Syntheses of 7*H*-pyrido- and 7*H*-pyrano[2,3,4-*kl*]acridin-2(3*H*)-ones from 9-chloroacridines

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A method for *peri*-annulation of the pyridine or pyran ring to acridine was developed and used to obtain 7*H*-pyrido- and 7*H*-pyrano[2,3,4-*kl*]acridin-2(3*H*)-ones. The *peri*-groups were formed by a reaction of 9-chloro-1-nitroacridine with a CH-acid (malononitrile, ethyl cyanoacetate, and ethyl malonate) followed by reduction of the nitro group, or by a reaction of 1-amino-10-methylacridone with PCl_5 and then with a CH-acid. Replacement of the chlorine atom in 9-chloro-1-methoxyacridines by the residue of the CH-acid with subsequent heating in an acidic medium afforded 7*H*-pyrano[2,3,4-*kl*]acridin-2(3*H*)-ones, which belong to a novel heterocyclic system.

Key words: heterocyclization, pyridoacridines, pyranoacridines, acridines, CH-acids.

Acridine derivatives containing a *peri*-annulated heterocycle are of considerable interest for biological investigations. Earlier,[1] we have described the synthesis of pyrido[*kl*]acridines by cyclization of 1-acylaminoacridones. Here we present another route to these heterocycles *via* replacement of the halogen atom in 1-substituted 9-chloroacridine by a C-nucleophile followed by an attack of its electrophilic α-functional group on the substituent in position 1. A literature example of [*kl*]annulation of a heterocycle with acridine is a transformation of 9-ethynyl-1,4-dimethoxyacridine into 6-methoxy-3*H*-pyrido[2,3,4-*kl*]acridine in the presence of sodium diformylamide, which is regarded as electrocyclic ring closure in the enamide anion.[2]

9-Chloroacridine containing the amino group in position 1 was generated by a reaction of 1-amino-10-methylacridone (**1**) with PCl_5 (by analogy with a known[3] reaction of 1-aminoanthraquinone with PCl_5). Treatment of aminoacridone **1** with PCl_5 in benzene and then with a CH acid in the presence of a base directly gave pyrido[2,3,4-*kl*]acridine derivatives. With ethyl cyanoacetate as a CH acid, 1-cyano-2-ethoxy-7-methyl-7*H*-pyrido[2,3,4-*kl*]acridine (**2a**) and 1-cyano-7-methyl-7*H*-pyrido[2,3,4-*kl*]acridin-2(3*H*)-one (**3a**) were obtained in the ratio ~3 : 1 (Scheme 1). The total yield of both products was 78%.

Apparently, in an intermediate with plausible[3] structure **A**, which is initially formed by the action of PCl_5, the Cl atom is replaced by the C-nucleophile, whereupon the N atom in position 1 is attacked by the ethoxycarbonyl rather than cyano group. Elimination of a water molecule from the resulting tetracyclic intermediate **B** is the major process leading to 1-cyano-2-ethoxypyridoacridine **2a**, while elimination of an ethanol molecule gives 1-cyanopyridoacridinone **3a**.

In the case of ethyl malonate, the cyclization yielded a mixture of 2-ethoxy-1-ethoxycarbonyl-7-methyl-7*H*-pyrido[2,3,4-*kl*]acridine (**2b**) and 1-ethoxycarbonyl-7-methyl-7*H*-pyrido[2,3,4-*kl*]acridin-2(3*H*)-one (**3b**) in approximately the same ratio as for products **2a** and **3a**. With malononitrile as a CH acid, the cyclization through the cyano group gave 1-cyano-2-imino-7-methyl-2,3-dihydro-7*H*-pyrido[2,3,4-*kl*]acridine (**4**) as the sole product. Pyridoacridines **3a,b** were identical with compounds obtained by acylation of 1-amino-10-methylacridone with ethyl cyanoacetate and ethyl malonate, respectively, followed by base-catalyzed cyclization.[1]

A reaction of 9-chloro-1-nitroacridine (**5**) with malononitrile in the presence of KOH in DMSO afforded 9-dicyanomethylidene-1-nitro-9,10-dihydroacridine (**6**) in high yield (Scheme 2). The existence of compound **6** in the dicyanomethylidene form rather than in the tautomeric 9-dicyanomethyl-1-nitroacridine form was evident from the presence of the band of the N—H stretching vibrations in its IR spectrum.

Methylation of compound **6** followed by reduction of *N*-methyl derivative **7** gave the same iminopyridoacridine **4** as in the reaction of 1-amino-10-methylacridone (**1**) with PCl_5 and malononitrile.

The reduction of the nitro group to an amino group in both acidic and alkaline media was accompanied by intramolecular cyclization. For instance, treatment of com-

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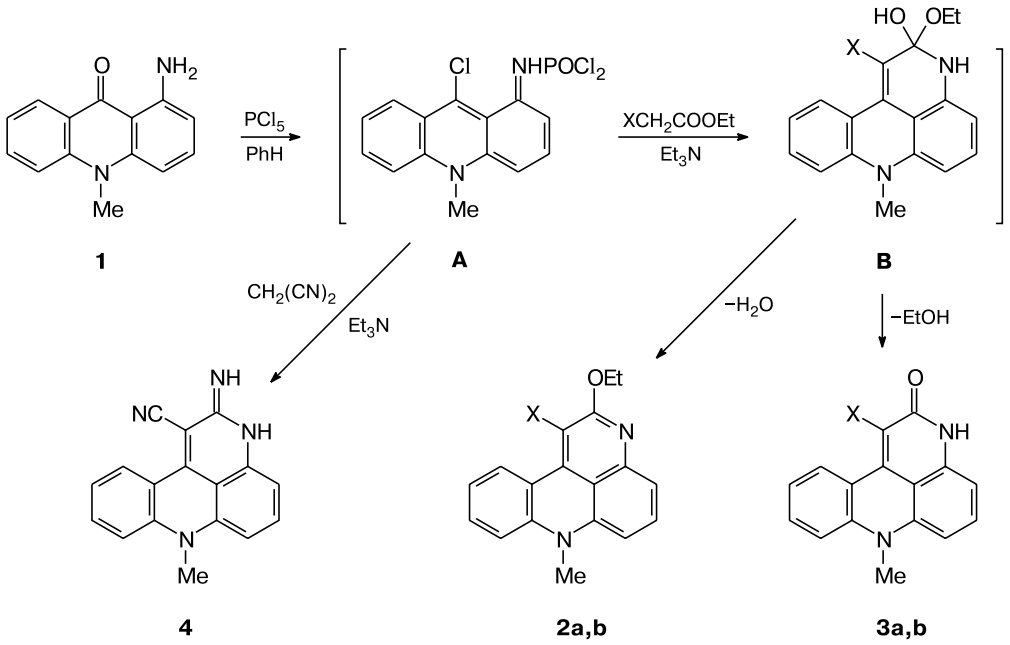
Scheme 1



X = CN (**a**), COOEt (**b**)

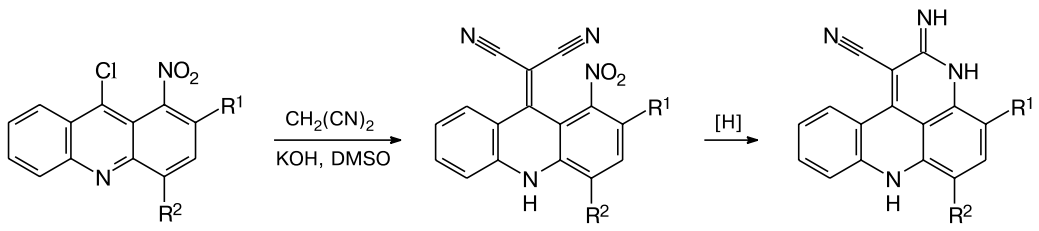
pound **6** with $SnCl_2$ in HCl, or with an iron powder in aqueous ethanol containing acetic acid, or with sodium dithionite in the presence of NaOH gave the same product, *viz.*, 1-cyano-2-imino-2,3-dihydro-7*H*-pyrido[2,3,4-*kl*]acridine (**8**) in good yields (see Scheme 2).

Starting from 9-chloroacridines, one can obtain pyridoacridines with substituents in the acridine moiety. The literature routes to such compounds are very complicated. For instance, a nine-step synthesis of 4-methoxy-7*H*-pyrido[2,3,4-*kl*]acridin-2(3*H*)-one includes intramolecular insertion of a nitrene as a key step in the thermal decomposition of 5-azido-8-methoxy-4-phenylquinolin-2(1*H*)-one.[4]

9-Chloro-1-nitroacridines containing desired substituents are prepared according to a standard procedure[5] while constructing the acridine fragment from appropriate derivatives of *m*-nitroaniline and *o*-chlorobenzoic acid. For illustration, we synthesized 4- and 6-methoxypyridoacridines. Replacement of the Cl atom in 9-chloro-2-methoxy- (**9**)[6] and 9-chloro-4-methoxy-1-nitroacridines (**10**)[7] by malononitrile in DMSO in the presence of KOH yielded 9-dicyanomethylidene-2-methoxy- (**11**) and 9-dicyanomethylidene-4-methoxy-1-nitro-9,10-dihydroacridines (**12**), respectively. Subsequent reduction of the nitro group was accompanied by cyclization into 1-cyano-2-imino-4-methoxy- (**13**) and 1-cyano-2-imino-6-methoxy-2,3-dihydro-7*H*-pyrido[2,3,4-*kl*]acridines (**14**), respectively, in good yields (see Scheme 2).

Imines **4**, **8**, **13**, and **14** can potentially exist as tautomeric aminopyridines and ketones **3a,b**, as hydroxypyridines. The structures of these compounds were confirmed by a comparison of their IR spectra with the spec-

Scheme 2



$R^1 = R^2 = H$ (**5**, **6**, **8**); R^1 = OMe, R^2 = H (**9**, **11**, **13**); R^1 = H, R^2 = OMe (**10**, **12**, **14**)

tra of *O*-alkyl derivatives **2a,b** and *N*-alkyl derivatives[1] with the fixed pyridine and pyridone forms. Like the IR spectra of *N*-alkyl derivatives, the spectra of the compounds obtained show a band due to the stretching vibrations of the exocyclic C=N or C=O double bond at 1641—1651 cm^{-1}, which is absent in the spectra of *O*-alkyl derivatives **2a,b**.

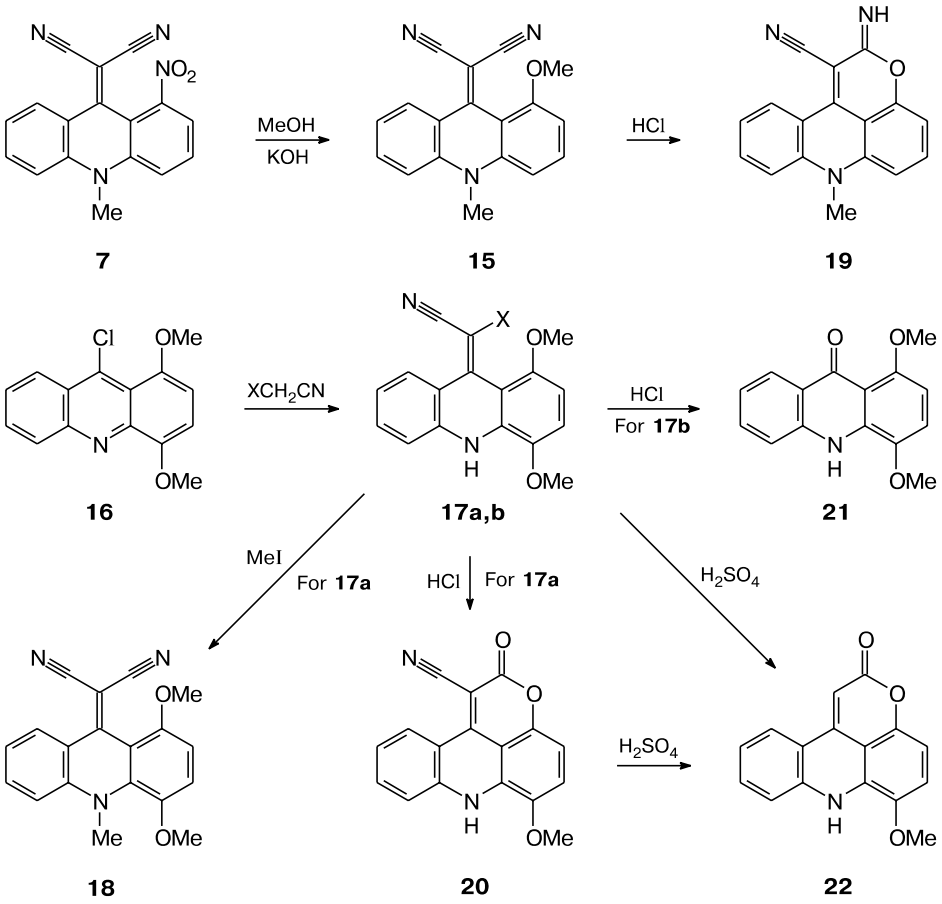
The presence of a nucleophilic heteroatom in position 1 of acridine allows the design of other tetracyclic compounds, which has been illustrated with the synthesis of first representatives of the pyrano[*kl*]acridine system from *peri*-methoxy derivatives.

We found that the nitro group in 9-dicyanomethylidene-10-methyl-1-nitro-9,10-dihydroacridine (**7**) can be easily replaced by a methoxy group in a methanolic solution of KOH, giving 9-dicyanomethylidene-1-methoxy-10-methyl-9,10-dihydroacridine (**15**) (Scheme 3). Starting from 9-chloro-1,4-dimethoxyacridine (**16**) and appropriate CH acids, we obtained 9-dicyanomethylidene-1,4-dimethoxy-9,10-dihydroacridine (**17a**) and 9-cyano(ethoxycarbonyl)methylidene-1,4-dimethoxy-9,10-dihydroacridine (**17b**). Methylation of compound **17a** gave *N*-methyl derivative **18** (see Scheme 3).

The methoxy group that is *peri* to the methylidene substituent is involved in acid-catalyzed intramolecular cyclization leading to pyranoacridinones. Being structurally similar, compounds **15**, **17a,b**, and **18** behaved differently in aqueous HCl. When heated, 1-methoxy derivative **15** promptly yielded 1-cyano-2-imino-7-methyl-2,3-dihydro-7*H*-pyrano[2,3,4-*kl*]acridine (**19**), 1,4-dimethoxy derivative **17a** somewhat more slowly turned into 1-cyano-6-methoxy-7*H*-pyrano[2,3,4-*kl*]acridin-2(3*H*)-one (**20**), compound **17b** underwent hydrolysis to 1,4-dimethoxyacridone **21**, while *N*-methylated 1,4-dimethoxy derivative **18** remained unchanged. Refluxing of 2-iminopyranoacridine **19** in aqueous HCl did not give pyranoacridin-2-one. An analysis of the intramolecular electronic and steric effects that are responsible for the aforementioned differences in reactivity between these structurally similar compounds are beyond the scope of this study.

These differences were eliminated in H_2SO_4. Compounds **17a,b** and 1-cyanopyranoacridine **20** in

Scheme 3

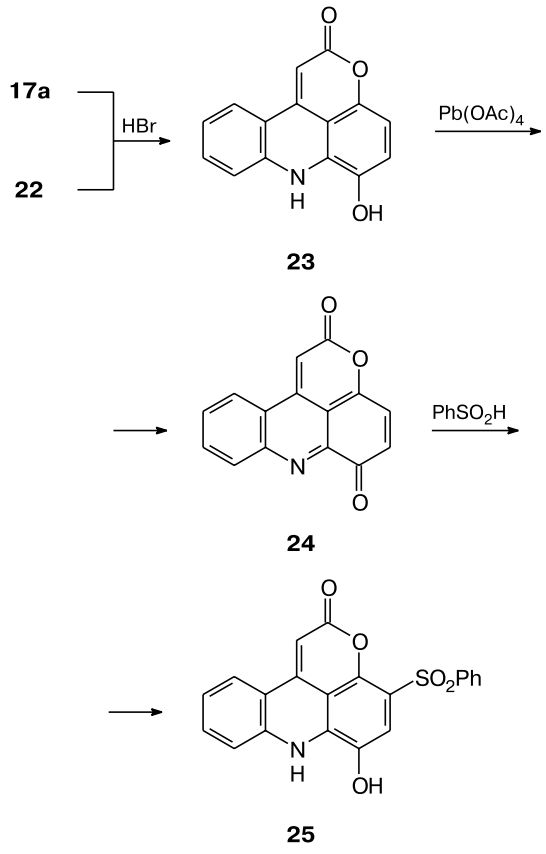


X = CN (**a**), COOEt (**b**)

65% H_2SO_4 at 140 °C yielded 6-methoxy-7*H*-pyrano[2,3,4-*kl*]acridin-2(3*H*)-one (**22**). Under these conditions, *N*-methylated 1,4-dimethoxy derivative **18** underwent cyclization into a 7-methylated analog of pyranoacridine **22**. The cyano group in position 1 of pyranoacridines was eliminated through hydrolysis followed by decarboxylation.

The methoxy group in position 6 of pyranoacridinone **22** was retained under the cyclization conditions in HCl or H_2SO_4. It can be transformed into a hydroxy group (Scheme 4, compound **23**) by heating methoxy derivative **22** with pyridine hydrochloride or hydrobromic acid. Prolonged refluxing in HBr afforded 6-hydroxy-7*H*-pyrano[2,3,4-*kl*]acridin-2(3*H*)-one (**23**) directly from 9-dicyanomethylidene-1,4-dimethoxyacridine **17a**, combining cyclization, elimination of the cyano group, and demethylation in one step.

Scheme 4



23 **24** **25**

Pyrano[2,3,4-*kl*]acridine-2,6-dione (**24**) with a quinonoid structure was obtained by oxidation of 6-hydroxy derivative **23** with lead tetraacetate. This unstable compound was characterized by IR and electronic absorption spectra (λ_{max} = 510 and 550 nm). Like quinones, pyranoacridinedione **24** can be involved in nucleophilic addition reactions. For instance, its reaction with benzenesulfinic acid gave 6-hydroxy-4-phenylsulfonyl-7*H*-pyrano[2,3,4-*kl*]acridin-2(3*H*)-one **25** (see Scheme 4). *O*-Phenylsulfonylation, which is inherent in some quinones,[8] did not take place here, because the reaction product was not hydrolyzed to a hydroxy derivative and was inaccessible *via* treatment of compound **24** with benzenesulfonyl chloride. The $PhSO_2$ group seems to be in position 4 (conjugated in pyranoacridinedione **24** with the carbonyl group).

The possibilities of the synthesis of tetracyclic systems from *peri*-substituted 9-chloroacridines can be enhanced by variation of the CH acid, introduction of substituents into the acridine moiety, and replacement of the heteroatom in position 1.

Experimental

Mass spectra were recorded on a Kratos MS 30 instrument (EI, 70 eV, ion source temperature 250 °C, direct inlet probe). IR spectra were recorded on a FSM 1201 FTIR-spectrometer (in KBr pellets). Electronic absorption spectra were recorded on a Specord M40 spectrophotometer. The course of the reactions was monitored and the purity of the products was checked by TLC on Silufol UV-254 plates. Preparative chromatography was carried out on silica gel (60/100 μm) with chloroform as an eluent. The products were identified by TLC (from R_f values) and IR spectroscopy. 1-Amino-10-methylacridone (**1**),[9] 9-chloro-1-nitroacridine (**5**),[10] 9-chloro-2-methoxy-1-nitroacridine (**9**),[6] 9-chloro-4-methoxy-1-nitroacridine (**10**),[7] and 9-chloro-1,4-dimethoxyacridine (**16**)[11,12] were prepared according to known procedures.

1-Cyano-2-ethoxy-7-methyl-7*H*-pyrido[2,3,4-*kl*]acridine (2a) and 1-cyano-7-methyl-7*H*-pyrido[2,3,4-*kl*]acridin-2(3*H*)-one (3a). Phosphorus pentachloride (0.46 g, 2.2 mmol) was added at 40 °C to a solution of aminoacridone **1** (0.45 g, 2 mmol) in benzene (60 mL). The reaction mixture was stirred for 45 min and the resulting red suspension was added at 5 °C to a solution of ethyl cyanoacetate (1.13 g, 10 mmol) and triethylamine (1.52 g, 15 mmol) in benzene (30 mL). After 30 min, the mixture was filtered and concentrated *in vacuo*. The residue was chromatographed in $CHCl_3$ to give ethoxypyridoacridine **2a** (0.36 g, 60%) and then in ethyl acetate to give pyridoacridinone **3a** (0.10 g, 18%) (*cf.* Ref. 1). Compound **2a**, m.p. 172—174 °C (from methanol). Found (%): C, 76.06; H, 4.97; N, 14.19. $C_{19}H_{15}N_3O$. Calculated (%): C, 75.73; H, 5.02; N, 13.94. IR, ν/cm^{-1}: 2205 (CN).

2-Ethoxy-1-ethoxycarbonyl-7-methyl-7*H*-pyrido[2,3,4-*kl*]acridine (2b) and 1-ethoxycarbonyl-7-methyl-7*H*-pyrido[2,3,4-*kl*]acridin-2(3*H*)-one (3b) were obtained analogously from a potassium salt of diethyl malonate (10 mmol) and triethylamine (15 mmol). Column chromatography gave ethoxypyridoacridine **2b** (0.36 g, 52%) and pyridoacridinone **3b** (0.09 g, 14%) (*cf.* Ref. 1). Compound **2b**, m.p. 157 °C (from methanol). Found (%): C, 72.17; H, 5.83; N, 7.97. $C_{21}H_{20}N_2O_3$. Calculated (%): C, 72.40; H, 5.79; N, 8.04. IR, ν/cm^{-1}: 1717 (COOEt). MS, *m/z*: 348 $[M]^+$.

9-Dicyanomethylidene-1-nitro-9,10-dihydroacridine (6). A solution of nitroacridine **5** (0.52 g, 2 mmol) in DMSO (20 mL)

was added to a solution of malononitrile (0.33 g, 5 mmol) and KOH (0.28 g, 5 mmol) in DMSO (15 mL). The reaction mixture was stirred for 1 h, diluted with water (100 mL), and acidified with acetic acid. The precipitate was filtered off, washed with water, and dried. The yield was 0.49 g (85%), m.p. >350 °C (from butanol). Found (%): C, 66.48; H, 2.76; N, 19.18. $C_{16}H_8N_4O_2$. Calculated (%): C, 66.67; H, 2.80; N, 19.44. IR, ν/cm^{-1}: 1377, 1531 (NO_2); 2212 (CN); 3281 (NH).

9-Dicyanomethylidene-10-methyl-1-nitro-9,10-dihydroacridine (7). Finely powdered KOH (1.20 g) was added to a solution of compound **6** (0.46 g, 1.6 mmol) in DMF (30 mL). To the resulting blue-violet solution MeI (1.2 mL, 20 mmol) was added and the reaction mixture was stirred at 30—35 °C for 1 h and then poured into water (100 mL). The precipitate was filtered off, washed with water, and dried. The yield was 0.37 g (75%), m.p. 308 °C. Found (%): C, 67.48; H, 3.30; N, 18.62. $C_{17}H_{10}N_4O_2$. Calculated (%): C, 67.55; H, 3.33; N, 18.53. IR, ν/cm^{-1}: 1368, 1524 (NO_2); 2212 (CN).

1-Cyano-2-imino-7-methyl-2,3-dihydro-7*H*-pyrido[2,3,4-*kl*]acridine (4). ***A.*** A mixture of 9-dicyanomethylidene-10-methyl-1-nitroacridine (**7**) (0.45 g, 1.5 mmol), conc. HCl (10 mL), and $SnCl_2 \cdot 2H_2O$ (2.5 g) was refluxed for 1 h, cooled, and diluted with water (50 mL). The precipitate of iminopyridoacridine **4** was filtered off, washed with water, and dried. The yield was 0.31 g (75%), m.p. 288—290 °C (from aqueous Pr^{i}OH). Found (%): C, 74.90; H, 4.27; N, 20.60. $C_{17}H_{12}N_4$. Calculated (%): C, 74.98; H, 4.44; N, 20.57. IR, ν/cm^{-1}: 1644 (C=N); 2187 (C≡N); 3406, 3472 (NH).

B. Compound **4** was obtained from aminoacridone **1**, PCl_5, and malononitrile (10 mmol) as described for compounds **2a** and **3a**. The yield of product **4** purified by column chromatography was 0.34 g (62%).

1-Cyano-2-imino-2,3-dihydro-7*H*-pyrido[2,3,4-*kl*]acridine (8). ***A.*** Nitro compound **6** (0.29 g, 1 mmol) was added for 10 min to a mixture of an iron powder (0.5 g), water (20 mL), conc. HCl (0.5 mL), and propan-2-ol (20 mL). The reaction mixture was refluxed with stirring for 1 h and diluted with water (40 mL). Sodium carbonate was added to pH 8.5 and the precipitate was filtered off and triturated with DMF (50 mL). The mixture was filtered and imine **8** was precipitated from the filtrate with water (150 mL). The yield was 0.18 g (70%), m.p. 350—353 °C (from aqueous Pr^{i}OH). Found (%): C, 74.42; H, 4.25; N, 21.43. $C_{16}H_{10}N_4$. Calculated (%): C, 74.41; H, 3.90; N, 21.69. IR, ν/cm^{-1}: 1639 (C=N), 2200 (C≡N), 3348 (NH). MS, *m/z*: 258 $[M]^+$.

B. A mixture of nitro compound **6** (0.44 g, 1.5 mmol), conc. HCl (10 mL), and $SnCl_2 \cdot 2H_2O$ (2.5 g) was refluxed for 1 h, cooled, and diluted with water (50 mL). The precipitate was filtered off and washed with water and propan-2-ol. The yield of imine **8** was 0.30 g (77%).

C. Sodium dithionite (1 g) was added to a suspension of nitro compound **6** (0.29 g, 1 mmol) in aqueous 1.5% NaOH (20 mL). The reaction mixture was stirred at 50 °C for 30 min and diluted with water (30 mL). The precipitate was filtered off, washed with water, and dried. The yield of imine **8** was 0.16 g (62%).

9-Dicyanomethylidene-2-methoxy-1-nitro-9,10-dihydroacridine (11) was obtained from chloroacridine **9** as described for compound **6**. The yield was 0.51 g (80%), red needles (from pentanol), m.p. 283—285 °C. Found (%): C, 64.33; H, 3.31; N, 17.38. $C_{17}H_{10}N_4O_3$. Calculated (%): C, 64.15; H, 3.17; N, 17.60. IR, ν/cm^{-1}: 1320, 1580 (NO_2); 1616 (C=C); 2210 (CN); 3305 (NH).

9-Dicyanomethylidene-4-methoxy-1-nitro-9,10-dihydroacridine (12) was obtained from acridine **10** as described for compound **6**. The yield was 0.40 g (63%), m.p. >350 °C (from aqueous acetone). Found (%): C, 64.10; H, 3.18; N, 17.27. $C_{17}H_{10}N_4O_3$. Calculated (%): C, 64.15; H, 3.17; N, 17.60. IR, ν/cm^{-1}: 1320, 1580 (NO_2); 1612 (C=C); 2210 (CN); 3274 (NH).

1-Cyano-2-imino-4-methoxy-2,3-dihydro-7*H*-pyrido[2,3,4-*kl*]acridine (13) was obtained by reduction of dicyanomethylideneacridine **11** with iron as described for imine **8** (procedure ***A***). The yield was 49%, m.p. >350 °C (from aqueous DMF). Found (%): C, 70.64; H, 4.05; N, 19.06. $C_{17}H_{12}N_4O$. Calculated (%): C, 70.82; H, 4.20; N, 19.43. IR, ν/cm^{-1}: 1635 (C=N), 2190 (C≡N), 3293 (NH). MS, *m/z*: 288 $[M]^+$.

1-Cyano-2-imino-6-methoxy-2,3-dihydro-7*H*-pyrido[2,3,4-*kl*]acridine (14) was obtained by reduction of dicyanomethylideneacridine **12** with $SnCl_2 \cdot 2H_2O$ as described for imine **8** (procedure ***B***). The yield was 54%, m.p. >350 °C (from aqueous DMF). Found (%): C, 70.62; H, 4.05; N, 19.14. $C_{17}H_{12}N_4O$. Calculated (%): C, 70.82; H, 4.20; N, 19.43. IR, ν/cm^{-1}: 1639 (C=N), 2206 (C≡N), 3318 (NH). MS, *m/z*: 288 $[M]^+$.

9-Dicyanomethylidene-1-methoxy-10-methyl-9,10-dihydroacridine (15). Potassium hydroxide (0.70 g, 12 mmol) was added to a boiling solution of 1-nitroacridone **7** (0.36 g, 1.2 mmol) in MeOH (100 mL). The reaction mixture was stirred for 30 min and concentrated by partially removing the solvent (60 mL). The residue was cooled and the precipitate was filtered off and washed with water. The yield of compound **15** was 0.28 g (81%), m.p. 235 °C (from MeOH). Found (%): C, 74.96; H, 4.54; N, 14.82. $C_{18}H_{13}N_3O$. Calculated (%): C, 75.25; H, 4.56; N, 14.62. IR, ν/cm^{-1}: 2204 (CN). MS, *m/z*: 287 $[M]^+$.

9-Dicyanomethylidene-1,4-dimethoxy-9,10-dihydroacridine (17a). A mixture of malononitrile (0.66 g, 10 mmol) and powdered KOH (1.40 g, 25 mmol) in DMSO (30 mL) was stirred for 1 h. A suspension of acridine **16** (2.74 g, 10 mmol) in DMSO (30 mL) was added. The reaction mixture was heated at 50 °C for 1 h, poured into water with ice (250 mL), and acidified with acetic acid. The orange precipitate was filtered off, washed with water, and dried. The yield of compound **17a** was 2.52 g (83%), m.p. 218—220 °C (from butanol—hexane). Found (%): C, 71.29; H, 4.19; N, 13.72. $C_{18}H_{13}N_3O_2$. Calculated (%): C, 71.28; H, 4.32; N, 13.85. IR, ν/cm^{-1}: 2202 (CN), 3289 (NH).

9-Cyano(ethoxycarbonyl)methylidene-1,4-dimethoxy-9,10-dihydroacridine (17b) was obtained analogously from acridine **16** and ethyl cyanoacetate. The yield was 0.22 g (62%), m.p. 290—292 °C (from benzene—hexane). Found (%): C, 68.24; H, 4.88; N, 8.03. $C_{20}H_{18}N_2O_4$. Calculated (%): C, 68.56; H, 5.18; N, 8.00. IR, ν/cm^{-1}: 1701 (C=O); 2192 (CN); 3310, 3327 (NH).

9-Dicyanomethylidene-1,4-dimethoxy-10-methyl-9,10-dihydroacridine (18). Powdered KOH (1.87 g) and MeI (4 mL, 6.4 mmol) were added to a solution of compound **17a** (1.52 g, 5 mmol) in DMSO (50 mL). The reaction mixture was stirred at 30—35 °C for 1 h and poured into water (200 mL). The precipitate was filtered off, washed with water, and dried. The yield of compound **18** was 1.27 g (80%), m.p. 233—235 °C (from Pr^{i}OH). Found (%): C, 71.97; H, 4.75; N, 13.30. $C_{19}H_{15}N_3O_2$. Calculated (%): C, 71.97; H, 4.76; N, 13.24. IR, ν/cm^{-1}: 2210 (CN).

1-Cyano-2-imino-7-methyl-2,3-dihydro-7*H*-pyrano[2,3,4-*kl*]acridine (19). 1-Methoxyacridine **15** (0.29 g, 1 mmol) was refluxed in conc. HCl (10 mL) for 30 min. The precipitate was filtered off and washed with water. The yield of compound **19** was 0.25 g (91%), m.p. >350 °C (from DMF). Found (%): C, 74.67; H, 4.24; N, 15.12. $C_{17}H_{11}N_3O$. Calculated (%): C, 74.71; H, 4.06; N, 15.38. IR, ν/cm^{-1}: 1641 (C=N), 2201 (C≡N), 3370 (NH). MS, *m/z* (I_{rel} (%)): 273 $[M]^+$ (100); 258 $[M - Me]^+$ (15).

1-Cyano-6-methoxy-7*H*-pyrano[2,3,4-*kl*]acridin-2(3*H*)-one (20). A mixture of compound **17a** (1.21 g, 4 mmol) and conc. HCl (70 mL) in Pr^{i}OH (35 mL) was heated at 80 °C for 2 h until the starting reagent was completely consumed. Water (100 mL) was added and the solvent was removed as an azeotrope. The residue was neutralized with aqueous ammonia and the precipitate was filtered off, washed with water, and dried. The yield of compound **20** was 0.91 g (78%), m.p. >350 °C (from DMF). Found (%): C, 69.92; H, 3.69; N, 9.78. $C_{17}H_{10}N_2O_3$. Calculated (%): C, 70.34; H, 3.47; N, 9.65. IR, ν/cm^{-1}: 1690 (C=O), 2195 (CN), 3230 (NH).

1,4-Dimethoxyacridone (21). Compound **17b** (0.35 g, 1 mmol) was refluxed in conc. HCl (20 mL) with Pr^{i}OH (10 mL) for 3 h until the starting reagent was completely consumed. Water was added and aqueous propan-2-ol was distilled off. The residue was neutralized with aqueous ammonia. The yield of compound **21** was 0.21 g (82%); the product was identical with the earlier reported one.[11]

6-Methoxy-7*H*-pyrano[2,3,4-*kl*]acridin-2(3*H*)-one (22). A mixture of dicyanomethylideneacridine **17a** (0.46 g, 0.15 mmol) and 65% H_2SO_4 (7 mL) was stirred at 140 °C for 30 min, cooled, and poured into water (170 mL). The precipitate was filtered off, washed with water, and dried. The yield of compound **22** was 0.27 g (71%), m.p. 263—265 °C (from Pr^{i}OH). Found (%): C, 72.64; H, 4.15; N, 5.31. $C_{16}H_{11}NO_3$. Calculated (%): C, 72.44; H, 4.18; N, 5.28. IR, ν/cm^{-1}: 1684, 1701 (C=O); 3234 (NH).

The identical compound was obtained under the same conditions from acridine **17b** or pyranoacridinone **20** in 85—90% yield.

6-Methoxy-7-methyl-7*H*-pyrano[2,3,4-*kl*]acridin-2(3*H*)-one was obtained analogously from dicyanomethylideneacridine **18**, m.p. 168—170 °C (from methanol). Found (%): C, 73.36; H, 4.80; N, 4.82. $C_{17}H_{13}NO_3$. Calculated (%): C, 73.11; H, 4.68; N, 5.01. IR, ν/cm^{-1}: 1684, 1701 (C=O).

6-Hydroxy-7*H*-pyrano[2,3,4-*kl*]acridin-2(3*H*)-one (23). ***A.*** Compound **22** (0.27 g, 1 mmol) was refluxed in conc. HBr (10 mL) for 5 h until the starting reagent was completely consumed. The reaction mixture was poured into water (100 mL) and neutralized with aqueous ammonia. The precipitate was filtered off and washed with water. The yield of compound **23** was 0.23 g (92%), m.p. 336—338 °C (from aqueous ethanol). Found (%): C, 71.58; H, 3.84; N, 5.30. $C_{15}H_9NO_3$. Calculated (%): C, 71.71; H, 3.61; N, 5.57. IR, ν/cm^{-1}: 1662 (C=O), 3300 (OH). UV-VIS (dioxane), λ_{max}/nm (ε): 435 (9700). MS, *m/z* (I_{rel} (%)): 251 $[M]^+$ (100); 223 $[M - CO]^+$ (25); 195 $[M - 2\,CO]^+$ (28).

The identical compound was obtained in 90% yield by refluxing 9-dicyanomethylidene-1,4-dimethoxyacridine **17a** in conc. HBr for 12 h.

B. A mixture of 6-methoxypyranoacridinone **22** (0.80 g, 3 mmol) and pyridine hydrochloride (7.5 g) was heated at 200 °C for 40 min and then cooled to 90 °C. A saturated solution of $NaHCO_3$ was added at this temperature. The precipitate was filtered off and refluxed in acetone (100 mL). After filtration, the filtrate was concentrated. The yield of hydroxy derivative **23** was 0.53 g (70%).

Pyrano[2,3,4-*kl*]acridine-2,6-dione (24). Lead tetraacetate (1.20 g, 27 mmol) in AcOH (30 mL) was added at 25 °C to a suspension of finely ground compound **23** (0.52 g, 2 mmol) in benzene (100 mL). The reaction mixture was stirred for 20 min. The resulting violet solution was diluted with water (200 mL). The benzene layer was separated and compound **24** was precipitated with hexane (100 mL). The yield was 0.12 g. IR, ν/cm^{-1}: 1721, 1682 (C=O). UV-VIS (dioxane in the presence of $Pb(OAc)_4$), λ_{max}/nm: 510, 550. Dione **24** was reduced with an aqueous solution of hydrazine hydrate or sodium dithionite to the starting compound **23**; product **24** is unstable in storage and in solutions.

6-Hydroxy-4-phenylsulfonyl-7*H*-pyrano[2,3,4-*kl*]acridin-2(3*H*)-one (25). A solution of compound **24** in benzene, which was prepared as described above, was mixed with a solution of benzenesulfinic acid (0.56 g, 4 mmol) in acetonitrile (40 mL). The resulting colorless mixture was stirred at 20 °C for 1 h and the precipitate was filtered off. An additional crop of the solid product was obtained by concentrating the filtrate. The total yield of compound **25** was 0.51 g (65%), m.p. 326—328 °C (from ethanol). Found (%): C, 64.47; H, 3.85; N, 3.54. $C_{15}H_9NO_3$. Calculated (%): C, 64.44; H, 3.35; N, 3.58. IR, ν/cm^{-1}: 1680 (C=O), 3250 br (OH, NH). MS, *m/z* (I_{rel} (%)): 391 $[M]^+$ (100), 251 $[M - PhSO_2 - CO]^+$ (23).

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