β-AROYL-α- AND -β-ARYLPROPIONIC ACIDS

PART I. THEIR PREPARATION AND LACTONIZATION[1]

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ABSTRACT

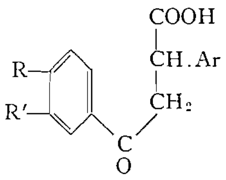
Bromobenzene reacts with phenyl- and *p*-methoxyphenyl-succinic anhydride in the presence of anhydrous aluminum chloride to give a mixture of β-*p*-bromobenzoyl-α- and -β-phenylpropionic acid, and a mixture of β-*p*-bromobenzoyl-α- and -β-*p*-hydroxyphenylpropionic acid, respectively.

Similarly, iodobenzene reacts with the same anhydrides to give a mixture of β-*p*-iodobenzoyl-α- and -β-phenylpropionic acid and β-benzoyl-α- and -β-phenylpropionic acid, and a mixture of β-benzoyl- and β-*p*-iodobenzoyl-α-*p*-methoxyphenylpropionic acid, respectively.

Phenyl- and diphenyl-succinic anhydride are cyclized by aluminum chloride to 1-ketoindane- and 1-keto-2-phenylindane-3-carboxylic acid, respectively.

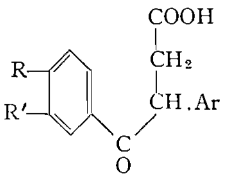
The above keto acids are converted by boiling acetic anhydride into β,γ-unsaturated γ-lactones.

Condensation of phenylsuccinic anhydride with bromobenzene in the presence of anhydrous aluminum chloride gave rise to a mixture of β-*p*-bromobenzoyl-α- and -β-phenylpropionic acid (I*a* and II*a*, respectively) in which the latter was predominant. The structure of the α-phenyl isomer was established by comparison with an authentic specimen prepared after Allen, Normington, and Wilson (1). The structure of the β-phenyl isomer was established by elemental analysis and by the production of *p*-bromobenzoic acid on oxidation with alkaline potassium permanganate. The reaction mixture contained a neutral product which was proved to be *p*-dibromobenzene, probably produced by the action of aluminum chloride on bromobenzene.



I

(*a*) R = Br; R′ = H; Ar = C_6H_5
(*b*) R = Br; R′ = H; Ar = *p*-HOC_6H_4
(*c*) R = I; R′ = H; Ar = C_6H_5
(*d*) R = R′ = H; Ar = C_6H_5
(*e*) R = R′ = H; Ar = *p*-$CH_3OC_6H_4$
(*f*) R = I; R′ = H; Ar = *p*-$CH_3OC_6H_4$
(*g*) R = R′ = Cl; Ar = C_6H_5
(*h*) R = R′ = Cl; Ar = H



II

(*a*) R = Br; R′ = H; Ar = C_6H_5
(*b*) R = Br; R′ = H; Ar = *p*-HOC_6H_4
(*c*) R = I; R′ = H; Ar = C_6H_5
(*d*) R = R′ = H; Ar = C_6H_5

When phenylsuccinic anhydride was replaced by *p*-methoxyphenylsuccinic anhydride, a mixture of β-*p*-bromobenzoyl-α- and -β-*p*-hydroxyphenylpropionic acid (I*b* and II*b*, respectively) was produced in which the latter was predominant. The structure of the α-*p*-hydroxyphenyl isomer was established by its identity with an authentic specimen prepared from *p*-bromophenyl 4-methoxystyryl ketone. The presence of the hydroxyl group was established by its infrared spectrum (see Experimental). The structure of the β-*p*-bromobenzoyl-β-*p*-hydroxyphenylpropionic acid was established by elemental analysis and by oxidation to *p*-bromobenzoic acid.

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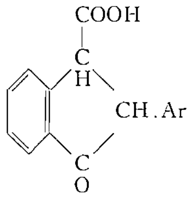
The condensation of phenylsuccinic anhydride with iodobenzene under the same conditions gave a mixture of β-*p*-iodobenzoyl-α- and -β-phenylpropionic acid (I*c* and II*c*, respectively) and β-benzoyl-α- and β-phenylpropionic acid (I*d* and II*d*, respectively). The structure of the first acid was established by comparison with an authentic specimen prepared from *p*-iodophenyl styryl ketone. The structure of the second acid was inferred from its elemental analysis, and from the fact that it gave, on oxidation with alkaline potassium permanganate, *p*-iodobenzoic acid. The structure of the halogen-free acids was established by comparison with authentic specimens (2). The formation of the halogen-free acids is due to the partial dehalogenation of iodobenzene to benzene, under the experimental conditions, and not to the partial dehalogenation of the β-aroylpropionic acids for the following reasons: (i) *o*- and *p*-diiodobenzene were isolated from the reaction mixture, and from a mixture of aluminum chloride and iodobenzene treated under the same conditions, and (ii) β-*p*-iodobenzoyl-α-phenylpropionic acid was recovered unchanged, when heated with aluminum chloride in toluene at 100° for 3 hours.

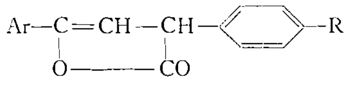
p-Methoxyphenylsuccinic anhydride reacted with iodobenzene in the presence of aluminum chloride to give a mixture of acids, which, after methylation and hydrolysis, was separated into β-benzoyl-α-*p*-methoxyphenylpropionic acid and β-*p*-iodobenzoyl-α-*p*-methoxyphenylpropionic acid (I*e* and I*f*, respectively); the former acid predominated. The structure of both acids was established by comparison with authentic specimens.

β-3,4-Dichlorobenzoyl-α-phenylpropionic acid (I*g*) was prepared by the addition of hydrogen cyanide to 3,4-dichlorophenyl styryl ketone and subsequent alcoholysis and hydrolysis of the corresponding nitrile.

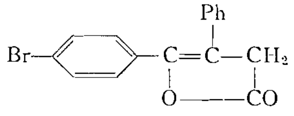
In the presence of aluminum chloride, succinic anhydride condensed with *o*-dichlorobenzene to give β-3,4-dichlorobenzoylpropionic acid (I*h*), the structure of which was established by oxidation with alkaline potassium permanganate to 3,4-dichlorobenzoic acid. However, under the same experimental conditions, phenylsuccinic anhydride failed to condense with *o*-dichlorobenzene, and instead it cyclized intramolecularly, giving 1-ketoindane-3-carboxylic acid (III*a*); this on decarboxylation gave α-hydrindone. Under the same conditions, α,β-diphenylsuccinic anhydride cyclized intramolecularly to give 1-keto-2-phenylindane-3-carboxylic acid (III*b*), the structure of which was established by comparison with an authentic specimen (3).



III



IV



V

(*a*) Ar = H
(*b*) Ar = C_6H_5

When the β-aroyl-α- and -β-arylpropionic acids were boiled with acetic anhydride, they were converted to the corresponding β,γ-unsaturated γ-lactones (4, 5) (IV and V, respectively). The lactone structure was established by the appearance of its characteristic stretching frequency (6, p. 153) in the infrared spectra of these compounds (see Experimental).

The results of the present investigation agree with those of Baddar and Sherif (4).

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were measured with a Perkin–Elmer Infracord spectrophotometer Model 137, using the potassium bromide wafer technique.

β-p-Bromobenzoyl-α-phenylpropionic Acid

A mixture of β-*p*-bromobenzoyl-α-phenylpropionitrile (7) (20 g), ethanol (150 ml), and concentrated sulphuric acid (30 ml) was refluxed for 6 hours on a steam bath. The ester (22 g), which solidified on being cooled, was filtered off and crystallized from light petroleum (b.p. 50–70°) to give ethyl β-*p*-bromobenzoyl-α-phenylpropionate in colorless crystals, m.p. 70–71°. Calc. for $C_{18}H_{17}BrO_3$: C, 59.85; H, 4.74; Br, 22.13. Found: C, 59.83; H, 4.61; Br, 22.00.

The ester (20 g) was hydrolyzed with 10% aqueous potassium hydroxide (200 ml) (1 hour reflux) to give β-*p*-bromobenzoyl-α-phenylpropionic acid (17 g) (from benzene), m.p. 160–161°; Allen and co-workers (1) give the same melting point. Calc. for $C_{16}H_{13}BrO_3$: C, 57.69; H, 3.93; Br, 24.00. Found: C, 57.85; H, 4.00; Br, 23.73.

When the acid was treated with 2,4-dinitrophenylhydrazine in a warm mixture of ethanol and concentrated sulphuric acid, it gave the 2,4-dinitrophenylhydrazone of the ethyl ester in orange-yellow crystals (from dilute acetic acid), m.p. 161–162°. Calc. for $C_{24}H_{21}BrN_4O_6$: C, 53.24; H, 3.91; N, 10.35. Found: C, 53.22; H, 3.75; N, 10.15.

Condensation of Bromobenzene with Phenylsuccinic Anhydride

A solution of phenylsuccinic anhydride (17.6 g, 0.1 mole) in bromobenzene (20 ml) was added gradually to a well-cooled and stirred mixture of anhydrous aluminum chloride (26.7 g, 0.2 mole) and bromobenzene (30 ml). The reaction mixture was heated at 100° for 3 hours, decomposed with ice-cold dilute hydrochloric acid, and the solvent was steam-distilled. The product (20 g, 60% yield), m.p. 85–100°, was crystallized from the least amount of glacial acetic acid, then from ether, to give β-*p*-bromobenzoyl-β-phenylpropionic acid (16 g, 48% yield) in colorless crystals, m.p. 156–157°, depressed to 130–140° when admixed with the α-phenyl isomer. Calc. for $C_{16}H_{13}BrO_3$: C, 57.69; H, 3.93; Br, 24.00. Found: C, 57.90; H, 3.83; Br, 24.00.

On oxidation with alkaline potassium permanganate (1 hour at 100°), it gave *p*-bromobenzoic acid, m.p. and mixed m.p. 250°.

The acetic acid mother liquor was diluted with water, and the precipitated solid was crystallized from benzene to give β-*p*-bromobenzoyl-α-phenylpropionic acid (2 g, 6% yield), m.p. and mixed m.p. 160–161°.

The steam-distillable fraction was dried (Na_2SO_4) and fractionally distilled to give mainly bromobenzene and *p*-dibromobenzene, m.p. and mixed m.p. 89°.

Action of Aluminum Chloride on Bromobenzene

Aluminum chloride was added to cold bromobenzene. The reaction mixture was kept at 25–30° for 3 days and then decomposed and worked up as usual to give bromobenzene and *p*-dibromobenzene.

β-p-Bromobenzoyl-α-p-methoxyphenylpropionitrile

To a solution of *p*-bromobenzoyl 4-methoxystyryl ketone (8) (5 g) in ethanol (150 ml), glacial acetic acid (2.3 ml) and aqueous potassium cyanide (3.5 g in 9 ml water) were added. The reaction mixture was kept at 60–65° for 5 hours, then left overnight. The nitrile (4 g) had m.p. 132–133° (from ethanol), depressed to 115–120° on admixing with the above chalcone. Calc. for $C_{17}H_{14}BrNO_2$: C, 59.31; H, 4.10; Br, 23.21; N, 4.07. Found: C, 59.20; H, 4.16; Br, 22.86; N, 4.00.

β-p-Bromobenzoyl-α-p-methoxyphenylpropionic Acid

A mixture of the above nitrile (4 g), methanol (50 ml), and concentrated sulphuric acid (7 ml) was refluxed for 8 hours and the product (4 g) crystallized from methanol to give methyl *β-p*-bromobenzoyl-*α-p*-methoxyphenylpropionate in colorless crystals, m.p. 79–80°. Calc. for $C_{18}H_{17}BrO_4$: C, 57.31; H, 4.55; Br, 21.18. Found: C, 57.11; H, 4.42; Br, 21.10.

The ester was hydrolyzed by refluxing for 2.5 hours with 5% aqueous potassium hydroxide (100 ml). The reaction mixture was cooled, acidified, and the precipitated acid was crystallized from ethanol to give *β-p*-bromobenzoyl-*α-p*-methoxyphenylpropionic acid (3.5 g) in colorless crystals, m.p. 134–135°. Calc. for $C_{17}H_{15}BrO_4$: C, 56.22; H, 4.17; Br, 22.02. Found: C, 56.00; H, 4.20; Br, 22.00.

When the acid was warmed with 2,4-dinitrophenylhydrazine in ethanol and concentrated sulphuric acid, and the product was crystallized from acetic acid, the 2,4-dinitrophenylhydrazone of the ethyl ester was obtained, in yellow crystals, m.p. 188–189°. Calc. for $C_{25}H_{23}BrN_4O_7$: C, 52.55; H, 4.06; Br, 14.00; N, 9.81. Found: C, 52.41; H, 3.91; Br, 14.20; N, 10.08.

β-p-Bromobenzoyl-α-p-hydroxyphenylpropionic Acid

A mixture of *β-p*-bromobenzoyl-*α-p*-methoxyphenylpropionic acid (2.5 g), aluminum chloride (5 g), and bromobenzene (20 ml) was stirred at 100° for 2 hours, then worked up as usual. The product (2 g) was crystallized from ether to give *β-p*-bromobenzoyl-*α-p*-hydroxyphenylpropionic acid, in colorless crystals, m.p. 171–172°. It gave a deep blue color with warm concentrated sulphuric acid. Calc. for $C_{16}H_{13}BrO_4$: C, 55.05; H, 3.75; Br, 22.90. Found: C, 55.16; H, 3.75; Br, 22.90. Its infrared spectrum showed two bands at 3450 and 1670 cm^{-1} characteristic of a bonded OH group (6, p. 84) and the CO group of the aroyl group (6, p. 114), respectively.

p-Methoxyphenylsuccinic Anhydride

It was prepared from the acid (9) by refluxing with 3 times its weight of acetyl chloride for 6 hours. The excess of acetyl chloride was distilled off, and the residue fractionated, b.p. 205–208° at 5 mm (80% yield).

Condensation of Bromobenzene with p-Methoxyphenylsuccinic Anhydride

A solution of *p*-methoxyphenylsuccinic anhydride (20.6 g, 0.1 mole) in bromobenzene (40 ml) was gradually added to a well-cooled and stirred mixture of aluminum chloride (26.7 g, 0.2 mole) and bromobenzene (50 ml). The reaction mixture was left overnight, heated at 100° for 3 hours, then worked up as usual. The product (20 g, 57% yield) was crystallized from ether to give *β-p*-bromobenzoyl-*β-p*-hydroxyphenylpropionic acid, in colorless crystals, m.p. 198–199° (12 g, 34% yield), depressed to 150–155° when admixed with *β-p*-bromobenzoyl-*α-p*-hydroxyphenylpropionic acid. Calc. for $C_{16}H_{13}BrO_4$: C, 55.05; H, 3.75; Br, 22.90. Found: C, 55.32; H, 3.90; Br, 22.45. It gave a yellowish-green color with concentrated sulphuric acid. On oxidation with alkaline potassium permanganate, it gave *p*-bromobenzoic acid.

Concentration of the ether mother liquor gave *β-p*-bromobenzoyl-*α-p*-hydroxyphenylpropionic acid (6 g, 17% yield), m.p. and mixed m.p. 171–172°.

β-p-Iodobenzoyl-α-phenylpropionitrile

To a solution of *p*-iodophenyl styryl ketone (10) (3 g) in ethanol (75 ml), glacial acetic acid (2.3 ml) and aqueous potassium cyanide (3.5 g in 10 ml water) were added. The reaction mixture was kept at 70–75° for 4 hours, then left overnight. β-*p*-Iodobenzoyl-α-phenylpropionitrile (3 g) was crystallized from ethanol in colorless crystals, m.p. 148–149°. Calc. for $C_{16}H_{12}INO$: C, 53.21; H, 3.35; I, 35.15; N, 3.88. Found: C, 53.11; H, 3.45; I, 34.76; N, 3.80.

β-p-Iodobenzoyl-α-phenylpropionic Acid

A mixture of the above nitrile (2 g), methanol (25 ml), and concentrated sulphuric acid (5 ml) was refluxed on a steam bath for 8 hours. The reaction mixture was diluted with water and the precipitated methyl β-*p*-iodobenzoyl-α-phenylpropionate (2 g) was crystallized from methanol, in colorless crystals, m.p. 132–133°, depressed to 115–120° when admixed with the corresponding nitrile. Calc. for $C_{17}H_{15}IO_3$: C, 51.79; H, 3.84; I, 32.20. Found: C, 51.70; H, 3.77; I, 32.00.

The preceding ester was hydrolyzed by refluxing for 1.5 hours with 5% aqueous potassium hydroxide (100 ml) to give β-*p*-iodobenzoyl-α-phenylpropionic acid (1.7 g), which was crystallized from ether in colorless crystals, m.p. 155–156°. Calc. for $C_{16}H_{13}IO_3$: C, 50.55; H, 3.45; I, 33.40. Found: C, 50.37; H, 3.60; I, 33.15. Oxidation of the α-phenylpropionic acid with aqueous alkaline potassium permanganate gave *p*-iodobenzoic acid, m.p. and mixed m.p. 270° (11).

Condensation of Iodobenzene with Phenylsuccinic Anhydride

The product from iodobenzene (60 ml), phenylsuccinic anhydride (17.6 g, 0.1 mole), and aluminum chloride (26.7 g, 0.2 mole) (3 hours at 100°) was extracted with boiling aqueous sodium carbonate solution. The extract, on being cooled and acidified, gave a semisolid residue (15 g). This was extracted several times with light petroleum (b.p. 50–70°), and the insoluble portion was crystallized from benzene to give β-benzoyl-β-phenylpropionic acid (2 g), m.p. and mixed m.p. 168° (2). Concentration of the benzene mother liquor gave β-benzoyl-α-phenylpropionic acid (3 g), m.p. and mixed (2) m.p. 154°. Evaporation of the benzene layer gave a semisolid residue which was crystallized several times from light petroleum (b.p. 70–90°) to give β-*p*-iodobenzoyl-β-phenylpropionic acid (2 g, 5.3% yield) in colorless crystals, m.p. 160–161°, depressed to 130–135° when admixed with its α-phenyl isomer. Calc. for $C_{16}H_{13}IO_3$: C, 50.55; H, 3.45; I, 33.40. Found: C, 50.82; H, 3.60; I, 32.47. Oxidation of the β-phenylpropionic acid with alkaline potassium permanganate gave *p*-iodobenzoic acid.

The light petroleum mother liquor was evaporated and the residue left was crystallized from ether to give β-*p*-iodobenzoyl-α-phenylpropionic acid (1.5 g, 4% yield), m.p. and mixed m.p. 156°.

The residue insoluble in sodium carbonate solution was dissolved in hot ethanol, and the oil and crystals, which were precipitated when the solution was cooled, were mechanically separated. The crystals, after crystallization from light petroleum (b.p. 50–70°), melted at 128°, not depressed when admixed with an authentic specimen of *p*-diiodobenzene. The oil was distilled under vacuum, b.p. 153–155° at 15 mm, and the solidified product was crystallized from light petroleum (b.p. below 40°) to give *o*-diiodobenzene in plates, m.p. and mixed m.p. 27° (12).

Action of Aluminum Chloride on β-p-Iodobenzoyl-α-phenylpropionic Acid

The acid (2 g) was dissolved in toluene (15 ml) and the cooled mixture was treated with aluminum chloride (5 g); the reaction mixture was stirred at 100° for 3 hours, then decomposed as usual. β-*p*-Iodobenzoyl-α-phenylpropionic acid was recovered unchanged, m.p. and mixed m.p. 156°.

Action of Aluminum Chloride on Iodobenzene

Iodobenzene was cooled to 0–5° and treated gradually with aluminum chloride. The reaction mixture was kept at room temperature (25–30°) for 3 days, then decomposed in the usual manner. *p*-Diiodobenzene and *o*-diiodobenzene were isolated from the reaction mixture as already mentioned.

p-Iodophenyl 4-Methoxystyryl Ketone

A mixture of *p*-iodoacetophenone (13) (18.4 g), ethanol (175 ml), water (60 ml), sodium hydroxide (7.5 g), and anisaldehyde (10.2 g) was stirred at 20–25° for 1.5 hours. *p*-Iodophenyl 4-methoxystyryl ketone (27 g) was obtained from ethanol in pale yellow crystals, m.p. 172–173°. Calc. for $C_{16}H_{13}IO_2$: C, 52.77; H, 3.60; I, 34.86. Found: C, 52.55; H, 3.51; I, 34.52.

β-p-Iodobenzoyl-α-p-methoxyphenylpropionitrile

To a solution of the above chalcone (3 g) in ethanol (175 ml), acetic acid (2.3 ml) and aqueous potassium cyanide (3.5 g in 10 ml water) were added. The reaction mixture was kept at 70–75° for 4 hours, then left overnight. The crystalline precipitate (3 g) was collected and crystallized from ethanol to give *β*-*p*-iodobenzoyl-*α*-*p*-methoxyphenylpropionitrile in colorless crystals, m.p. 164–165°. Calc. for $C_{17}H_{14}INO_2$: C, 52.21; H, 3.60; N, 3.58. Found: C, 52.10; H, 3.70; N, 3.41.

β-p-Iodobenzoyl-α-p-methoxyphenylpropionic Acid

A mixture of the preceding nitrile (2 g), methanol (25 ml), and concentrated sulphuric acid (4 ml) was refluxed for 10 hours. The reaction mixture was poured onto ice water and the crude methyl ester was directly hydrolyzed with 10% aqueous potassium hydroxide (100 ml) (1-hour reflux) to *β*-*p*-iodobenzoyl-*α*-*p*-methoxyphenylpropionic acid (1 g) from ether, m.p. 156–157°. Calc. for $C_{17}H_{15}IO_4$: C, 49.75; H, 3.69; I, 30.95. Found: C, 50.00; H, 3.60; I, 30.84.

Condensation of Iodobenzene with p-Methoxyphenylsuccinic Anhydride

The product from iodobenzene (60 ml), *p*-methoxyphenylsuccinic anhydride (20.6 g, 0.1 mole), and aluminum chloride (26.7 g, 0.2 mole) (3 hours at 100°) was steam-distilled and the residue extracted with boiling 10% aqueous sodium carbonate solution. The extract, on acidification, gave a semisolid residue (10 g), which was methylated with methyl iodide, potassium carbonate, and acetone. Hydrolysis of the esters (5% aqueous potassium hydroxide) gave a semisolid mass which, after crystallization from benzene, gave *β*-benzoyl-*α*-*p*-methoxyphenylpropionic acid (6 g), m.p. and mixed (9) m.p. 158°. Evaporation of the benzene mother liquor gave a gummy acid which, on crystallization from ether, gave *β*-*p*-iodobenzoyl-*α*-*p*-methoxyphenylpropionic acid (2 g), m.p. and mixed m.p. 156–157°.

The steam-distillable fraction was dried (Na_2SO_4) and fractionally distilled to give iodobenzene and *o*- and *p*-diiodobenzene.

β-3,4-Dichlorobenzoylpropionic Acid

A stirred mixture of aluminum chloride (53.4 g, 0.4 mole) and *o*-dichlorobenzene (75 ml) was treated portionwise with a solution of succinic anhydride (20 g, 0.2 mole in 25 ml of *o*-dichlorobenzene). The reaction mixture was heated at 100° for 3 hours, then worked up as usual. *β*-3,4-Dichlorobenzoylpropionic acid (30 g, 61% yield) came down from ethanol in colorless crystals, m.p. 167–168°. Calc. for $C_{10}H_8Cl_2O_3$: C, 48.61; H, 3.26; Cl, 28.70. Found: C, 48.57; H, 3.11; Cl, 28.61. Oxidation of this acid with alkaline potassium permanganate gave 3,4-dichlorobenzoic acid, m.p. and mixed (14) m.p. 208–209°.

3,4-Dichlorophenyl Styryl Ketone

A mixture of 3,4-dichloroacetophenone (15) (9.5 g), ethanol (100 ml), water (40 ml), sodium hydroxide (5 g), and benzaldehyde (5.3 g) was stirred at 50–55° for 1 hour, then allowed to cool. 3,4-Dichlorophenyl styryl ketone (10 g) was obtained in pale yellow crystals, m.p. 116–117° (from ethanol). Bradsher and co-workers (16) and Lutz and co-workers (17) gave m.p. 112–113° and 110–112°, respectively. Calc. for $C_{15}H_{10}Cl_2O$: C, 65.03; H, 3.63; Cl, 25.60. Found: C, 64.73; H, 3.60; Cl, 25.00.

β-3,4-Dichlorobenzoyl-α-phenylpropionitrile

To a solution of the above chalcone (2 g) in ethanol (50 ml), acetic acid (2 ml) and aqueous potassium cyanide (2 g in 5 ml water) were added. The reaction mixture was heated to the boiling point, then left overnight. The nitrile (2 g) was crystallized from ethanol in colorless crystals, m.p. 119–120°, depressed to 105–110° when admixed with the corresponding chalcone. Calc. for $C_{16}H_{11}Cl_2NO$: C, 63.19: H, 3.65; Cl, 23.31; N, 4.60. Found: C, 63.00; H, 3.60; Cl, 23.11; N, 4.45.

β-3,4-Dichlorobenzoyl-α-phenylpropionic Acid

A mixture of the above nitrile (2 g), methanol (25 ml), and concentrated sulphuric acid (5 ml) was heated on a steam bath for 10 hours. The ester that precipitated on cooling was hydrolyzed with 5% aqueous potassium hydroxide (100 ml) (1.5 hours reflux) to give β-3,4-dichlorobenzoyl-α-phenylpropionic acid (1.5 g) as colorless crystals from methanol, m.p. 170–171°. Calc. for $C_{16}H_{12}Cl_2O_3$: C, 59.47; H, 3.74; Cl, 21.95. Found: C, 59.21; H, 3.75; Cl, 21.46.

1-Ketoindane-3-carboxylic Acid

Phenylsuccinic anhydride (17.6 g) in *o*-dichlorobenzene (20 ml) was added gradually to a well-cooled and stirred mixture of aluminum chloride (26.7 g) and *o*-dichlorobenzene (30 ml). The reaction mixture was heated at 100° for 2 hours, then worked up as usual. The colorless crystalline acid, m.p. 85° (from water), was dried in vacuum to give 1-ketoindane-3-carboxylic acid (12.5 g, 71% yield), m.p. and mixed (18) m.p. 120°.

α-Hydrindone

A mixture of 1-ketoindane-3-carboxylic acid (2 g), quinoline (15 ml), and copper bronze (0.5 g) was refluxed for 1 hour, cooled, and decomposed as usual. The reaction mixture was extracted with benzene. The removal of the solvent left an oil (ca. 1.5 g) which, on trituration with light petroleum (b.p. below 40°), gave colorless crystals, m.p. 42°; it was converted into α-hydrindone 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 260° (decomp.).

1-Keto-2-phenylindane-3-carboxylic Acid

A mixture of diphenylsuccinic anhydride (8.5 g) and aluminum chloride (10 g) in *o*-dichlorobenzene (30 ml) was heated at 100° for 2 hours, decomposed, and the solvent was steam-distilled. 1-Keto-2-phenylindane-3-carboxylic acid monohydrate (ca. 8 g) was crystallized from dilute ethanol in colorless crystals, m.p. and mixed (3) m.p. 116–117° (decomp.).

Lactonization of β-Aroyl-α- and -β-arylpropionic Acids

The solution of the acid (1 g) in acetic anhydride (10 ml) was refluxed for 2 hours and, after cooling, poured into water. The solid was filtered off and washed with dilute sodium carbonate solution. The lactone (ca. 100% yield) was then crystallized from a suitable solvent (see Table I).

TABLE I

Lactone							Analysis (%)					
							Calculated			Found		
No.	Ar	R	Solvent	M.p.	$\nu_{\max}$§ (cm^{-1})	Formula	C	H	Halogen	C	H	Halogen
IV	C_6H_5	OCH_3	C_6H_6–Pet†	107–108°	1750	$C_{17}H_{14}O_3$	76.68	5.31	—	76.44	5.30	—
IV	β-Naphthyl*	H	C_6H_6–Pet†	123–124°	1745	$C_{20}H_{14}O_2$	83.90	4.93	—	83.82	4.84	—
IV	2-Fluorenyl*	H	Ether	159–160°	1745	$C_{23}H_{16}O_2$	85.18	4.98	—	85.05	5.00	—
IV	p-Br·C_6H_4	H	C_6H_6	158–159°	1745	$C_{16}H_{11}BrO_2$	60.95	3.52	25.35	61.00	3.60	25.85
IV	p-Br·C_6H_4	OCH_3	C_6H_6–Pet†	149–150°	1755	$C_{17}H_{13}BrO_3$	59.16	3.80	23.15	59.04	3.64	22.93
IV	p-I·C_6H_4	H	C_6H_6	173–174°	1755	$C_{16}H_{11}IO_2$	53.07	3.06	35.05	53.41	3.22	34.57
IV	3,4-Cl_2·C_6H_3	H	C_6H_6	157–158°‡	1750	$C_{16}H_{10}Cl_2O_2$	63.00	3.30	23.25	63.40	3.25	22.84
V	—	—	C_6H_6	141–142°	1755 & 1786	$C_{16}H_{11}BrO_2$	60.95	3.52	25.35	61.01	3.51	24.54

*The corresponding keto acids were prepared after Hidayetulla and co-workers (19) and Baddar and his students (2), respectively.
†Pet = light petroleum (b.p. 50–70°).
‡Decomp.
§Stretching frequency for β,γ-unsaturated γ-lactones.

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