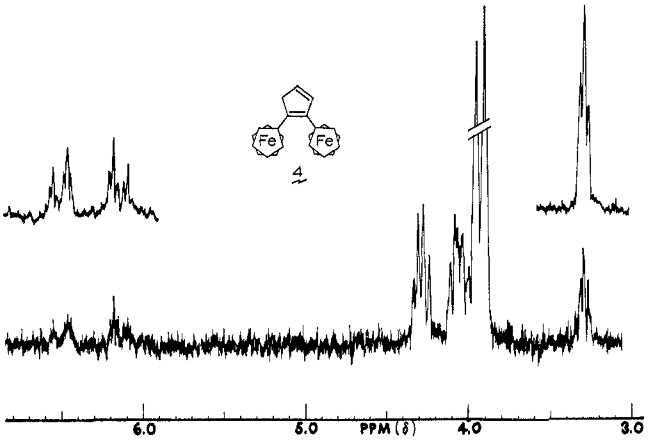

Figure 3.—Nmr spectrum of 1,2-diferrocenyl-1,3-cyclopentadiene.

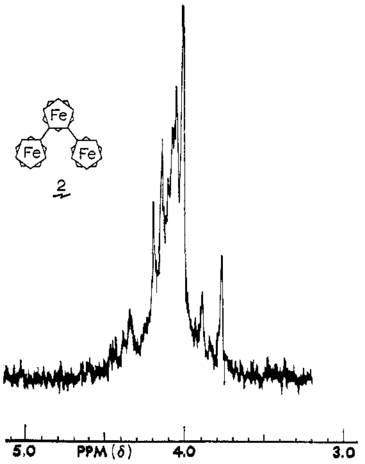

Figure 4.—Nmr spectrum of 1,2-terferrocene.

1,2-Terferrocene (2).—In a thoroughly dried three-necked flask, equipped with a stirrer, nitrogen inlet, condenser, and a rubber septum injection port, was mixed a solution of 1,2-diferrocenyl-1,3-cyclopentadiene (4) (348 mg, 0.802 mmol) in 20 ml of anhydrous ether and a solution of *n*-butyllithium [4 ml (6 mmol) of a 15% (w/w) solution in hexane (Foote Mineral Co.)] in 100 ml of anhydrous ether. The mixture was stirred at room temperature for 1 hr before freshly prepared cyclopentadiene (3.3 g, 50 mmol) and *n*-butyllithium (10 ml, 16 mmol) were added. The mixture was stirred for an additional 3-hr period when iron(II) chloride[16] (1.0 g, 7.9 mmol) was added, and the whole mixture was stirred overnight. After addition of 25 ml of 5% aqueous ammonium chloride solution, the separated aqueous phase was exhaustively extracted with ether, and the ether extracts were combined with the original ethereal phase before the whole mixture was dried ($CaCl_2$) and evaporated. The residue, a brown solid, was chromatographed on alumina (Merck, acid-washed). Elution with hexane gave ferrocene, 1.4 g. Further column development and elution with a mixture of hexane and benzene (1:1 (v/v)] produced 46 mg of crude 1,2-terferrocene (2) which was initially obtained as an orange-brown solid. This material was successively (five times) recrystallized from hexane–benzene to yield a 10-mg orange crystalline, constant-melting (mp 191–193°, sealed, evacuated capillary) sample of 1,2-terferrocene which was chromatographically pure (R_f 0.90) and characterized by the following spectral properties: ir (CH_2Cl_2) 3100, 3050, 1100, and 1000 cm^{-1}; uv (EtOH) 215 nm broad (ϵ 24,000) and 290 sh (5000); nmr ($CDCl_3$) showed only a complex cluster of signals centered at δ 4.05 indicating the presence of only ferrocenyl protons (see Figure 4) [determination of the spectrum at 45° (near 36° initially) caused significant changes in the detailed structure of the signal complex indicating perhaps a rather facile and complex conformational equilibria]; mass spectrum[9] m/e (intensity relative to M^+) 556 ($M^+ + 2$, 8.5), 555 ($M^+ + 1$, 38), 554 (M^+, 100), 553 ($M^+ - 1$, 7.3), and 552 ($M^+ - 2$, 23) [calcd[15] for $C_{30}H_{26}Fe_3$: 556 ($M^+ + 2$, 8.9), 555 ($M^+ + 1$, 40), 554 (M^+, 100), 553 ($M^+ - 1$, 6.7), and 552 ($M^+ - 2$, 19)].

Anal. Calcd for $C_{30}H_{26}Fe_3$: C, 65.03; H, 4.73. Found: C, 64.92; H, 4.86.

Registry No.—**2**, 12504-91-5; **4**, 12504-84-6; **5**, 12504-88-0; **7**, 12504-87-9; **8**, 12504-90-4; **9**, 12113-85-8; **10**, 12504-86-8; **11**, 12504-85-7; desoxyferrocoin, 12504-83-5.

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A Facile Synthesis of 3-Acylaminoisocoumarins[1a]

J. N. Wells,* W. J. Wheeler,[1b] and L. M. Davisson[1c]

Department of Medicinal Chemistry and Pharmacognosy, School of Pharmacy and Pharmacal Sciences, Purdue University, Lafayette, Indiana 47907

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The synthesis of some 3-acylaminoisocoumarins is reported. Spectral data and chemical reactivity are discussed. 3-Aminoisocoumarin was prepared and acylated to afford 3-acylaminoisocoumarin by an alternative route.

During a program for the synthesis of some tetracyclic indole compounds, we had need of 5-(2-carboxy-5-chlorophenyl)levulinic acid (**1**) as a precursor. It was hoped that 3-carbethoxypropionic 5-chloro-α-cyano-2-toluic anhydride (**2**) could be condensed under basic conditions to form ethyl 5-(2-carboxy-5-chlorophenyl)-5-cyanolevulinate (**3**). Hydrolysis of **3** and subsequent decarboxylation would yield **1**.

It was planned to synthesize **2** by the reaction of 5-chloro-α-cyano-2-toluic acid (**4**) with 3-carbethoxypropionyl chloride[2] in the presence of pyridine. Attempts to prepare **4** by the reaction of 5-chlorophthalide,[3] with potassium cyanide utilizing Price's procedure,[4] yielded only tars. Adequate yields of **4** could be obtained when the reaction was carried out in dimethyl sulfoxide at 100–110°.

Upon reaction of **4** with 3-carbethoxypropionyl chloride[2] in the presence of 2 equiv of pyridine, no anhydride was isolated. Instead a high-melting solid, mp 198–199°, **5** was isolated in 39.6% yield. The infrared spectrum indicated loss of the nitrile and showed no absorption below 5.7 μ (the characteristic carbonyl

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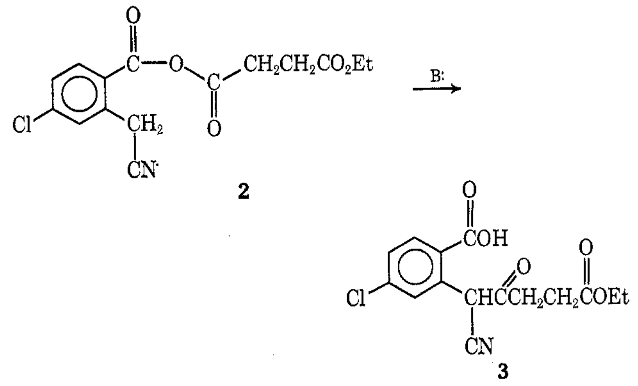
[1] (a) Abstracted in part from the Ph.D. thesis of W. J. Wheeler, Purdue University, June 1970; (b) Fellow of the American Foundation for Pharmaceutical Education, 1968–1970; (c) NSF Undergraduate Research Participant, 1969.

[2] I. Heilbron and H. M. Bunbury, Ed., "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, p 384.

[3] L. P. Levy and H. Stephan, *J. Chem. Soc.*, 867 (1931).

[4] C. C. Price, *Org. Syn.*, **22**, 61 (1942).

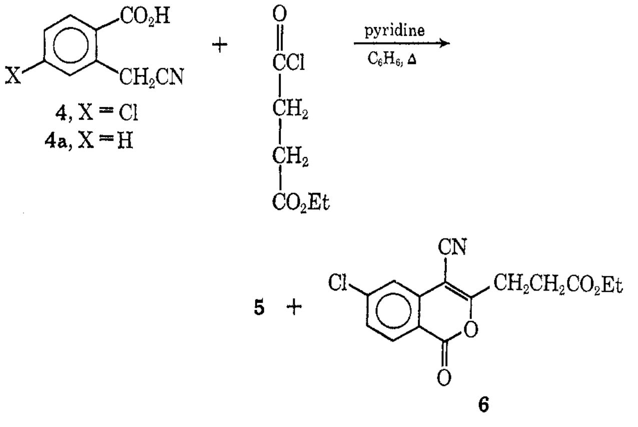


2

3

doublet of anhydrides[5] was absent). The nmr spectrum (DMSO-d_6) showed a three-proton triplet at δ 1.07 ppm (ester methyl) and a four-proton singlet at δ 2.58 ppm (superimposed on the DMSO-d_5 signal) which is presumably the methylene protons of the succinate residue. In addition, there were a two-proton quartet at δ 4.04 ppm (ester methylene) and a one-proton singlet at δ 7.05 ppm, as well as additional aromatic protons. There was also a broad one-proton singlet at δ 11.06 ppm. The mass spectrum indicated an apparent molecular ion at m/e 323 as well as a large M − 128 peak at m/e 195 (base peak). There were also significant peaks at m/e 129 and 101. Reaction of **4a** with acetyl chloride similarly yielded **5b**.

A minor product (**6**, the enol lactone of **3**) was also obtained from this reaction. The nmr spectrum of **6** ($CDCl_3$) showed a three-proton triplet at δ 1.25 ppm (ester methyl), a four-proton A_2B_2 multiplet at δ 3.05 ppm (ethylene), a two-proton quartet at δ 4.2 ppm (ester methylene), and the aromatic signals centered at δ 7.90 ppm. The mass spectrum had an apparent molecular ion at m/e 305 as well as a reasonable fragmentation pattern.

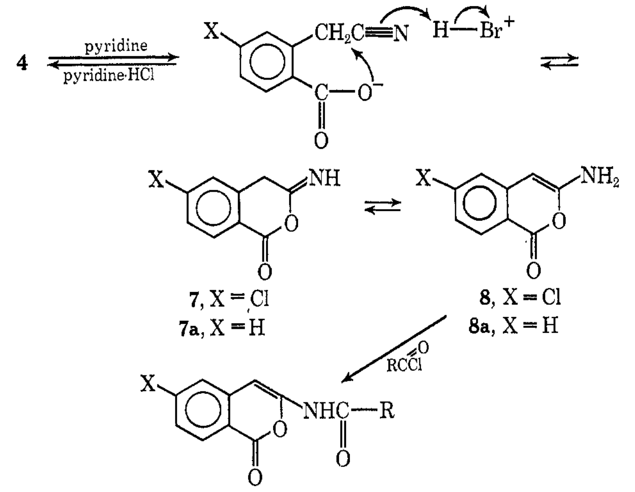


4, X = Cl
4a, X = H

6

Since condensations under similarly mild conditions are known (*e.g.*, the intramolecular condensation of 2,4-dibenzoyloxyacetophenone in the presence of $NaHCO_3$[6]), **5** was initially postulated to be **3**. The following evidence indicated otherwise. The material was slowly dissolved in base but could not be recovered upon acidification. The conversion of **5** to **6** was unsuccessful under a variety of conditions. Additionally, hydrolysis of **5** under both acidic and basic conditions yielded 5-chlorohomophthalic acid and succinic acid. Ethanolysis of **5** yielded diethyl 5-chlorohomophthalate and diethyl succinate.

On the basis of both the spectral and chemical data, **5** is postulated to be an acylated 3-aminoisocoumarin. The formation of **5** could be visualized to proceed *via* the following mechanism.



7, X = Cl
7a, X = H

8, X = Cl
8a, X = H

5, X = Cl, R = $CH_2CH_2CO_2Et$
5a, X = H, R = $CH_2CH_2CO_2CH_3$
5b, X = H, R = CH_3

Although other pathways could be envisioned, carbon acylation of **7** could also explain the formation of **6** (*via* **3**) since isoimides are thought to give rise to nitriles under similar conditions.[7] 3-Aminoisocoumarin (**8a**) has recently been proposed as an intermediate in the thermolysis of 2-carboxyphenylacetonitrile.[8]

Formulation of the product as **5** explains the lack of –C≡N absorption in the ir spectrum, as well as the facile hydrolysis to 5-chlorohomophthalic acid and succinic acid. Although 3-aminoisocoumarins have not been reported in the literature, there is ample precedence for the intermediacy of isoimide **7**. Alkyl-[9] and aryl-substituted 3-iminophthalides[10,11] have been synthesized and isolated. Isoimides have been proposed as intermediates in the conversion of phthalamic acid to ethyl 2-cyanobenzoate,[12] in the reaction of ketenimines with carboxylic acids,[13] in the interconversion of aromatic acids and arylnitriles,[14] and in the reaction of amides with acid anhydrides and acid chlorides.[15] It has been suggested that isoimides are easily acylated in the presence of acid chlorides.[15]

Careful examination of the fragments of the mass spectrum of **5** further substantiates the 3-acylaminoisocoumarin structure. The base peak m/e 195 results from hydrogen migration and expulsion of a ketene (the usual base peak from acylanilides[16]) and corresponds to **8**.

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[5] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, pp 125–129.

[6] W. Baker, *J. Chem. Soc.*, 1381 (1933).

[7] B. Liberek, *Bull. Acad. Polo. Sci., Ser. Sci. Chim.*, **10**, 227 (1962).

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[9] Hoogewerff and W. A. van Dorp, *Recl. Trav. Chim. Pays-Bas*, **13**, 93 (1894).

[10] W. A. Roderick and P. L. Bhatia, *J. Org. Chem.*, **28**, 2018 (1963).

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[12] C. K. Sauers and R. J. Cotter, *J. Org. Chem.*, **26**, 6 (1961).

[13] C. L. Stevens and M. Munk, *J. Amer. Chem. Soc.*, **80**, 4065 (1959).

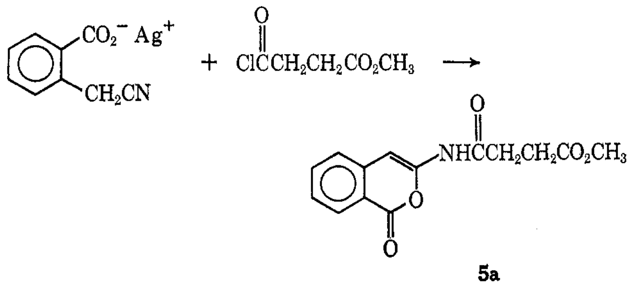
[14] W. G. Toland and L. Ferstandig, *J. Org. Chem.*, **23**, 1350 (1958).

[15] D. Davidson and H. Skovronck, *J. Amer. Chem. Soc.*, **80**, 376 (1958).

[16] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 350.

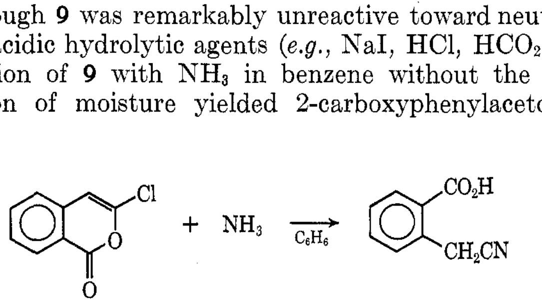
The uv spectrum of **5** showed maxima at 224, 251, 290, 298 sh, and 347 mμ. The uv spectrum of an acylated 3-hydroxyisocoumarin, 3-ethoxycarbonyloxyisocoumarin, showed maxima at 240, 263, 370 sh, and 324 mμ.[17] These spectra are quite similar except for a bathochromic shift of the maxima in that of **5**. This is not unexpected, however, since the maxima for aniline appear at longer wavelengths than those of phenol.[18]

Additional evidence for structure **5** arises from the following experiments. When the silver salt of 2-carboxyphenylacetonitrile was treated with 3-carbomethoxypropionyl chloride,[19] the corresponding 3-acylaminoisocoumarin **5a** was formed. When 2-carbomethoxyphenylacetonitrile[20] was treated with 3-carbomethoxypropionyl chloride,[19] no **5** was isolated or detected, indicating participation of the carboxyl group in the formation of **5**.



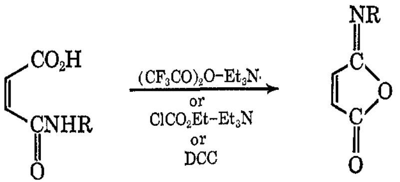
5a

In hope to further substantiate the 3-acylaminoisocoumarin structure **5** and perhaps shed some light on the mechanism of the reaction, attempts were made to synthesize isoimide **7a** or its tautomer **8a**. Davies and Poole attempted the synthesis of **8a** by the reaction of 3-chloroisocoumarin (**9**) with anhydrous ammonia.[21] Although **9** was remarkably unreactive toward neutral and acidic hydrolytic agents (*e.g.*, NaI, HCl, HCO_2H), reaction of **9** with NH_3 in benzene without the exclusion of moisture yielded 2-carboxyphenylacetonitrile.



9

Sauer and Cotter[12] synthesized the five-membered isoimide **10** under a variety of conditions.



10

Homophthalamic acid, readily obtained from the reaction of 2-carboxyphenylacetonitrile with basic hydrogen peroxide,[22] was dehydrated with dicyclohexylcarbodiimide to yield **8a**.

The nmr spectrum of **8a** showed a one-proton singlet at δ 5.30 ppm and a two-proton singlet at δ 6.50 ppm, which were exchangeable with D_2O. The ir spectrum showed N–H absorption at 2.95 μ and C=O absorption at 5.88 μ as well as the 6.05, 6.49 μ maxima characteristic of isocoumarins.[16] The uv spectrum showed maxima at 232, 291, and 380 mμ. The mass spectrum had a molecular ion at *m/e* 161 and a fragmentation pattern similar to the acylated analogs.

Acylation of **8a** with 3-carbomethoxypropionyl chloride[19] in the presence of pyridine at room temperature yielded **5a**. The compounds (**5a**) from the two different reactions showed no depression of mixture melting point and identical spectra.

It was hoped that **4a** could be converted to **8a** with pyridine; however, reaction of both **4a** and **8a** with pyridine under identical conditions yielded the same equilibrium mixture as evidenced by tlc (silica gel PF_{254}, developed with $CHCl_3$–MeOH 95:5, visualized with short wavelength uv light).

Experimental Section[23]

5-Chloro-2-carboxyphenylacetonitrile (4).—5-Chlorophthalide[3] (74.5 g, 0.44 mol) and potassium cyanide (43.2 g, 0.66 mol) were mixed in 475 ml of dimethyl sulfoxide. After an initial exothermic reaction, the mixture was warmed to 100°. The color of the solution gradually darkened from yellow to dark red. Heating was continued for 18 hr, whereupon the mixture was allowed to cool to room temperature.

The mixture was neutralized with 150 ml of 6 *N* hydrochloric acid. The acidified solution was poured over 2 l. of ice and a solid gradually precipitated (87 g) which was collected by filtration and washed with water. The solid was dissolved in 10% aqueous sodium bicarbonate and treated with charcoal. Precipitation with 6 *N* hydrochloric acid yielded 62 g (72%) of **4**: mp 121–125° dec (recrystallization from ether–*n*-hexane raised this to 143–145° dec); nmr ($CDCl_3$-DMSO) δ 4.17 (2, s, CH_2), 7.2 (1, d, J = 2.5 cps, 6 H), 7.4 (1, dd, J = 2.5 cps and J = 9 cps, 4 H), 7.95 (1, d, J = 9 cps, 3 H), and 13.34 ppm (1, bs, COOH, exchangeable with D_2O); ir (KBr) 2.3 (OH), 3.35 (CH), 4.45 (C≡N), 5.95 μ (C=O).

Anal. Calcd for $C_9H_6ClNO_2$: C, 55.26; H, 3.09. Found: C, 55.07; H, 3.28.

Attempted Synthesis of 3-Carbethoxypropionic 5-Chloro-α-cyano-2-toluic Anhydride (2).—3-Carbethoxypropionyl chloride[2] (10.8 g, 0.06 mol) was added dropwise (over 0.5 hr) to a mixture of **4** (12 g, 0.06 mol) and pyridine (10.32 g, 0.13 mol) in 200 ml of anhydrous benzene. There was a slight exothermic reaction and an initial precipitate of pyridine hydrochloride formed. After the addition was complete, stirring was continued at room temperature for 1 hr, followed by heating at reflux for 36 hr.

The mixture was filtered to remove the pyridine hydrochloride and the filtrate was allowed to cool to room temperature. An initial precipitate (3.8 g) was formed. An additional 6.6 g of compound was isolated after concentration of the benzene solution. Recrystallization of the combined fractions from absolute ethanol yielded 7.7 g (39.6%) of 6-chloro-3-(3-carbethoxypropionylamino)isocoumarin (**5**): mp 198–199°; nmr (DMSO-d_6) δ 1.17 (3, t, ester methyl), 2.68 (>4, s, CH_2CH_2 and DMSO-d_5), 4.14 (2, q, OCH_2), 7.05 (1, s, =CH), 7.4 (1, dd, J = 9 and 1.5 cps, 7 H), 7.63 (1, d, J = 1.5 cps, 5 H), 8.02 (1, d, J = 9 cps,

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(21) W. Davies and H. G. Poole, *ibid.*, 1616 (1928).

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(23) Melting points were determined using a Büchi capillary melting point apparatus with open capillary tubes and were uncorrected. Infrared spectra were obtained with a Perkin-Elmer Model 21 or Model 237-B infrared spectrophotometer. Mass spectral data were obtained on a Perkin-Elmer Hitachi RMU-6A mass spectrometer. A Varian Associates A-60-A spectrometer was used at a sweep width of 500 cps using TMS as an internal standard. The samples were dissolved in the solvent specified. Ultraviolet spectra were determined on a Bausch and Lomb Model 505 or Cary 14 ultraviolet spectrophotometer. Elemental analyses were determined by Midwest Microlabs, Inc., Indianapolis, Ind.

8 H), and 11.16 ppm (1, bs, NH); ir ($CHCl_3$) 5.75 (ester C=O), 5.80 (lactone C=O), 6.05 (amide C=O and C=C), and 6.25 μ (C=C stretch); mass spectrum M^+ 323 (10), 277 (54), 249 (20), 221 (10), 195 (100), 179 (28), 167 (60), 139 (19), 129 (71), 123 (56), 101 (94); uv λ_M^{EtOH} 244, 251, 290, 298 sh, and 347 mμ (log ϵ_M 4.58, 4.58, 4.39, 4.28, and 4.01, respectively).

Anal. Calcd for $C_{15}H_{14}ClNO_5$: C, 55.65; H, 4.36. Found, C, 55.44; H, 4.53.

Further evaporation of the benzene from above yielded 800 mg of 6-chloro-3-(3-carbethoxyethyl)-4-cyanoisocoumarin (**6**): mp 104.5–105.5° after recrystallization from 95% ethanol; nmr ($CDCl_3$) δ 1.25 (3, t, ester methyl), 3.05 (4, A_2B_2 sextet, CH_2, CH_2), 4.2 (2, q, ester methylene), and 7.9 ppm (3, m, aromatic); ir ($CHCl_3$) 3.42 (CH str), 3.5 (CH str), 4.47 (CN), 5.67 (lactone C=O), and 5.75 μ (ester C=O); mass spectrum M^+ 305 (14), 260 (13), 231 (100), 190 (10), 148 (15), 122 (17).

Anal. Calcd for $C_{15}H_{12}ClNO_4$: C, 58.78; H, 4.21. Found: C, 58.76; H, 4.18.

Hydrolysis of 5. Method A.—A mixture of **5** (3.23 g, 0.01 mol), concentrated hydrochloric acid (7.5 ml), water (7.5 ml), and acetic acid (30 ml) was stirred at reflux under nitrogen for 24 hr. The water and acetic acid were removed *in vacuo*, whereupon a light yellow solid was obtained. The solid was partially dissolved in ether and filtered to remove the ammonium chloride. Evaporation of the ether left a residue, mp 157–161°. Recrystallization from ether–hexane yielded 1.8 g of 5-chlorohomophthalic acid: mp 153.5–156.5°; nmr ($CDCl_3$–pyridine) δ 4.1 ppm (2, s, CH_2), in addition to the aromatic protons from the sample and pyridine. There was also contamination from succinic acid.

From the recrystallization there was also obtained an ether-insoluble fraction, mp 178–182°, 800 mg. This compound was identical in all respects with authentic succinic acid.

Method B.—A mixture of **5** (6.46 g, 0.02 mol), potassium hydroxide (4.93 g, 0.09 mol), and 150 ml of 80% aqueous ethanol was stirred under reflux until ammonia evolution ceased (approximately 48 hr). The ethanol was removed and the residue was dissolved in water. Acidification to pH 2 with 6 *N* hydrochloric acid yielded a solid which was extracted with ether. The ether was dried (Na_2SO_4) and removed *in vacuo* to yield 4.1 g of a white solid which the nmr spectrum indicated to be a mixture of succinic acid and 5-chlorohomophthalic acid. Thin layer chromatography (silica gel, developed with ethanol–ammonia–water 80:4:16, visualized with ceric sulfate) confirmed this result.

Attempted Synthesis of 3-Carbomethoxypropionic α-Cyano-2-toluic Anhydride.—Following the directions of Vogel,[24] the silver salt of 2-carboxyphenylacetonitrile[4] (15.1 g, 0.1 mol) was prepared and suspended in benzene (200 ml) in the dark. 3-Carbomethoxypropionyl chloride[19] was added dropwise. The mixture was then stirred with refluxing for 7 hr.

The mixture was filtered to remove silver chloride (15.35 g, 100%). Upon cooling a light yellow solid (3 g) slowly crystallized: mp 199–201°; nmr (DMSO-d_6) δ 2.5 (>4, m, CH_2CH_2 and DMSO-d_5), 3.55 (3, s, OMe), 6.9 (1, s, =CH), 7.0–8.2 (4, m, aromatic), and 10.7 ppm (1, bs, NH). This material was shown to be 3-(3-carbomethoxypropionylamino)isocoumarin (**5a**).

Evaporation of the benzene yielded unreacted starting material as well as a fraction with carbonyl absorption at 5.57, 5.65, and 5.75 μ in the ir spectrum. There was not a sufficient quantity of this material for identification.

3-Acetylaminoisocoumarin (5b).—Acetyl chloride (4.8 g, 0.06 mol) was reacted with 2-carboxyphenylacetonitrile[4] (9 g, 0.06 mol) in the presence of pyridine as above to yield 4.65 g (40%) of **5b** which was recrystallized from DMSO: mp 230–231°; nmr (DMSO-d_6) δ 1.94 (s, 3, CH_3), 6.88 (s, 1, =CH), 7.1–8.0 (4, m, aromatic), and 10.6 ppm (1, bs, NH).

Anal. Calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89. Found: C, 64.91; H, 4.45; N, 6.68.

3-Aminoisocoumarin (8a).—Dicyclohexylcarbodiimide (28 g, 0.13 mol) in 50 ml of ethyl acetate was added dropwise to a suspension of homophthalamic acid[22] (21 g, 0.12 mol) in 450 ml of ethyl acetate at room temperature. The white suspension gradually became yellow. The mixture was stirred at room temperature for 12 hr.

The dicyclohexylurea was removed by filtration [28 g, mp 230–232° (lit.[25] mp 229–230°)] and the filtrate was concentrated *in vacuo* to yield **8a**, as a yellow solid. Recrystallization from ethyl acetate yielded 6.7 g (35%): mp 127–128.5°; nmr (DMSO-d_6) δ 5.32 (1, s, =CH), 6.5 (2, s, NH_2), and 6.9–8.0 ppm (4, m, aromatic) (the signals at δ 5.32 and 6.5 were removed slowly by washing the sample with D_2O); ir (Nujol mull) 2.95 μ (NH); uv λ_M^{EtOH} 232, 291, and 390 mμ (log ϵ_M 4.36, 4.26, and 3.60, respectively); mass spectrum M^+ 161 (86), 133 (100), 105 (56), 104 (86), 89 (48).

Anal. Calcd for $C_9H_7NO_2$: C, 67.08; H, 4.38; N, 8.69. Found: C, 67.17; H, 4.61; N, 8.55.

Reaction of 2-Carboxyphenylacetonitrile and 3-Aminoisocoumarin (8a) with Pyridine.—2-Carboxyphenylacetonitrile[4] (1.0 g, 6 mmol) and pyridine (0.47 g, 6 mmol) were dissolved in benzene (100 ml) and stirred under reflux for 48 hr. Likewise, **8a** (1.0 g, 6 mmol) was reacted in the same manner. Thin layer chromatography (silica gel PF_{254}, developed with $CHCl_3$–MeOH 95.5, visualized with short wavelength uv light) showed that these systems were identical.

3-(3-Carbomethoxypropionylamino)isocoumarin (5a). Method A.—Acylation of **8a** (1.0 g, 6 mmol) with 3-carbomethoxypropionyl chloride[19] (0.9 g, 6 mmol) in the presence of pyridine (0.5 ml, 6 mmol) yielded 0.38 g (23%) of **5a** after recrystallization from acetonitrile: mp 199–201°; nmr (DMSO-d_6) δ 2.6 (4, s, CH_2CH_2), 3.6 (3, s, OMe), 7.0 (1, s, =CH), 7.5 (5, m, aromatic), and 11.06 ppm (1, bs, NH).

Anal. Calcd for $C_{14}H_{13}NO_5$: C, 61.09; H, 4.76; N, 5.09. Found: C, 61.28; H, 4.82; N, 5.03.

This material was identical in all respects with that material from the silver salt reaction above (mp 199–201°, nmr identical).

Method B.—Reaction of 2-carboxyphenylacetonitrile (1.0 g, 6 mmol) with 3-carbomethoxypropionyl chloride[19] (0.9 g, 6 mmol) as above yielded 0.37 g (23%) of **5a** after recrystallization from acetonitrile, mp 199–201°. This material was identical with **5a** prepared above (mp 199–201°, nmr identical).

Registry No.—**4**, 28519-70-2; **5**, 28519-71-3; **5a**, 28519-72-4; **5b**, 28519-73-5; **6**, 28519-74-6; **8a**, 28607-63-8.

Acknowledgments.—The authors are grateful to the Purdue Research Foundation for financial support (David Ross Predoctoral Research Fellowship to W. J. W.).

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