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Synthetic Routes to 1,5-Dihydro-5-oxo-4,1-benzoxazepines and to 5-Oxooxazolo*[3,2-a]*quinolines

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Dedicated to Professor Hans Suschitzky on the occasion of his 80th birthday.

Abstract: The literature concerning phenacyl anthranilate, *N*- phenacylanthranilic acid and phenacyl *N*-phenacylanthranilate is clarified. Phenacyl anthranilate is dehydrated to 1,5-dihydro-5-oxo-2-phenyl-4,1-benzoxazepine by treatment with phosphoryl chloride; other examples of this reaction are described.

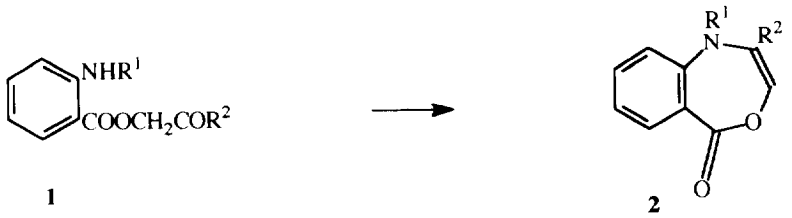
A preparation of 4-methyl-5-oxo-2-phenyloxazolo*[3,2-a]*quinoline from *N*-phenacylanthranilic acid and propionic anhydride is reported.

INTRODUCTION

The 4,1-benzoxazepines have attracted modest attention over the years, in part because of interest in their potential physiological properties. Synthetic work has been mainly directed to derivatives in which the heterocyclic ring is fully hydrogenated (1,2,3,5-tetrahydrobenzoxazepines), with one or more carbon atoms functionalised as a carbonyl group. These include 5-oxo derivatives,[1-3] 2-oxo derivatives,[4,5] 2,5-dioxo derivatives[6] and a 3,5-dioxo derivative.[7] 1,2,3,5-Tetrahydrobenzoxazepines with no oxo function in the heterocyclic ring have also been described.[4,8] Prior to 1983, when we set out to develop a synthesis of 1,5-dihydrobenzoxazepines, no work on dihydrobenzoxazepines had been reported. Subsequently, 2-chloro- and 2-methanethio-3,5-dihydrobenzoxazepines have been described,[5] and a route to 1,5-dihydrobenzoxazepines has been reported which, though similar to ours, employs different starting materials and reagents.[9]

RESULTS AND DISCUSSION

Phenacyl anthranilate was the starting point chosen for our work (**Scheme**). Two phenacyl derivatives of anthranilic acid had been described prior to 1983. The first, *N*-phenacylanthranilic acid, was prepared by Scholtz[10] from anthranilic acid (2 mole) and phenacyl bromide (1 mole) in hot ethanol. Its structure was later confirmed by Franck and Gilligan[11] by an alternative synthesis from isatoic anhydride and phenacyl chloride. Scholtz also noted that reaction of anthranilic acid with phenacyl bromide in ethanol in presence of potassium hydroxide gave a small amount of the disubstituted product, phenacyl *N*-phenacylanthranilate. The second, phenacyl anthranilate, is listed among a series of phenacyl derivatives of carboxylic acids by Rather and Reid,[12] but the compound was not adequately characterised. The procedure used for preparing these derivatives was to react the carboxylic acid with phenacyl bromide in aqueous ethanol in presence of sodium carbonate, and we noticed that the melting point recorded for the anthranilic acid derivative was close to that given by Scholtz for the



1 **2**

a; $R^1 = H$; $R^2 = C_6H_5$

b; $R^1 = H$; $R^2 = 4\text{-}ClC_6H_4$

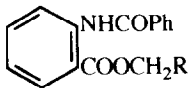
c; $R^1 = H$; $R^2 = 4\text{-}BrC_6H_4$

d; $R^1 = H$; $R^2 = 4\text{-}CH_3C_6H_4$

e; $R^1 = H$; $R^2 = 4\text{-}CH_3OC_6H_4$

f; $R^1 = CH_3$; $R^2 = C_6H_5$

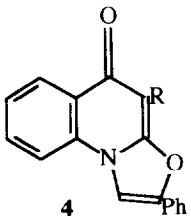
Scheme



3

a; $R = CO_2CH_3$

b; R = CN



4

a; R = H

b; $R = CH_3$

disubstituted product. Repetition of the Rather-Reid experiment gave a material of the reported melting point, and both thin layer chromatographic and spectroscopic comparisons confirm that the product is mainly phenacyl *N*-phenacylanthranilate. We prepared the true phenacyl anthranilate **1a** by reacting anthranilic acid with phenacyl bromide and potassium fluoride in anhydrous DMF; a chromatographic purification was necessary and the yield was low, and a better procedure was found using potassium carbonate with anhydrous acetone as solvent. Data for **1a**, prepared by catalytic hydrogenation of phenacyl 2-nitrobenzoate, have since been reported[9] and tally with our data (melting point and ^{1}H NMR spectrum; the IR absorption reported[9] at 1615 cm^{-1} should be assigned to arom C=C, not to C=O, as we observe the second carbonyl absorption at 1710 cm^{-1}). We have shown that both *N*-phenacylanthranilic acid and **1a** react with phenacyl bromide to give phenacyl *N*-phenacylanthranilate. We used the potassium carbonate in acetone method to prepare a number of substituted phenacyl anthranilates, while α-phenylphenacyl anthranilate was prepared by reacting isatoic anhydride with benzoin.

We explored a variety of acidic conditions for the cyclodehydration of phenacyl anthranilate. By far the best results (yield, reproducibility) were obtained when we used phosphoryl chloride in benzene (2 h reflux). Cyclisation was also achieved using trifluoroacetic acid in benzene (2.5 h reflux), but both yield and purity of product were lower. Minimal success attended the use of polyphosphoric acid (2.5 h, 110 °C), with much of the starting material **1a** recovered. This last result is surprising, given the success with this reagent reported by Sicker,[9] and it may be that he used a reagent containing a higher concentration of phosphorus pentoxide. The properties of the cyclodehydration product reported by Sicker[9] (melting point; IR, ^{1}H NMR and mass spectra) correspond with those that we observed and support structure **2a**, *i.e.*, the enamine tautomer. In addition, all signals in the ^{13}C NMR spectrum of the compound lie in the range δ 118—170 ppm, with only one signal near 170 ppm (C=O). By contrast, the ketimine tautomer would be expected to show an upfield signal near 70 ppm (CH_2) and a second downfield signal near 165 ppm (C=N). The IR spectrum of **2a** is of interest in showing the carbonyl frequency at 1630 cm^{-1} which, though low for enol benzoates, is consistent with carbonyl frequencies of 4-quinolones.[11] The low frequency can be attributed to electron delocalisation involving the nitrogen atom, ring and carbonyl group, perhaps supplemented by intermolecular hydrogen bonding. Hydrolysis of **2a** with methanolic sodium hydroxide gave anthranilic acid, confirming that cyclisation had not involved an aromatic position. We prepared benzoxazepines **2b-f** by the phosphoryl chloride method, and also converted **2a** to **2f** by methylation with iodomethane in presence of potassium fluoride. These benzoxazepines also exhibit carbonyl frequencies near 1630 cm^{-1} (*cf.* ref [9]). Of the α-substituted phenacyl anthranilates, the α-phenyl compound resisted dehydration, but the α-methyl compound could be converted to a benzoxazepine, albeit in poor yield.

We also prepared compounds **3a** and **3b**. Two modes of cyclisation of **3a** to a benzoxazepine can be envisaged; one involves the amide carbonyl and ester methylene groups, and the other (with greater steric demands) involves the amide nitrogen and the ester carbonyl group. A pilot experiment with **3a** using sodium hydride as base suggests that the former course is followed, but the structure of the product requires confirmation.

The availability of *N*-phenacylanthranilic acid allowed us to repeat the reaction with acetic anhydride[10,11] to obtain 5-oxo-2-phenyloxazolo[*3,2-a*]quinoline **4a**. The properties of this compound agree with those reported[10,11] and the ^{13}C NMR spectrum provides additional support for the structure, with the signal for C-4 appearing upfield at δ 89.7. A similar reaction using propionic anhydride gave **4b**, with the signal for C-4 now appearing at δ 99.7. For each of these compounds, hydrolysis with sodium hydroxide opens the oxazole ring and yields the corresponding 1-phenacylhydroxyquinolone. In a related case, it has been shown that the oxazole ring

is not reformed when this type of hydroxyquinolone is refluxed with acetic anhydride.[7] In this reaction sequence leading to the oxazolo[*3,2-a*]quinoline ring system, formation of the oxazole ring thus occurs prior to that of the six-membered ring; intramolecular acylation by a mixed anhydride of an oxazolium cation or its conjugate base is a likely possibility.

EXPERIMENTAL

General

Thin layer chromatography (TLC) was performed on Merck silica gel 60F 254 slides. IR spectra were recorded on an Analect 6260 FTIR spectrophotometer. ^{1}H NMR spectra were recorded at 60 MHz on a WP-60 FT or at 200 MHz on a 200 MHz Bruker AC200 spectrometer using tetramethylsilane as internal standard; the same instruments were used to obtain ^{13}C NMR spectra (15 MHz and 50 MHz respectively) using the solvent as internal standard. Mass spectra were recorded on an AEI MS30 double beam mass spectrometer or a Kratos Concept 1S double focussing mass spectrometer; *m/z* values are quoted for the lowest isotopic species. Representative spectra are quoted below for each compound type.

Preparation of N-Phenacylanthranilic Acid

This compound was prepared by *(a)* Scholtz' method[10] (15% yield; mp 188—192 °C; lit[10] mp 190 °C), and *(b)* Franck and Gilligan's method[11] (33%, variable; mp 195—197 °C; lit[11] mp 183—184 °C); MS: *m/z* (%) 255 (M^+, 7), 150 (43), 137 (11), 132 (100), 119 (19) and 105 (37).

Preparation of Phenacyl N-Phenacylanthranilate

(a) A solution of phenacyl anthranilate (1.0 g, 3.9 mmole) and phenacyl bromide (0.78 g, 3.9 mmole) in ethanol (35 mL) was refluxed for 5 h. The solid that separated was collected, dried, and crystallised from acetic acid to give phenacyl *N*-phenacyl- anthranilate (0.88 g, 60%) as plates, mp 176—179 °C (lit[10] mp 180 °C); ^{1}H NMR ($CDCl_3$) δ 4.65 (d, 2 H, CH_2), 5.53 (s, 2 H, CH_2), 6.63—6.90 (m, 2 H, arom H), 7.35—7.90 (m, 7 H, arom H), 8.00—8.38 (m, 5 H, arom H) and 8.68 (br s, 1 H, NH, exchangeable with D_2O); MS: *m/z* (%) 373 (M^+, 3), 268 (32), 132 (100) and 105 (52).

(b) *N*-Phenacylanthranilic acid (0.26 g, 1.02 mmole) was converted to its anthranilate by the general procedure described in the following experiment. The ester (0.10 g, 26%) crystallised from acetic acid as plates, mp 176—180 °C, identical (mp and mixed mp, TLC, and IR spectrum) with the foregoing sample.

Preparation of Phenacyl Anthranilate and Related Compounds

(a) A mixture of anthranilic acid (4.0 g, 29 mmole) and anhydrous potassium carbonate (2.66 g, 19.3 mmole) in dry acetone (100 mL) was stirred for 30 min. Phenacyl bromide (5.8 g, 29 mmole) was added, and the stirred mixture was refluxed for 5 h. The mixture was filtered while hot, and the solid inorganic material was washed with acetone (35 mL). The combined filtrate and washings were concentrated to *ca.* 50 mL and the solution was poured into water (200 mL). The solid was filtered off, washed with water, dried, and crystallised from ethanol, giving phenacyl anthranilate **1a** (6.0 g, 81%) as light yellow needles, mp 128—129 °C (lit[9] mp 122.5—124 °C); IR (KBr) 1585 (arom C=C), 1615 (arom C=C), 1690 (C=O), 1710 (C=O), 3375 (NH) and 3490 (NH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.02 (s, 2 H, CH_2), 6.19 (br s, 2 H, NH_2, exchangeable with D_2O), 7.14—7.20 (m, 2 H, arom H), 7.75—7.82 (m, 1 H, arom H), 7.95—8.11 (m, 3 H, arom H) and 8.44—8.52 (m, 3 H, arom H); ^{13}C

NMR ($CDCl_3$) δ 66.1 (CH_2), 110.1, 116.5, 116.8, 127.9, 128.9, 131.7, 133.9, 134.4, 134.6, 150.6, 167.3 (CO) and 192.6 (CO); MS: *m/z* (%) 255 (M^+, 44), 120 (90) and 105 (100). Anal. Calc. for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found C, 70.32; H, 5.37; N, 5.35.

Prepared in the same way, **1b** (57%) crystallised from ethanol as needles, mp 135—136 °C; ^{13}C NMR ($CDCl_3$:DMSO-d_6) δ 65.8, 108.2, 114.7, 116.4, 128.7, 129.3, 130.7, 132.4, 134.0, 139.0, 151.4, 166.5 and 192.5; MS: *m/z* (%) 289 (M^+, 24), 139 (100), 120 (95) and 111 (39). Anal. Calc. for $C_{15}H_{12}ClNO_3$: C, 62.19; H, 4.17; Cl, 12.24; N, 4.83. Found C,62.00; H, 3.54; Cl, 11.87; N, 4.71.

Compound **1c** (71%) crystallised from ethanol as needles, mp 129—130 °C (lit[9] mp 133—134.5 °C). Anal. Calc. for $C_{15}H_{12}BrNO_3$: C, 53.91; H, 3.62; N, 4.19. Found C, 53.69; H, 3.68; N, 4.06.

Compound **1d** (56%) crystallised from ethanol as needles, mp 118—119 °C (lit[9] mp 112—113 °C). Anal. Calc. for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found C, 71.27; H, 5.80; N, 5.06.

Compound **1e** (52%) crystallised from ethanol as needles, mp 124—125 °C (lit[9] mp 114—115 °C). Anal. Calc. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found C, 67.29; H, 5.16; N, 5.09.

Compound **1f** (76%) crystallised from ethanol as needles, mp 101—103 °C; IR (KBr) 1680 (C=O), 1710 (C=O) and 3370 (NH) cm^{-1}; ^1H NMR (CF_3CO_2H) δ 3.40 (s, 3 H, CH_3), 5.88 (s, 2 H, CH_2) and 7.28—8.35 (m, 9 H, arom H); MS: *m/z* (%) 269 (M^+, 39), 134 (78) and 105 (100). Anal. Calc. for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found C, 71.34; H, 5.41; N, 5.14.

α-Methylphenacyl anthranilate (65%) crystallised from ethanol as needles, mp 96—97 °C; ^1H NMR ($CDCl_3$) δ 1.74 (d, 3 H, CH_3), 5.69 (br s, 2 H, NH_2, exchangeable with D_2O), and 6.23 (q, 1 H, CH) and 6.72—8.11 (m, 9 H, arom H); ^{13}C NMR ($CDCl_3$) δ 17.2 (CH_3), 71.5 (CH), 110.4, 116.6, 116.8, 128.5, 128.8, 131.5, 133.5, 134.4, 150.3, 167.3 and 197.0; MS: *m/z* (%) 269 (M^+, 48), 120 (100) and 105 (37).

(b) A solution of crystallised isatoic anhydride (4.0 g, 25 mmole), benzoin (5.3 g, 25 mmole) and sodium hydroxide (0.05 g, 1.3 mmole) in freshly distilled dioxan (100 mL) was refluxed for 2 h, then cooled, and poured into water (300 mL). Next day, the solid was filtered off, dried, and crystallised from methanol, giving α-phenylphenacyl anthranilate as needles (1.2 g, 15%), mp 129—134 °C; ^1H NMR ($CDCl_3$) δ 4.63 (s, 1 H, CH), 5.5 (br s, 2 H, NH_2, exchangeable with D_2O) and 6.54—8.14 (m, 14 H, arom H); MS: *m/z* (%) 331 (M^+, 19), 225 (27), 120 (100) and 105 (33).

Reaction of N-Benzoylanthranilic Acid with (a) Methyl Bromoacetate and (b) Bromoacetonitrile

(a) Reaction of *N*-benzoylanthranilic acid (0.50 g, 2.0 mmole) with methyl bromoacetate (0.32 g, 2.1 mmole) as described for the preparation of phenacyl anthranilate gave the methyl ester **3a** (0.40 g, 63%) as a colorless solid which crystallised from ethylene glycol as needles, mp 109—113 °C; ^1H NMR ($CDCl_3$) δ 3.88 (s, 3 H, CH_3), 4.97 (s, 2 H, CH_2), 7.61—7.76 (m, 5 H, arom H), 8.12—8.28 (m, 3 H, arom H), 9.00—9.05 (m, 1 H, arom H) and 11.37 (br s, 1 H, NH, exchangeable with D_2O); ^{13}C NMR ($CDCl_3$) δ 52.3 (CH_3), 61.1 (CH_2), 114.3, 120.5 (CH), 122.7 (CH), 127.3 (CH), 128.7 (CH), 131.2 (CH), 131.9 (CH), 134.8, 135.3 (CH), 142.1, 165.6 (CO) and 167.7 (CO); MS: *m/z* (%) 313 (M^+, 28), 223 (16) and 105 (100).

(b) A similar reaction of *N*-benzoylanthranilic acid with bromoacetonitrile gave **3b** (67%), which crystallised from ethylene glycol as needles, mp 116—119 °C; ^{13}C NMR ($CDCl_3$) δ 49.0 (CH_2), 113.0 (CN), 114.0, 120.7 (CH), 122.8 (CH), 127.3 (CH), 128.9 (CH), 131.1 (CH), 132.2 (CH), 134.5, 136.2 (CH), 142.4, 165.7 (CO) and 166.9 (CO); MS: *m/z* (%) 280 (M^+, 22), 223 (24) and 105 (100).

Preparation of 1,5-Dihydro-5-oxo-2-phenyl-4,1-benzoxazepine and Related Compounds

A mixture of phenacyl anthranilate (3.0 g, 12 mmole), phosphoryl chloride (9 mL) and dry benzene (50 mL) was refluxed for 2 h (steam bath). The reaction mixture was cooled, the solution was decanted off, and the gummy residue was washed several times with light petroleum. The residual solid was dissolved in aqueous ethanol (70 mL) and the solution was basified to pH 7 by adding 5% aqueous sodium hydroxide solution, whereupon crude 1,5-dihydro-5-oxo-2-phenyl-4,1-benzoxazepine **2a** separated as a light yellow solid (1.65 g, 59%), mp 265—268 °C. Crystallisation from ethanol raised the mp to 273—275 °C (lit[9] mp 271—275 °C); IR (KBr) 1630 (C=O) and 3250 (br, NH) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.26—8.21 (m, 10 H, arom H and =CH) and 11.64 (br s, 1 H, NH, exchangeable with D_2O); ^{13}C NMR (DMSO-d_6) δ 118.4, 121.7, 124.3, 128.2, 129.1, 130.4, 131.4, 132.3, 137.7, 138.0 and 170.0 (C=O); MS: *m/z* (%) 237 (M^+, 98), 236 (100), 209 (8), 208 (14), 180 (20), 104 (16) and 77 (32) (no peak was observed at *m/z* 474).[13] Anal. Calc. for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found C, 75.91; H, 4.66; N, 5.76.

Prepared in the same way, compound **2b** was obtained as a light yellow solid (78%), mp 249—251 °C. Crystallisation from ethanol and then from methanol raised the mp to 288—289 °C; IR (KBr) 1632 (C=O) and 3270 (br, NH) cm^{-1}; ^{13}C NMR (DMSO-d_6) δ 118.4, 121.9, 124.4, 128.3, 130.1, 130.6, 131.1, 133.9, 137.9, 138.1 and 170.1; MS: *m/z* (%) 271 (M^+, 100), 270 (91), 236 (10), 208 (15), 180 (10), 103 (20) and 77 (25). Anal. Calc. for $C_{15}H_{10}ClNO_2$: C, 66.31; H, 3.71; N, 5.16. Found C, 66.13; H, 3.67; N, 5.04.

Compound **2c** (90%) had mp 293—295 °C after crystallisation from ethanol (lit[9] mp 297—300 °C). Anal. Calc. for $C_{15}H_{10}BrNO_2$: C, 56.99; H, 3.19; Br, 25.27; N, 4.43. Found C, 56.79; H, 3.69; Br, 25.38; N, 4.42.

Compound **2d** (61%) had mp 270—272 °C after crystallisation from ethanol (lit[9] mp 263—266.5 °C). Anal. Calc. for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found C, 76.05; H, 5.31; N, 5.50.

Compound **2e** (53%) had mp 285—286 °C after crystallisation from acetone and then from ethanol (lit[9] mp 281—284 °C). Anal. Calc. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found C, 71.57; H, 4.96; N, 5.53.

Prepared from phenacyl *N*-methylanthranilate, compound **2f** (34%, variable) was recovered from the crude product by removing sticky impurities by boiling with acetone; crystallisation from dimethyl sulfoxide gave yellow needles, mp 277—279 °C; ^{1}H NMR (CF_3CO_2H) δ 4.10 (s, 3 H, CH_3) and 7.25—8.25 (m, 10 H, arom H and =CH); MS: *m/z* (%) 251 (M , 61), 250 (100), 223 (15), 222 (11), 194 (7), 105 (27) and 77 (35). Anal. Calc. for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found C, 76.45; H, 5.30; N, 5.56.

Cyclodehydration of α-methylphenacyl anthranilate also gave a benzoxazepine, but much of the starting material did not react; leaching the crude product with hot ethanol to remove starting material, followed by crystallisation from acetic acid gave a yellow powder (25%), mp 208—212 °C; MS: *m/z* (%) 251 (M^+, 17), 207 (38), 179 (74) and 105 (100).

Alternative Preparation of 1,5-Dihydro-1-methyl-5-oxo-2-phenyl-4,1-benzoxazepine

A mixture of **2a** (250 mg, 1.05 mmole) and freshly dried potassium fluoride (500 mg, 8.61 mmole) in dry DMF was stirred for 20–30 min; iodomethane (1.75 g, 12.3 mmole) was then added and the mixture was stirred overnight. After filtering off suspended solids, the filtrate was concentrated *in vacuo* and water (60 mL) was added, whereupon a yellow solid separated. Filtration and washing with cold acetone gave a yellow solid (110 mg, 42%), mp 265—267 °C. Crystallisation from dimethyl sulfoxide gave **2f** as needles, mp 274—275 °C, identical with the foregoing sample.

Cyclodehydration of **3a**

Compound **3a** (0.50 g, 1.6 mmole) was added to a stirred suspension of sodium hydride (*ca* 30 mg) in dry benzene (50 mL). The stirred suspension was refluxed for 3 h, then cooled, and t-butanol (2 mL) was then added. The suspension was filtered, and the solid was washed with ether (50 mL). The combined filtrate and washings were evaporated *in vacuo*, and the residue was crystallised from acetic acid giving the dehydration product as an ivory solid (0.18 g, 38%), mp 289—294 °C; MS: *m/z* (%) 295 (M^+, 21), 264 (8) and 105 (100).

5-Oxo-2-phenyloxazolo[3,2-a]quinoline and its 4-Methyl-derivative

Compound **4a**, prepared by the literature method,[10,11] crystallised from pyridine as plates (83%), mp 283—285 °C (lit[10,11] mp 288 °C, 276.5—278 °C); ^{13}C NMR (CD_3CO_2D) δ 89.7 (CH, C-4), 107.7, 116.9 (CH), 124.2, 125.7 (CH), 126.5, 127.5 (CH), 130.2 (CH), 131.4 (CH), 133.0, 150.2 and 157.7; MS: *m/z* (%) 261 (M^+, 41), 152 (21) and 105 (100).

Similarly prepared from *N*-phenacylanthranilic acid and propionic anhydride, 4-methyl-5-oxo-2-phenyloxazolo[3,2-a]quinoline **4b** (26%) crystallised from pyridine as plates, mp 293—295 °C; ^{13}C NMR (CD_3CO_2D) δ 8.5 (CH_3), 99.7 (C-4), 107.9, 116.4 (CH), 124.4, 125.6 (CH), 126.9, 127.6 (CH), 130.2 (CH), 131.2 (CH), 131.9, 132.7 (CH), 149.8 and 156.3; MS: *m/z* (%) 275 (M^+, 100), 246 (41) and 105 (68).

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