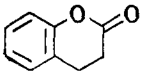
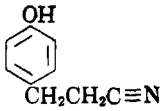
hydroxyphenyl)propionitrile, II, was obtained in 72% yield. In addition, a careful fractional distillation of the products of the reaction gave the δ-lactone of β-(o-hydroxyphenyl)propionic acid, I, in 3% yield.


I


II

Although several experiments were made, at no time under the reaction conditions used, was any trace of the *ortho*-cyanoethylphenol observed. It is reasonable to expect that this compound or its tautomeric imine was attacked by the neighboring *ortho*-phenolate ion in the aluminum chloride complex or during the subsequent hydrolysis of the complex ions. The relatively low yield of this *ortho* addition compound suggests steric hindrance.

EXPERIMENTAL

Four hundred grams (3 moles) of anhydrous C.P. aluminum chloride was added slowly with rapid mechanical stirring at 15° to 564 g. (6 moles) of freshly distilled phenol and 387 g. (6 moles) of freshly distilled acrylonitrile. Dry hydrogen chloride was passed into the rose-colored viscous slurry over a period of about 1.5 hr. during which time there was a pronounced decrease in viscosity of the mixture.

The slurry was heated to 80° whereupon it dissolved to a dark red fluid solution. Although further external heating was discontinued the reaction was strongly exothermic and refluxed at 105°. Addition of dry gas was continued over a period of 1.5 hr. after which the mixture was allowed to cool.

The contents of the reaction vessel were poured over 2 kg. of cracked ice and stirred until the precipitated salts redissolved. The dark red phenolic layer was removed by means of a separatory funnel and the aqueous portion was extracted with two 250-ml. portions of toluene which were combined with the phenolic material. The organic mixture was washed several times with 10% potassium chloride solution and stripped of solvent at reduced pressure.

Vacuum distillation of the residue through a 24-in. helix-packed column connected to a distillation head equipped for partial take-off gave 374 g. of phenol, b.p. 69° at 7 mm.; 15 g. of melilotol (containing phenol as a contaminant), b.p. 84–109° at 1 mm.; and 317 g. of β-(p-hydroxyphenyl)-propionitrile, b.p. 157–163° at 1 mm., m.p. 58–59°, which is in agreement with that recorded in the literature.[7] Alkaline hydrolysis of this nitrile gave phloretinic acid, m.p. 127–129°.[8]

Redistillation of the second fraction gave melitolol, b.p. 111–112° at 2.5 mm., identified by comparison of its infrared spectrum with that of an authentic sample prepared by an independent method.[9,10]

Strong bands in the infrared spectrum of the lactone were noted at 1775, 1242, 1227, 1140, and 760 cm.$^{-1}$ Hydrolysis of the lactone with aqueous KOH followed by acidification gave melilotic acid, m.p. 81–83°. A mixed melting point with an authentic sample[9] showed no depression.

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NEWARK COLLEGE OF ARTS AND SCIENCES
RUTGERS, THE STATE UNIVERSITY
NEWARK 2, N. J.

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α-Phenylcycloalkylideneacetic Acids

F. F. BLICKE AND R. H. COX

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α-Phenyl-3-methylcyclohexylidenaecetic, α-phenyl-4-methylcyclohexylideneacetic and α-phenylcycloöctylideneacetic acids have been prepared by dehydration of the required α-phenyl-α-(1-hydroxycycloalkyl)acetic acids[1] with acetic anhydride according to the procedure described for α-phenylcyclohexylideneacetic acid.[2] The ultraviolet absorption spectra of the new acids were compared with those of α-phenylcyclohexylideneacetic acid[2,3] and α-phenyl-1-cyclohexenylacetic acid.[3] The spectrum of each new acid was essentially coincident with that of α-phenylcyclohexylideneacetic acid,[4] which indicated that each possessed the α-phenylcycloalkylideneacetic acid structure rather than that of the corresponding α-phenyl-1-cycloalkenylacetic acid. The much lower adsorption above 220 mμ shown by α-phenyl-1-cyclohexenylacetic acid was expected, since the ethylenic bond in this compound is not in conjugation with the benzene nucleus.

EXPERIMENTAL

α-Phenyl-3-methylcyclohexylideneacetic acid. This acid, obtained in 22% yield after recrystallization from petroleum ether (90–100°), melted at 142–148°; it was undoubtedly a mixture of geometric isomers.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.24; H, 7.86: neut. equiv., 230.3. Found: C, 78.20; H, 8.10; neut. equiv., 230.1.

α-Phenyl-4-methylcyclohexylideneacetic acid. This acid melted at 122–124° after recrystallization from absolute ethanol; yield 36%.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.24; H, 7.86; neut. equiv., 230.3. Found: C, 78.28; H, 8.19; neut. equiv., 229.3.

α-Phenylcycloöctylideneacetic acid. This acid, obtained in 11% yield, melted at 139–141° after recrystallization from absolute ethanol.

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[3] α-Phenylcyclohexylideneacetic acid and α-phenyl-1-cyclohexenylacetic acid, which are structural isomers, were prepared and characterized by oxidative degradation by Phalnikar and Nargund.[2]

[4] The ultraviolet absorption spectrum determined by us for α-phenylcyclohexylideneacetic acid was in agreement with that reported by K. Scholz, M. Spillman, E. Tagmann, and K. Hoffman [*Helv. Chim. Acta*, **35**, 2016 (1952)] for a basic ester of this acid.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25; neut. equiv., 244.3. Found: C, 78.17; H, 8.34; neut. equiv., 245.4.

The ultraviolet absorption spectra were determined between 220 and 300 mμ with a Beckman DU spectrophotometer. A concentration of 0.01% in absolute ethanol was employed in each case.

COLLEGE OF PHARMACY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICH.

Reactions of Vanillin and Its Derived Compounds. XXVIII.[1] Coniferaldehyde and *p*-Coumaraldehyde

IRWIN A. PEARL AND STEPHEN F. DARLING[2]

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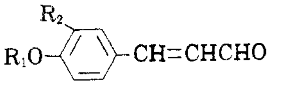
In connection with other studies in these laboratories on reactions of lignin, wood, and wood extractives, it was necessary to prepare substantial quantities of coniferyl aldehyde (I) and *p*-coumaraldehyde (II). These aldehydes had been prepared recently by Freudenberg and co-workers[3,4] by the stannous chloride reduction of the phenylimidochlorides of the corresponding acetylated acids, but the procedures involved did not lend themselves to quantity production. Attempts to adapt the Rosenmund procedure as used by Freudenberg and Hübner[5] for the preparation of the closely related sinapyl aldehyde resulted only in the recovery of the acid chlorides as their parent acids. The elegant method of Brown and McFarlin[6] for the production of aldehydes by the reduction of acid chlorides with lithium tri-*t*-butoxyaluminohydride was tried on acetylferulic and acetyl *p*-coumaric acid chlorides. These acid chlorides gave good yields of acetylconiferyl aldehyde (III) and acetyl *p*-coumaraldehyde (IV), respectively, and the acetylated aldehydes yielded the desired coniferyl aldehyde and *p*-coumaraldehyde upon hydrolysis with sodium methylate in chloroform solution.



I, $R_1 = H$; $R_2 = CH_3O$
II, $R_1 = R_2 = H$
III, $R_1 = CH_3CO$; $R_2 = CH_3O$
IV, $R_1 = CH_3CO$; $R_2 = H$

EXPERIMENTAL

All melting points are uncorrected, and ultraviolet spectral data are for solution in 95% ethanol (concentration, 0.02 g. per liter).

Lithium tri-t-butoxyaluminohydride. The reagent was prepared by treating a filtered solution of lithium aluminum hydride in absolute ether with dry *t*-butyl alcohol with stirring. The white precipitate was filtered, washed with anhydrous ether, and dried at 60°.

Acetylconiferylaldehyde (III). A solution of 12.2 g. (0.05 mole) of acetylferuoyl chloride[3] in 75 ml. of dry tetrahydrofuran was placed in a 250-ml. 3-neck flask fitted with a dropping funnel, thermometer, and mercury-sealed stirrer, and immersed in a Dry Ice–acetone bath. The solution was cooled to $-65°$ and treated dropwise with stirring with a solution of 12.7 g. (0.05 mole) of lithium tri-*t*-butoxyaluminohydride in 50 ml. of dry tetrahydrofuran while maintaining the temperature at $-65°$. After addition was complete the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature with stirring. With rise in temperature, the turbid mixture became clear. When the temperature reached 20° the mixture was poured onto a mixture of crushed ice and water. The precipitate was filtered, and the filtrate deposited colorless platelets upon standing. These were collected, and the filtrate was concentrated and cooled to give more platelets. The total yield of platelets melting at 95–96° was 1.2 g. The original aluminum hydroxide precipitate was extracted with boiling ethanol, and the ethanol was concentrated in a rotating evaporator to yield 5.0 g. of product melting at 81–97°. Both of these products, when adsorbed on aluminum oxide and eluted with ether, yielded pure pale yellow crystals of III melting at 97–98° and having the following maxima in its ultraviolet absorption spectrum: λ_{max} 240 mμ, ϵ 11800; λ_{max} 290 mμ, ϵ 19440.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.67; H, 5.49.

Freudenberg and Dillenburg[3] reported a melting point of 102–103° for III prepared by acetylation of isolated I, but repetition of their work in this laboratory confirmed the 97–98° melting point.

This experiment was repeated with diglyme as the solvent with essentially the same results.

Coniferaldehyde (I). A solution of 2 g. of III in 50 ml. of chloroform was treated with cooling with a solution of 0.5 g. of sodium in 10 ml. of anhydrous methanol. The mixture was allowed to stand at 20° for 30 min., and then treated with 50 ml. of water. The mixture was shaken, and the aqueous layer was separated and acidified with dilute sulfuric acid. The acidified mixture was extracted with chloroform, and the chloroform was dried and concentrated to dryness. The residual sirup was covered with a little benzene and scratched to induce crystallization. The crude crystals melted at 70–72°, and the material obtained upon recrystallization from benzene melted at 80–81° and did not depress the melting point of authentic coniferaldehyde.[3] The yield was 75%.

Acetyl p-coumaraldehyde (IV). Similar reduction of 11.2 g. of acetyl *p*-coumaroyl chloride (m.p. 119–121° from benzene–petroleum ether) in diglyme or tetrahydrofuran as a solvent yielded 7 g. of crude IV melting at 70–75° which, upon recrystallization from ether–petroleum ether, yielded colorless crystals of IV melting at 77–78° and having the following maxima in its ultraviolet absorption spectrum: λ_{max} 223 mμ, ϵ 14800; λ_{max} 293 mμ, ϵ 24750.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.32; H, 5.17.

The *semicarbazone*, after crystallization from ethanol, melted at 213–215°.

Anal. Calcd. for $C_{12}H_{13}O_3N_3$: C, 58.29; H, 5.30. Found: C, 58.46; H, 5.26.

p-Coumaraldehyde (II). Reduction of IV with a solution of sodium methylate in methanol-chloroform as described

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