

α -NAPHTHYL- AND α -TETRALYL-CINNAMIC ACIDS

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In connection with studies on the reduction of substituted naphthalene compounds with Raney's alloy and aqueous alkali (1), several naphthyl- and tetralyl-cinnamic acids as well as the corresponding α -naphthyl- and α -tetralyl-propionic acids were required. The Perkin condensation of naphthylacetic acids and nitrobenzaldehydes has been extensively applied for the synthesis of naphthyl-nitrocinnamic acids (2), the latter substances being intermediates in the Pschorr synthesis of polycyclic hydrocarbons (3). Halogen and alkyl substituted naphthylcinnamic acids (4) have also been secured by this synthesis. However, the preparation and characterization of α (1- and 2-naphthyl)- and α (1- and 2-*ar*-tetralyl)-cinnamic acids and the *p*-hydroxy derivatives have apparently not been described.

The Perkin condensation of benzaldehyde and *p*-hydroxybenzaldehyde with the anhydrous alkali metal salts of α - and β -naphthaleneacetic acids gave the naphthylcinnamic acids in crude yields of 60–93%. Similarly, the *ar*-tetralyl-cinnamic acids were obtained in 58–73% yields. The requisite α -*ar*-tetralylacetic acid was secured by Raney alloy reduction of α -naphthaleneacetic acid (1), whereas the β -*ar*-tetralylacetic acid was obtained from 6-acetyltetralin by the morpholine modification of the Willgerodt reaction (5).

In previous publications, it has been shown that cycloalkene- (6) and aryloxyacetic acids (7) may be condensed in fair yield with aromatic aldehydes using equimolecular amounts of potassium acetate or triethylamine. This method has been found applicable to the naphthyl- and *ar*-tetralyl-acetic acids. In the three condensations in which the free arylacetic acids were used, yields comparable to those obtained by the conventional condensation procedure were secured.

Reduction of the α -naphthylcinnamic acids to the α -naphthyl- β -phenylpropionic acids proceeded smoothly in dilute alkali with either Raney's catalyst at 25–30 pounds hydrogen pressure or with sodium amalgam. Somewhat better yields and purer products were obtained with the Raney catalyst reduction. The α -*ar*-tetralyl- β -phenylpropionic acids were secured in practically quantitative yields from the corresponding cinnamic acids by Raney alloy reduction (8).

EXPERIMENTAL

The Perkin condensations were carried out in 3-necked flasks equipped with stirrer, thermometer, and condenser carrying a calcium chloride tube. All melting points are corrected.

α -(α -Naphthyl)cinnamic acid. Method I. A mixture of 93 g. (0.5 mole) of α -naphthaleneacetic acid, 53 g. (0.5 mole) of freshly distilled benzaldehyde, 50 g. (0.5 mole) of anhydrous triethylamine, and 300 cc. of acetic anhydride was heated for 20 hours at 110–115°. After cooling the reaction mixture to 60°, the excess acetic anhydride was decomposed cautiously with water and then the mixture was poured into two liters of 5% hydrochloric acid.

After standing overnight, the supernatant liquid was decanted and the solid cake dissolved in hot sodium carbonate solution. Norit was added and the alkaline solution filtered and acidified; yield 82 g. (60%); m.p. 140–146°. The crude cinnamic acid was dissolved in 500 cc. of 10% sodium hydroxide, the resulting solution saturated with sodium chloride and cooled overnight at 5°. The precipitated sodium salt was filtered, dissolved in water and, after treating with Norit, was filtered. On acidification, the cinnamic acid was obtained as a white crystalline solid, yield 64 g.; m.p. 160–162°. The analytical sample was recrystallized from benzene-petroleum ether, m.p. 165–166°.

Anal. Calc'd for $C_{19}H_{14}O_2$: C, 83.18; H, 5.11.

Found: C, 82.94; H, 5.38.

Method II. The condensation of 44.8 g. (0.2 mole) of anhydrous potassium α -naphthylacetate and 21.2 g. (0.2 mole) of benzaldehyde in 200 cc. of acetic anhydride for eight hours at 105–110° gave 38 g. (69%) of the crude cinnamic acid, m.p. 152–154°. Recrystallized from benzene-petroleum ether, yield 30 g. (55%); m.p. 163–164°.

α -(α -Naphthyl)- β -phenylpropionic acid. This compound was secured from the corresponding cinnamic acid by reduction with Raney's catalyst in 2% sodium hydroxide solution at a pressure of 25–30 lbs. An 80% yield of the propionic acid was obtained, m.p. 136–137°, after recrystallization from benzene-petroleum ether or *n*-hexane.

Anal. Calc'd for $C_{19}H_{16}O_2$: C, 82.57; H, 5.98.

Found: C, 82.40; H, 6.12.

α -(β -Naphthyl)cinnamic acid. This compound was secured from β -naphthaleneacetic acid (9) by method II in 65% yield, m.p. 204–205°. Recrystallized from aqueous alcohol for analysis, m.p. 209.5–210.5°.

Anal. Calc'd for $C_{19}H_{14}O_2$: C, 83.18; H, 5.11.

Found: C, 83.02; H, 5.36.

α -(β -Naphthyl)- β -phenylpropionic acid. A quantitative yield of this compound was obtained by preparing it as described for the corresponding α -compound. Recrystallized from a mixture of ether-petroleum ether, m.p. 148–149°.

Anal. Calc'd for $C_{19}H_{16}O_2$: C, 82.57; H, 5.98.

Found: C, 83.02; H, 5.90.

*α -(α -Naphthyl)-*p*-hydroxycinnamic acid.* A mixture of 22.4 g. (0.1 mole) of anhydrous potassium α -naphthaleneacetate, 12.2 g. (0.1 mole) of *p*-hydroxybenzaldehyde and 300 cc. of acetic anhydride was heated for eight hours at 105–110° with stirring. The reaction product, after decomposition with water, was poured into 5% hydrochloric acid and allowed to stand overnight. The crude condensation product was filtered and then dissolved in 300 cc. of 20% sodium hydroxide. The alkaline solution was heated, treated with Norit and filtered. To the filtrate, 100 g. of sodium chloride was added, the mixture heated to boiling, Norit added and the solution then filtered through a heated funnel. On cooling the filtrate, the sodium salt of the cinnamic acid precipitated. It was filtered, dissolved in hot water and treated with Norit. After filtering, the aqueous solution was acidified, yield 26.8 g. (93%); m.p. 170–175°. Recrystallized from acetone-water, yield 18 g. (62%); m.p. 216–216.5°. The product crystallized with a molecule of water.

Anal. Calc'd for $C_{19}H_{14}O_3 \cdot H_2O$: C, 74.02; H, 5.23.

Found: C, 74.04; H, 5.24.

Recrystallized from a mixture of benzene-petroleum ether, the substituted *p*-hydroxycinnamic acid melted at 213–214° after drying *in vacuo* over xylene.

Anal. Calc'd for $C_{19}H_{14}O_3$: C, 78.59; H, 4.86.

Found: C, 78.56; H, 5.05.

The condensation of the free acid, *p*-hydroxybenzaldehyde and triethylamine by method I gave a 66% yield of the crude substituted cinnamic acid, m.p. 180–192°.

*α -(α -Naphthyl)- β -(*p*-hydroxyphenyl)propionic acid.* This compound was obtained in 78% yield from the corresponding cinnamic acid (5 g.) by reduction with 200 g. of 5% sodium amalgam in dilute sodium hydroxide solution. The propionic acid melted at 161–162° after recrystallization from ether-petroleum ether.

Anal. Calc'd for $C_{19}H_{16}O_2$: C, 78.05; H, 5.52.

Found: C, 78.23; H, 5.57.

α -(β -Naphthyl)-*p*-hydroxycinnamic acid. In accordance with method II, a mixture of 61 g. (0.5 mole) of *p*-hydroxybenzaldehyde, 112 g. (0.5 mole) of anhydrous potassium β -naphthylacetate, and 450 cc. of acetic anhydride was heated with stirring for eight hours at 110°. After decomposing the excess acetic anhydride with water, the crude condensation product was purified by solution in sodium carbonate, yield 125 g. (85%); m.p. 211–215°. Recrystallized from aqueous ethanol, yield 105 g.; m.p. 232.5–233.5°. The analytical sample melted at 238–239°.

Anal. Calc'd for $C_{19}H_{14}O_2$: C, 78.59; H, 4.87.

Found: C, 78.62; H, 5.27.

α -(β -Naphthyl)- β -(*p*-hydroxyphenyl)propionic acid. By reduction with Raney catalyst in alkaline solution at 35–40 pounds, this compound was obtained from the cinnamic acid in quantitative yield, m.p. 198–200°. The analytical sample melted at 206–207° after recrystallization from benzene-petroleum ether.

Anal. Calc'd for $C_{19}H_{16}O_2$: C, 78.05; H, 5.52.

Found: C, 78.15; H, 5.65.

α -(5,6,7,8-Tetrahydro- α -naphthyl)cinnamic acid. Using method II, this compound was obtained from anhydrous potassium α -*ar*-tetralylacetate (1) and benzaldehyde, yield 68%; m.p. 160–162°. Recrystallized from benzene-petroleum ether, m.p. 172–173°.

Anal. Calc'd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52.

Found: C, 82.28; H, 6.60.

α -(5,6,7,8-Tetrahydro- α -naphthyl)- β -phenylpropionic acid. This compound was obtained by Raney alloy reduction of the corresponding cinnamic acid in 95% yield; m.p. 100–106°. Recrystallized from ligroin (b.p. 65–68°), m.p. 111–112°.

Anal. Calc'd for $C_{19}H_{20}O_2$: C, 81.38; H, 7.19.

Found: C, 81.08; H, 7.07.

α -(5,6,7,8-Tetrahydro- β -naphthyl)cinnamic acid. This acid was secured by method II from anhydrous potassium β -*ar*-tetralylacetate and benzaldehyde, yield 65%; m.p. 160–166°. Recrystallized from aqueous ethanol, m.p. 179–180°.

Anal. Calc'd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52.

Found: C, 81.93; H, 6.52.

The β -*ar*-tetralylacetic acid was obtained from 6-acetyltetralin (10) by the morpholine modification of the Willgerodt reaction (7). The 6-tetralylthioacetmorpholide was obtained in 94% yield, m.p. 96–104°. Recrystallized from benzene-petroleum ether, m.p. 115–116°.

Anal. Calc'd for $C_{16}H_{21}NOS$: N, 5.09. Found: N, 5.40.

Hydrolysis with alcoholic alkali gave an 84% yield of the crude β -*ar*-tetralylacetic acid. Recrystallized from benzene, m.p. 98.5–99.5°, literature m.p. 97.2–97.5° (10).

α -(5,6,7,8-Tetrahydro- β -naphthyl)- β -phenylpropionic acid. This compound was obtained from the corresponding cinnamic acid by reduction with Raney's alloy and aqueous alkali, yield 90%; m.p. 88–89° after recrystallization from ligroin (b.p. 65–68°).

Anal. Calc'd for $C_{19}H_{20}O_2$: C, 81.38; H, 7.19.

Found: C, 81.20; H, 6.82.

α -(5,6,7,8-Tetrahydro- α -naphthyl)-*p*-hydroxycinnamic acid. A mixture of 22.8 g. (0.1 mole) of anhydrous potassium *ar*-tetrahydro- α -naphthylacetate and 12.2 g. (0.1 mole) of *p*-hydroxybenzaldehyde in 300 cc. acetic anhydride was heated for eight hours at 110–115° with stirring. The crude α -(5,6,7,8-tetrahydro- α -naphthyl)-*p*-hydroxycinnamic acid, after recrystallization from benzene-petroleum ether, melted at 221–221.5°; yield 17 g. (58%).

Anal. Calc'd for $C_{19}H_{18}O_2$: C, 77.53; H, 6.17.

Found: C, 77.72; H, 6.35.

α -(5,6,7,8-Tetrahydro- α -naphthyl)- β -(*p*-hydroxyphenyl)propionic acid. This acid was

obtained from the corresponding cinnamic acid either by reduction with Raney's catalyst in alkaline solution at 25 lbs. pressure or by treating with Raney's alloy and aqueous alkali. Recrystallized from benzene, m.p. 175-176°.

Anal. Calc'd for $C_{19}H_{20}O_2$: C, 76.99; H, 6.87.

Found: C, 77.06; H, 7.13.

α -(5,6,7,8-Tetrahydro- β -naphthyl)-*p*-hydroxycinnamic acid. Using method I, this compound was obtained from β -*ar*-tetralylacetic acid and *p*-hydroxybenzaldehyde in 73% yield, m.p. 201-202° after recrystallization from aqueous ethanol.

Anal. Calc'd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.17.

Found: C, 77.66; H, 6.20.

α -(5,6,7,8-Tetrahydro- β -naphthyl)- β -(*p*-hydroxyphenyl)propionic acid. This compound was obtained from the corresponding cinnamic acid by Raney alloy reduction, yield 95%; m.p. 205-206° after recrystallization from aqueous ethanol.

Anal. Calc'd for $C_{19}H_{20}O_3$: C, 76.99; H, 6.87.

Found: C, 76.81; H, 6.80.

SUMMARY

The Perkin synthesis of naphthyl- and *ar*-tetralyl-cinnamic acids and the *p*-hydroxy derivatives is described. The naphthylcinnamic acids were reduced to the corresponding propionic acids by sodium amalgam or Raney's catalyst, whereas the *ar*-tetralylcinnamic acids were reduced with Raney's alloy in aqueous alkali.

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