g. of potassium hydroxide, 0.5 g. of sulfur and 0.5 g. of hydroquinone in 25 cc. of ethyl alcohol was boiled under reflux for one-half hour. It was then diluted with 200 cc. of water, acidified with 5 cc. of glacial acetic acid and twice extracted with benzene. The combined extracts were filtered and distilled to yield 1 g. (38%) of *p*-vinylbenzyl alcohol, b. p. 132–137° (15 mm.), n^{25}_{D} 1.5697. The sample was redistilled at 5 mm. before analysis.

Anal. Calcd. for $C_9H_{10}O$: C, 80.6; H, 7.47. Found: C, 79.8; H, 7.37.

Summary

The liquid phase oxidation of *p*-ethylbenzyl acetate to *p*-acetylbenzyl acetate has been effected in 23% conversion and 55% yield. This reaction, followed by hydrogenation, acetylation and pyrolysis, constitutes a convenient synthesis of *p*-vinylbenzyl acetate.

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(9) Emerson and Agnew, THIS JOURNAL, **67**, 518 (1945).