145–147° dec; uv λ_{max} (H_2O) 248 nm (ϵ 3638), 333 (20,789); λ_{max} (pH 1) 246 nm (ϵ 4020), 335 (21,026); λ_{max} (pH 11) 318 nm (ϵ 20,906).

Anal. Calcd for $C_9H_{12}N_2O_4S$: C, 44.25; H, 4.95; N, 11.47. Found: C, 44.49; H, 5.15; N, 11.51.

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Registry No.—Arabinofuranosylisocytosine, 10212-30-3; isocytosine, 674-97-5; isocytidine, 489-59-8; H_2Se, 7783-07-5.

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Indeno[1,2-*c*]isocoumarin

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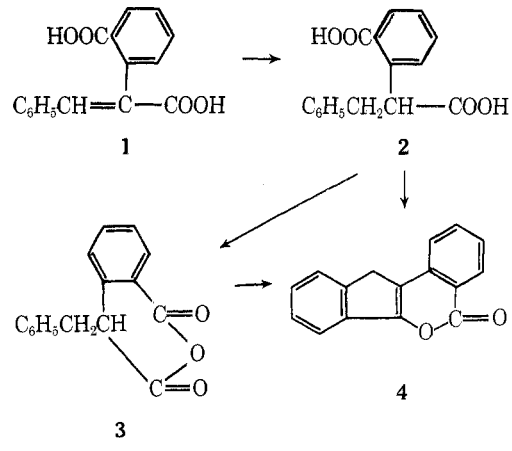
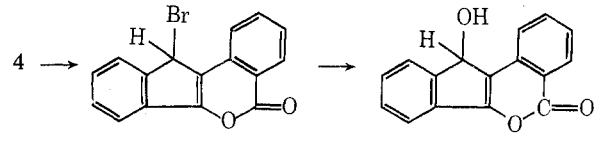
In studies dealing with the preparation of stabilized 2-arylindenones,[2,3] the synthesis of 2-*o*-carboxyphenylindanone, the precursor of 2-*o*-carboxyphenylindenone, from α-(*o*-carboxyphenyl)cinnamic acid (**1**) was investigated and found to give indeno[1,2-*c*]isocoumarin (**4**) instead of the desired product. α-(*o*-Carboxyphenyl)cinnamic acid (**1**) was prepared in two ways by the hydrolysis of α-(*o*-carboxyphenyl)cinnamonitrile and by the condensation of *o*-carboxyphenylacetic acid with benzaldehyde. Reduction of **1** with Raney nickel alloy in alkali gave α-(*o*-carboxyphenyl)-β-phenylpropionic acid (**2**), which was converted to the anhydride **3** by heating in toluene. Treatment of the acid **2** with polyphosphoric acid gave indeno[1,2-*c*]isocoumarin (**4**). The same product was formed by treating the anhydride **3** with aluminum chloride. Proofs for structure **4** were



1 **2** **3** **4**

the spectral data and the conversion of **4** to the known 11-keto[1,2-*c*]isocoumarin.[4] Bromination of **4** with *N*-bromosuccinimide gave 11-bromoindeno[1,2-*c*]isocoumarin (**5**), which when treated with alkali gave upon acidification 11-hydroxyindeno[1,2-*c*]isocoumarin (**6**). Evidence for this



5 **6**

structure was the NMR spectrum, which showed two doublets for the alcohol grouping. These doublets became a singlet in the presence of deuterium oxide.

The infrared spectrum in Nujol for **6** varied with the solvent used for recrystallization of this compound. A sample from benzene showed a sharp free hydroxyl absorption at 3484 cm^{-1} and carbonyl absorptions at 1739 and 1706 cm^{-1} with a shoulder at 1681 cm^{-1}. Compound **6** from ethanol gave two broad absorptions for the hydroxyl at 3268 and 3125 cm^{-1} and carbonyl absorptions at 1761 and 1712 cm^{-1}; the carbonyl at 1712 cm^{-1} was very small. Both samples, however, showed an absorption for the carbon–carbon double bond at 1637 cm^{-1}; its intensity when compared with that for the aromatic double bond at 1616 cm^{-1} was the same. One percent solutions of both samples in tetrahydrofuran, however, gave identical infrared spectra between 2.5 and 7 μ.

The alcohol **6** dissolved in alkali and the resulting solution when allowed to stand exposed to air for 7 days and then acidified gave 11-ketoindeno[1,2-*c*]isocoumarin.

Compound **6** was also formed by the reduction of 11-ketoindeno[1,2-*c*]isocoumarin with zinc and acetic acid.

Experimental Section

Melting points are corrected. The ir spectra were recorded with Model 21 and 137 Perkin-Elmer spectrometers, and the NMR spectra were obtained with a Varian A-60 spectrometer.

α-(*o*-Carboxyphenyl)cinnamonitrile. This nitrile was prepared from *o*-carboxyphenylacetonitrile[5] and benzaldehyde using the directions given for the preparation of α-phenylcinnamoni-

trile.[6] Recrystallization from 50% ethanol gave a 73% yield of a pale yellow solid, mp 170–171°.

Anal. Calcd for $C_{16}H_{11}O_2N$: C, 77.09; H, 4.45; N, 5.62. Found: C, 77.00; H, 4.75; N, 5.72.

α-(o-Carboxyphenyl)cinnamic Acid (1). A. α-(o-Carboxyphenyl)cinnamonitrile (11.4 g) was refluxed with concentrated hydrochloric acid (300 ml) for 48 hr. The mixture upon cooling gave a pale yellow solid, mp 197–201°. Purification by dissolving the solid in 10% sodium hydroxide, decolorizing with decolorizing carbon, and acidifying with hydrochloric acid gave 8.8 g of a white solid melting at 215–216°.

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.69; H, 4.29.

B. A mixture of o-carboxyphenylacetic acid (36.0 g), benzaldehyde (75 ml), and acetic anhydride (28.4 ml) at 70–80° was treated dropwise with triethylamine (50 ml) over a period of 1.5 hr. Heating and stirring were continued for another 4 hr and the resulting dark brown mixture was poured into 10% hydrochloric acid (700 ml) and allowed to stand overnight at 0°. The resulting brown oil was separated and dissolved in benzene (300 ml). Extraction with 5% sodium hydroxide followed by acidification gave a resinous solid which was filtered and treated with benzene (400 ml). The resulting pale tan solid melted at 185–190° and was purified by the method used in part A. The white solid melted at 215–216°, yield 25.8 g.

α-(o-Carboxyphenyl)-β-phenylpropionic Acid (2). α-(o-Carboxyphenyl)cinnamic acid (1, 15.5 g) was dissolved in 10% sodium hydroxide (275 ml) and the resulting solution was treated at 90° with small amounts of nickel–aluminum alloy (Raney catalyst, 27 g) during the course of 2 hr. The mixture was heated for an additional 1 hr and filtered, and the residue was washed with hot 10% sodium hydroxide (25 ml) and hot water (50 ml). The filtrate was added dropwise with stirring to 150 ml of concentrated hydrochloric acid at a rate such that the temperature did not exceed 80–85°. The resulting acid (13.5 g) melted at 166–167°.

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.79; H, 5.31.

α-(o-Carboxyphenyl)-β-phenylpropionic Anhydride (3). α-(o-Carboxyphenyl-β-phenylpropionic acid (2, 27.0 g) was refluxed with toluene in a flask fitted with a Dean-Stark for 24 hr or until 1.82 ml of water was formed. Removal of the toluene gave a quantitative yield of the anhydride 3, mp 114–116°, ir (Nujol) 1780, 1740 cm^{-1} (anhydride).

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.17; H, 4.79. Found: C, 75.97; H, 4.55.

Indeno[1,2-c]isocoumarin (4). A. A solution of α-(o-carboxyphenyl)-β-phenylpropronic acid anhydride (3, 5.0 g) in nitrobenzene (100 ml) was treated with aluminum chloride (10.7 g) and heated at 60° for 15 min. The resulting mixture was poured into dilute hydrochloric acid (300 ml) containing ice and then steam distilled to remove the nitrobenzene. The resulting solid was filtered and purified by dissolving in 10% sodium carbonate, treating the solution with decolorizing carbon, and acidifying. The crude product upon recrystallization from 70% ethanol gave 0.88 g of indeno[1,2-c]isocoumarin (4) melting at 175–176°; ir (Nujol) 1740 (C=O), 1685 cm^{-1} (C=C); NMR ($CDCl_3$) δ 4.10 (s, 2, CH_2), 7.68 (m, 8, aromatic H).

Anal. Calcd for $C_{16}H_{10}O_2$: C, 81.06; H, 4.53. Found: C, 81.16; H, 4.32.

B. α-(o-Carboxyphenyl)-β-phenylpropionic acid (2, 10 g) was added quickly with stirring to a mixture of concentrated phosphoric acid (80 g) and phosphorus pentoxide (80 g) at 160° and maintained at this temperature for 12 hr. The mixture was cooled and added to water (300 ml) and ice (300 g) and the resuling solid was extracted with ether. Removal of the ether gave a product which upon crystallization from 70% ethanol gave 5.14 g of indeno[1,2-c]isocoumarin (4), mp 175–176°.

11-Bromoindeno[1,2-c]isocoumarin (5). A solution of 4 (0.60 g) in carbon tetrachloride (15 ml) was treated with N-bromosuccinimide (0.46 g) and a trace of benzoyl peroxide and the resulting mixture was refluxed and irradiated for 6 hr. Upon cooling a pale yellow solid (0.8 g) was obtained and purified by stirring with water (20 ml) for 2 hours and recrystallizing from hexane: yield 0.49 g; mp 216–217°; ir (Nujol) 1760 (C=O), 1705 cm^{-1} (C=C); NMR ($CDCl_3$) δ 4.44 (s, 1 H, CHBr), 7.67 (m, 8, aromatic protons).

Anal. Calcd for $C_{16}H_9BrO_2$: C, 59.82; H, 3.01. Found: C, 59.71; H, 2.96.

6a,11a-Dihydro-11-ketoindeno[1,2-c]isocoumarin (6). A. A solution of 5 (0.25 g) in absolute ethanol (15 ml) was stirred at room temperature with 10% sodium hydroxide (1 ml) for 12 hr. Acidification with dilute hydrochloric acid gave a pale orange solid which upon recrystallization from benzene gave a pale green solid melting at 183–184°; yield 0.15 g. Two recrystallizations from ethanol gave a white solid melting at 186–187°; ir (1% in tetrahydrofuran) 3367 (OH), 1754, 1695 (very small, CO), 1639 (C=C), 1645 cm^{-1} (aromatic C=C); NMR (Me_2SO-d_6) δ 5.48 (d, 1, CH, J = 8 Hz), 5.97 (d, 1, OH, J = 8 Hz), 7.17–8.25 (m, 8, aromatic); NMR (Me_2SO-d_6 + D_2O) δ 5.45 (s, 1, CH), 7.17–8.25 (m, 8, aromatic).

Anal. Calcd for $C_{16}H_{10}O_3$: C, 76.79; H, 4.03. Found: C, 76.83; H, 4.23.

B. A solution of 11-ketoindeno[1,2-c]isocoumarin, (0.2 g) in glacial acetic (30 ml) was treated at reflux with zinc dust until the orange color of the solution disappeared. The resulting mixture was filtered into water (70 ml) and the solid formed was recrystallized from benzene, yield 0.14 g, mp 183–184°. A mixture melting point with the sample prepared in procedure A melted at the same point.

11-Ketoindeno[1,2-c]isocoumarin[4]. A solution of 6 in ethanol (15 ml) and 10% sodium hydroxide (1 ml) was stirred at room temperature for 7 days. Acidification with hydrochloric acid gave an orange solid which when recrystallized from benzene melted at 260–261°. A mixture melting point with an authentic sample melted at the same point.

Registry No.—1, 39585-13-2; 2, 2897-88-3; 3, 2897-89-4; 4, 5651-52-5; 5, 5614-25-1; 6, 56114-26-2; α-(o-carboxyphenyl)cinnamonitrile, 5614-27-3; o-carboxyphenylacetonitrile, 6627-91-4; benzaldehyde, 100-52-7; o-carboxyphenylacetic acid, 89-51-0; N-bromosuccinimide, 128-08-5; 11-ketoindeno[1,2-c]isocoumarin, 5651-60-5.

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The O,2-Dilithio Derivative of Allyl Alcohol, a Useful Synthetic Reagent

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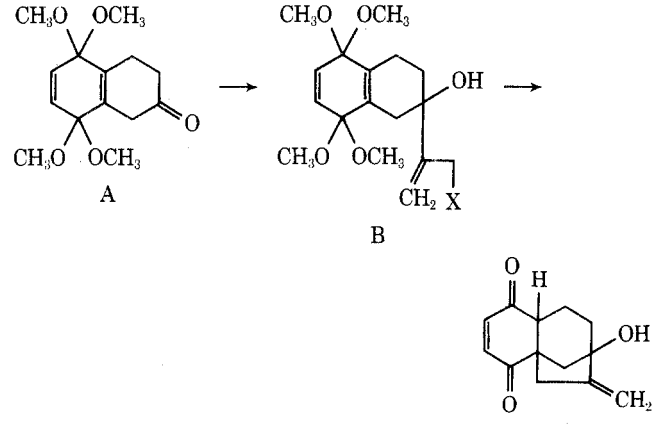
In connection with research directed toward a synthesis of gibberellic acid,[1] a reagent was required for effecting the sequence A → B → C. The ideal candidate seemed to be



the previously unknown O,2-dilithio derivative of allyl alcohol, $H_2C{=}C(Li)CH_2O^-Li^+$ (1). A similar reagent,