Annulation Reactions of 3-Aminoisoquinolin-1(2*H*)-one. Synthesis of Pyrimido[1,2-*b*]isoquinolines, Pyrido-[2,3-*c*]isoquinolines and Pyrrolo[2,3-*c*]isoquinolines

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Reactions of the title compound with the malonic acid derivatives diethyl ethoxymethylenemalonate (EMME), ethyl ethoxymethylenecyanoacetate (EMCA) and ethoxymethylenemalononitrile (EMMN) are reported. Condensations occur at the amino group or C-4, depending on conditions and the former intermediate was successfully cyclized to the pyrimido[1,2-*b*]isoquinoline system. Reactions with 2,4-pentanedione and *p*-bromophenacyl bromide gave only the angular systems, pyrido[2,3-*c*]isoquinoline and pyrrolo[2,3-*c*]isoquinoline, respectively.

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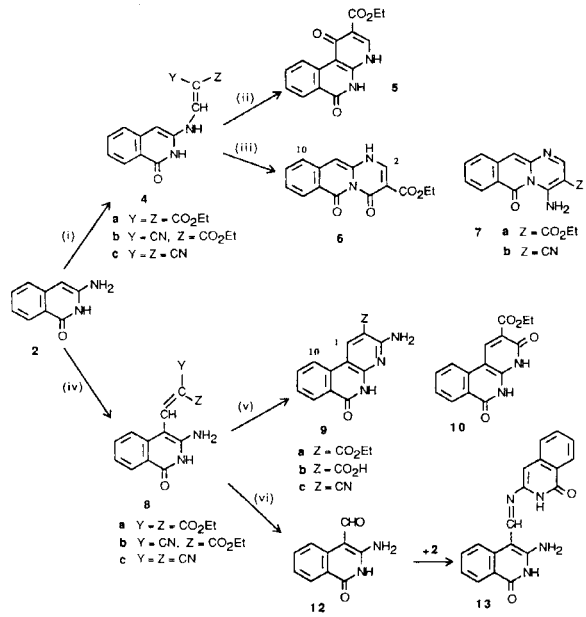
We have looked extensively at the use of isoquinolin-3-amines **1** as intermediates in the formation of polycyclic systems [1]. Reactions have invariably led to angular systems, either through bridging of the amino group and a suitable 4-substituent previously introduced [1] or by direct closure onto C-4 [2]. In principle, cyclizations onto N-2 is possible to give linear fused systems. There are few references to pyrimido[1,2-*b*]isoquinolines, being restricted to saturated pyrimidine rings [3]. We have therefore prepared **2** and report here on some ring annulation reactions which reveal a complex situation but where some examples of the desired linear systems were successfully prepared. Our preparation of **2** was by controlled basic hydrolysis of the available aryloxy compound **1** [4]. The related 1-bromoisoquinolin-3-amine [5] readily gave **3** under acid conditions, and an analogous reaction of this compound is also included. It is clear that **2** and **3** contain various nucleophilic sites so that a range of possible products may arise from reaction with a bis electrophile. Not all were found but reaction with the malonic acid derivatives diethyl ethoxymethylenemalonate (EMME), ethyl ethoxymethylenecyanoacetate (EMCA) and ethoxymethylenemalononitrile (EMMN) reveal some of the complexities.

Reactions of amines with EMME has been carried out under many conditions to give $ArNHCH=C(CO_2Et)_2$ products which can usually be isolated [6]. In the present work with **2** and all three reactants, results were condition dependent. In the reactions discussed below, the reaction times and temperatures are optimum-isolable yields in some cases were quite sensitive to variations.

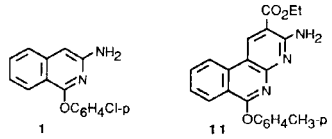
Pyridine as solvent gave generally clean reactions and competition occurred in the initial condensation between reaction at NH_2 and C-4, paths (i) and (iv) in Scheme 1. The least reactive EMME required reflux conditions to get reaction and this gave only **4a**, a 'normal' reaction at the NH_2 group. Reactions of the more reactive EMCA and EMMN were more complex. Products arising from both pathways were isolated and their ^1H nmr spectra contained sufficient key signals (H-4 and NCH=C of **4**, H-11 of **6**, and CHO of **12**) that quite complex crude mixtures could be largely assigned.

Scheme 1



Thus, with EMCA, milder conditions (room temperature/2 hours) favored path (iv). Compound **8b** was not detected as competitive breakdown apparently occurred readily to give a mixture of **9a** and **12**. The former is the expected tricycle and this structure was proved by obtaining the same oxo acid **9b** from hydrolysis of **9a** and the previously obtained **11** [7]. It is not surprising that intramolecular cyclization of **8b** is faster than initial alkylation at C-4, accounting for the failure to detect **8b**. Compound **12** is a hydrolysis product of **8b**. This sequence is a method for formylation of highly activated aromatics (see more below) and has been reported for pyrrole and indole

[8]. Higher temperature reaction with EMCA (90°/1 hour) gave more reaction by path (i) and **9a** and **4b** were isolated in approximately equal yields.



The more reactive EMMN gave complex crude mixtures; no products from path (iv) were positively identified and under mild conditions (50°/5 minutes, then to room temperature for 25 minutes) **4c** was isolated in 32% yield.

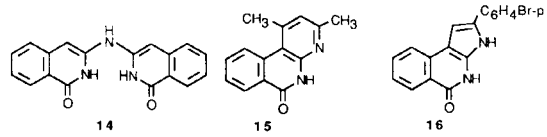
The effect of solvent was well demonstrated by the reaction of **2** with EMME under reflux in acetic acid. Significant reaction now occurred initially at C-4 [path (iv)], as **10** was formed, along with **4a** [path (i)] and a compound assigned structure **14**, all in approximately equal amounts. A related effect of change in solvent on EMME reaction at ring carbon and amine substituent has been reported for an aminopyrimidinedione [9]. Compound **10** obtained in this way was not able to be separated from trace impurities. The structure was confirmed, however, by preparation of the same compound in pure form by diazotization of **9a**. Compound **14** was an extraneous product; it could also be formed by heating **2** alone in acetic acid.

Dimethyl sulfoxide was a neutral solvent in which fairly clean reactions occurred, and which again revealed interesting reactivity differences. Reaction with EMME (100°/1 hour) again gave a mixture of products from both pathways; **4a** was produced, but in lesser amount than in pyridine solvent, and small amounts of **12** and **13** were detected. The compound assigned structure **13** arises from reaction between aldehyde **12** and unreacted **2**, and so the relative amounts of **12** and **13** varied with conditions such as the starting concentration of **2**.

The more reactive EMCA and EMMN were each similar, but different to EMME, in that reaction occurred only by path (iv) in clean reactions (especially EMCA). While no evidence for cyclization of the undetected **8b** (or **8c**) to **9a** (or **9c**) were found (different from the pyridine result), the hydrolysis product **12** (and further **13**) were formed in high yield. With proper control of conditions, the EMCA reaction is in fact a viable synthesis of the aldehyde **12**.

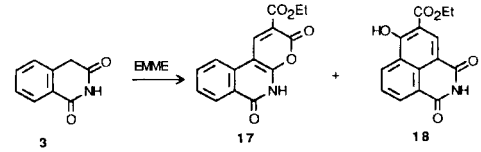
At this point then, conditions for obtaining the precursors **4** of the originally targeted linear compounds had been established but, in cyclization in boiling diphenyl ether, further competition between the two possible modes of ring closure, paths (ii) and (iii), was found, with differences between EMCA/EMMN and EMME intermediates.

Thus, when a cyano group was involved, only linear tricycle formation occurred to the deep-red **7a** and **7b**. On the other hand, the EMME intermediate **4a** gave only **5**. At lower temperature, this latter reaction became more complex, both pathways were followed, and it was possible to optimise conditions (140°/12 hours) so that 33% of the green **6** could be isolated.



Reactions of **2** with these malonic acid derivatives have proved to be complex and difficult to sort out. The initial aim to produce linear tricycles of type **6** has been realised under certain conditions and the chemistry of this pyrimido[1,2-*b*]isoquinoline system can now be further investigated. Two cyclization reactions of **2** with non-malonic acid derivatives were also carried out and each gave only angular products. Thus reaction with neat 2,4-pentanedione gave **15** while *p*-bromophenacyl bromide in ethanol gave **16**. Structure **16**, rather than the isomeric 1-aryl isomer was assigned from ^{13}C nmr; a CH peak at 99.7 ppm is consistent with a free β-type indole position [10].

Since **3** was unlikely to lead to linear compounds of the same sort, we have only had a limited look at an analogous reaction. The existence of this tautomeric form favors condensation reactions at C-4 [11]. Reaction with neat EMME at 190°/4 hours occurred initially through C-4. No intermediate was detected as it rapidly cyclized to **17**. Whereas **9** and **10** are stable, lactone **17** rearranged to the more stable **18** under these conditions and, experimentally, a mix of **17** and **18** was obtained. The isomerization was not a simple thermal process, however. Compound **17** was isolated and shown to give **18** on being boiled for 5 hours in EMME, but not in nitrobenzene or diphenyl ether. Compound **17** had previously been formed by a different route [12] (though some of the data for our compound did not agree) and related compounds were known to isomerise to the corresponding **18** [13].



EXPERIMENTAL

The ^1H nmr spectra are recorded at 300 MHz, in deuterated dimethyl sulfoxide unless otherwise stated. There was a common pattern of two doublets and two triplets (J = 8.5 Hz) for the aromatic protons of the benzo ring in all compounds. Chemical shifts alone are recorded below for these protons.

3-Aminoisoquinolin-1(2*H*)-one (**2**).

Potassium hydroxide solution (20 ml, 20%) was added to a solution of 1-(*p*-chlorophenoxy)isoquinolin-3-amine [4] (1 g) in dimethyl sulfoxide (20 ml) and the mixture was heated under reflux

for 80 minutes, then cooled immediately to 0° and taken to *p*H 7 with concentrated hydrochloric acid. The solid which separated was filtered off, washed with water and recrystallized from ethanol to give the pale yellow product (0.4 g, 67%), mp 265-266° (lit [14] 265°-dec); ^{1}H nmr: δ 5.42 (s, 1, H-4), 5.53 (s, 2, NH_2), 6.95 (H-6(7)), 7.19 (H-5), 7.37 (H-7(6)), 7.90 (H-8), 10.61 (s, 1, NH).

Isoquinoline-1,3(2H,4H)-dione (**3**).

A mixture of 1-bromoisoquinolin-3-amine [5] (1 g) in concentrated hydrochloric acid (40 ml) was heated under reflux for 2.5 hours and then cooled to 0°. The solid which separated was filtered off, washed with water and recrystallized from ethanol to give the greenish-yellow product (0.6 g, 84%), mp 233-235° (lit [11] 223°); ^{1}H nmr: δ 4.13 (s, 2, H-4), 7.47 (H-5), 7.55 (H-6(7)), 7.72 (H-7(6)), 8.11 (H-8), 11.40 (s, 1, NH).

Diethyl (1,2-Dihydro-1-oxoisoquinolin-3-yl)aminomethylenemalonate (**4a**).

A solution of **2** (0.2 g) and EMME (0.4 g) in pyridine (10 ml) was heated under reflux for 2 hours and then poured onto ice and acidified to *p*H 6 with concentrated hydrochloric acid. The solid which separated was filtered off, washed with water and recrystallized from light petroleum (bp 90-110°)/toluene to give the yellow product (0.2 g, 50%), mp 150-152°; ^{1}H nmr (deuteriochloroform): δ 1.30 + 1.39 (t + t, 6, J = 7.2 Hz, CH_2CH_3), 4.27 + 4.37 (q + q, 4, CH_2CH_3), 6.25 (s, 1, H-4), 7.39 (H-6(7)), 7.48 (H-5), 7.62 (H-7(6), 8.43 (H-8), 8.54 (d, 1, J = 12.3 Hz, NHCH), 11.16 (d, 1, J = 12.3 Hz, NHCH), 12.36 (s, 1, NH).

Anal. Calcd. for $C_{17}H_{18}N_2O_5$: C, 61.8; H, 5.5; N, 8.5. Found: C, 61.9; H, 5.3; N, 8.7.

Reaction of **2** with EMCA.

EMCA (0.25 g) was added to a solution of **2** (0.2 g) in pyridine (10 ml), and the mixture was heated at 90° for 1 hour, then poured onto ice and the *p*H taken to 6 with concentrated hydrochloric acid. The solid which separated was filtered off, washed with water and dried to give 0.25 g of product mixture. This was extracted several times with hot toluene, the combined extracts concentrated and cooled to give ethyl (1,2-dihydro-1-oxoisoquinolin-3-yl)aminomethylenecyanoacetate (**4b**) (0.11 g, 28%), mp 192-194°; ^{1}H nmr (deuteriochloroform): δ 1.36 (t, 3, J = 7.2 Hz, CH_2CH_3), 4.30 (q, 2, CH_2CH_3), 6.75 (s, 1, H-4), 7.39 (H-6(7)), 7.51 (H-5), 7.65 (H-7(6)), 8.31 (H-8), 8.39 (s, 1, NHCH), 10.02 (br s, 1, NHCH), 11.56 (s, 1, NH).

Anal. Calcd. for $C_{15}H_{13}N_3O_3$: C, 63.6; H, 4.6; N, 14.8. Found: C, 63.8; H, 4.6; N, 15.0.

The toluene insoluble material was recrystallized from dimethyl sulfoxide to give ethyl 3-amino-5,6-dihydro-6-oxobenzo[*c*][1,8]-naphthyridine-2-carboxylate (**9a**) (0.1 g, 26%), mp >300°; ^{1}H nmr: δ 1.47 (t, 3, J = 7.2 Hz, CH_2CH_3), 4.43 (q, 2, CH_2CH_3), 7.52-7.63 (m, 3, H-8(9) + NH_2), 7.88 (H-9(8)), 8.29-8.36 (m, 2, H-7,10), 9.01 (s, 1, H 1), 11.88 (s, 1, NH).

Anal. Calcd. for $C_{15}H_{13}N_3O_3$: C, 63.6; H, 4.6; N, 14.8. Found: C, 63.4; H, 4.5; N, 14.9.

Samples of **9a** and **11**, when warmed with aqueous sodium hydroxide in dimethyl sulfoxide for 1 hour, and the solutions acidified, each gave the corresponding acid, **9b**, mp >300°.

(1,2-Dihydro-1-oxoisoquinolin-3-yl)aminomethylenemalononitrile (**4c**).

EMMN (0.23 g) was added to a solution of **2** (0.25 g) in pyridine (8 ml). The yellow mixture was stirred at 50° for 5 minutes, then without heat for 25 minutes, and was then poured onto ice. The yellow solid which separated was filtered off, washed with water and recrystallized from *n*-butanol to give the product (0.12 g, 32%), mp 270-271° (darkens and resolidifies); ^{1}H nmr: δ 6.89 (s, 1, H-4), 7.56 (H-6(7)), 7.78 (H-5), 7.87 (H-7(6)), 8.06 (s, 1, NHCH), 8.29 (H-8), 9.15 (br s, 1, NHCH), 11.16 (s, 1, NH).

Anal. Calcd. for $C_{13}H_8N_4O$: C, 66.1; H, 3.4; N, 23.7. Found: C, 66.1; H, 3.2; N, 23.9.

Reaction of **2** with EMME in Acetic Acid.

EMME (0.4 g) was added to a solution of **2** (0.2 g) in acetic acid (15 ml) and the mixture was heated under reflux for 1.5 hours and then concentrated to 1/3 volume under reduced pressure. Light petroleum (bp 60-90°) (40 ml) was added and the solid which separated was filtered off and washed with chloroform (100 ml). The chloroform extract was evaporated and the residue recrystallised from toluene/light petroleum (bp 90-110°) to give **4a** (0.06 g, 15%). The chloroform insoluble solid was extracted with hot toluene to give ethyl 3,4,5,6-tetrahydro-3,6-dioxobenzo[*c*][1,8]-naphthyridine-2-carboxylate **10** (0.05 g, 14%). (This sample could not be completely purified but a pure sample was obtained by another method. Hydrochloric acid/water (1:1, 4 drops) was added to a hot solution of **9a** (0.05 g) in dimethyl sulfoxide (10 ml). This was cooled, sodium nitrite (0.015 g) was added, with stirring, and the mixture was heated for 2 minutes. The solutions was poured onto ice and the solid (0.03 g) was filtered off, washed with water and recrystallized from ethanol to give **10**, mp 277-279°); ^{1}H nmr: δ 1.47 (t, 3, J = 7.2 Hz, CH_2CH_3), 4.46 (q, 2, CH_2CH_3), 7.70 (H-8(9)), 7.95 (H-9(8)), 8.35 (H-7(10)), 8.49 (H-10(7)), 9.12 (s, 1, H-1), 12.05 (br s, 1, NH).

Anal. Calcd. for $C_{15}H_{12}N_2O_4$: C, 63.4; H, 4.3; N, 9.9. Found: C, 63.1; H, 4.0; N, 10.1.

The toluene insoluble solid was recrystallised from acetic acid/-*n*-butanol to give **14** (0.03 g, 9%), mp >300° dec; ^{1}H nmr: δ 6.17 (s, 1, H-4), 7.27 (H-6(7)), 7.49 (H-5), 7.57 (H-7(6)), 8.00 (br s, 1, NH), 8.06 (H-8), 11.29 (br s, 1, NH).

Anal. Calcd. for $C_{18}H_{13}N_3O_2 \cdot 1.25H_2O$: C, 66.4; H, 4.8; N, 12.9. Found: C, 66.7; H, 4.8; N, 13.0.

Ethyl 1,6-Dioxo-1,4,5,6-tetrahydrobenzo[*c*][1,8]naphthyridine-2-carboxylate (**5**).

A solution of **4a** (0.1 g) in diphenyl ether was heated under reflux for 10 minutes, then cooled to room temperature. The solid which formed was filtered off and washed with ether to give the product (0.07 g, 79%), mp 290-292° (from dimethyl sulfoxide); ^{1}H nmr: δ 1.47 (t, 3, J = 7.2 Hz, CH_2CH_3), 4.52 (q, 2, CH_2CH_3), 7.76 (H-8(9)), 7.98 (H-9(8)), 8.45 (H-7), 8.83 (s, 1, H-3), 9.31 (H-10), 12.35 (s, 1, NH).

Anal. Calcd. for $C_{15}H_{12}N_2O_4 \cdot 0.25H_2O$: C, 62.4; H, 4.4; N, 9.7. Found: C, 62.4; H, 4.2; N, 9.8.

Ethyl 1,4-Dihydro-4,6-dioxo-6*H*-pyrimido[1,2-*b*]isoquinoline-3-carboxylate (**6**).

A solution of **4a** (0.1 g) in diphenyl ether (60 ml) was stirred at 140° for 12 hours. The greenish cloudy mixture was cooled to room temperature, ether (20 ml) was added, and the solid which separated was filtered off and washed with ether to give the product (0.03 g, 33%), mp 270-275° (from dimethyl sulfoxide); ^{1}H nmr: δ 1.36 (t, 3, J = 7.2 Hz, CH_2CH_3), 4.28 (q, 2, CH_2CH_3), 6.38 (s, 1, H-2), 7.47 (H-8(9)), 7.65 (H-10), 7.75 (H-9(8)), 8.22 (H-7), 8.39 (s, 1, H-11), 12.30 (s, 1, NH).

Anal. Calcd. for $C_{15}H_{12}N_2O_4 \cdot 0.25H_2O$: C, 62.4; H, 4.4; N, 9.7.

Found: C, 62.7; H, 4.2; N, 9.8.

Ethyl 4-Amino-6-oxo-6*H*-pyrimido[1,2-*b*]isoquinoline-3-carboxylate (**7a**).

A mixture of **4b** (0.1 g) in diphenyl ether (2 ml) was heated under reflux for 1 hour. The deep red solution was cooled, light petroleum (bp 40-70°) (10 ml) was added, and the deep red solid which separated was filtered, washed with light petroleum and recrystallized from toluene to give the product (0.08 g, 80%), mp 239-242°; ^{1}H nmr: (80°) δ 1.37 (t, 3, J = 7.2 Hz, CH_2CH_3), 4.38 (q, 2, CH_2CH_3), 6.26 (s, 1, H-2), 7.24 (H-8(9)), 7.45-7.70 (m, 4, NH_2 + H-9(8),10), 8.17 (H-7), 9.36 (s, 1, H-11).

Anal. Calcd. for $C_{15}H_{13}N_3O_3$: C, 63.6; H, 4.6; N, 14.8. Found: C, 63.8; H, 4.5; N, 14.7.

4-Amino-6-oxo-6*H*-pyrimido[1,2-*b*]isoquinoline-3-carbonitrile (**7b**).

A mixture of **4c** (0.1 g) and diphenyl ether (4 ml) was heated under reflux for 0.5 hour. The red solid which separated from the cooled solution was filtered off, washed with ether, and recrystallized from *n*-butanol to give the product (0.08 g, 80%), mp >300°; ^{1}H nmr: δ 6.39 (s, 1, H-2), 7.39 (H-8(9)), 7.65 (H-10), 7.76 (m, 3, H-9(8) + NH_2), 8.27 (H-7), 9.39 (s, 1, H-11).

Anal. Calcd. for $C_{13}H_8N_4O$: C, 66.1; H, 3.4; N, 23.7. Found: C, 65.8; H, 3.6; N, 24.0.

3-Amino-1,2-dihydro-1-oxoisoquinoline-4-carboxaldehyde (**12**) and 3-[*N*-(3-Amino-1,2-dihydro-1-oxoisoquinolin-4-ylidene)amino]-isoquinolin-1(2*H*)-one (**13**).

A mixture of **2** (0.1 g) and EMCA (0.23 g) in dimethylsulfoxide (8 ml) was stirred at 80° for 1 hour, then poured onto ice and the yellow solid which separated was filtered off, washed with water and then extracted several times with hot water. The combined extracts were concentrated and cooled to give the aldehyde **12** (0.05 g, 42%), mp 244-246°; ^{1}H nmr: δ 7.21 (H-6(7)), 7.58 (H-7(6)), 8.00 (H-5(8)), 8.12 (H-8(5)), 10.17 (s, 1, CHO), 11.19 (s, 1, NH).

Anal. Calcd. for $C_{10}H_8N_2O_2 \cdot H_2O$: C, 58.2; H, 4.9; N, 13.6. Found: C, 58.3; H, 4.7; N, 13.6.

The water insoluble material was the dimer **13** which was insoluble in most solvents and was not purified further; ^{1}H nmr: δ 6.76 (s, 1, H-4), 7.3-7.5 (t + t, 2), 7.65-7.75 (m, 3), 8.10-8.28 (d + d + d, 3), 9.49 (s, 1, CH=N).

1,3-Dimethylbenzo[*c*][1,8]naphthyridin-6(5*H*)-one (**15**).

A solution of **2** (0.1 g) in 2,4-pentanedione (10 ml) was heated under reflux for 3 hours. Light petroleum (bp 40-70°) (20 ml) was added and the mixture was allowed to stand at 4° overnight. The solid which separated was filtered off, washed with light petroleum and recrystallized from ethanol to give the product (0.1 g, 71%), mp 275-277°; ^{1}H nmr (deuteriochloroform): δ 2.54 + 2.88 (s + s, 6, $(CH_3)_2$), 6.92 (s, 1, H-2), 7.60 (H-8(9)), 7.78 (H-9(8)), 8.40 (H-7(10)), 8.59 (H-10(7)), 9.12 (s, 1, NH).

Anal. Calcd. for $C_{14}H_{12}N_2O$: C, 75.0; H, 5.4; N, 12.5. Found: C, 75.0; H, 5.2; N, 12.7.

2-(*p*-Bromophenyl)pyrrolo[2,3-*c*]isoquinoline-5(4*H*)-one (**16**).

A solution of **2** (0.2 g) and *p*-bromophenacyl bromide (0.4 g) in ethanol (20 ml) was heated under reflux for 1 hour, during which time a green solid separated. After being cooled to 0°, the mixture was filtered and the solid was recrystallized from *n*-butanol to give the product (0.1 g, 24%), mp 305-308°; ^{1}H nmr: δ 7.32 (d, 1, J = 1.8 Hz, H-1), 7.43 (H-7(8)), 7.65 (d, J = 8.5 Hz, H-2'(3')), 7.78-7.83 (m, 2, H-8(7) + H-3'(2')), 8.00 (H-9), 8.29 (H-6), 11.70 (s, 1, NH), 12.05 (br s, 1, NH); ^{13}C nmr: δ 99.7 (CH), 104.0 (C), 118.4 (C), 121.6 (C), 121.9 (CH), 123.6 (CH), 125.6 (CH), 128.0 (C), 128.1 (CH), 131.6 (CH), 131.7 (C), 132.5 (CH), 134.0 (2 x C), 161.3 (CO).

Anal. Calcd. for $C_{17}H_{11}BrN_2O$: C, 60.2; H, 3.3; N, 8.3. Found: C, 60.1; H, 3.0; N, 8.2.

The ethanol filtrate was concentrated to give **3** (0.1 g).

Reaction of **3** with EMME.

A mixture of **3** (0.2 g) and EMME (2 ml) was heated at 200° for 2 hours. The cooled mass was stirred with a mixture of diethyl ether and light petroleum (bp 40-70°) (5 ml, 1:1) and the solid which separated was filtered off and washed with ether (0.24 g). Recrystallization from dimethyl sulfoxide gave ethyl 2,3-dihydro-6-hydroxy-1,3-dioxo-1*H*-benz[*de*]isoquinoline-5-carboxylate, **18**, (0.09 g), mp 294-299° (then resolidifies and dec >300°); ^{1}H nmr: δ 1.43 (t, 3, J = 7.2 Hz, CH_2CH_3), 4.49 (q, 2, CH_2CH_3), 7.83 (t, 1, J = 8.5 Hz, H-5), 8.47-8.57 (m, 3, H-4,6,9), 11.49 (s, 1, OH), 12.3 (v, br s, 1, NH).

Anal. Calcd. for $C_{15}H_{11}NO_5$: C, 63.2; H, 3.9; N, 4.9. Found: C, 62.7; H, 3.8; N, 4.9.

Water was added to the filtrate to give ethyl 5,6-dihydro-3,6-dioxo-3*H*-pyrano[2,3-*c*]isoquinoline-2-carboxylate, **17**, (0.08 g), mp 284-287° (from ethanol); ^{1}H nmr: δ 1.41 (t, 3, J = 7.2 Hz, CH_2CH_2), 4.37 (q, 2, CH_2CH_3), 7.63 (H-8(9)), 7.91 (H-9(8)), 8.25-8.31 (m, 2, H-7,10), 9.12 (s, 1, H-1), 13.5 (s, 1, NH).

Anal. Calcd. for $C_{15}H_{11}NO_5$: C, 63.2; H, 3.9; N, 4.9. Found: C, 63.3; H, 4.2; N, 4.8.

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