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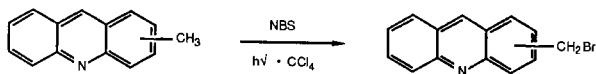
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The four acridinecarbaldehydes, namely, acridine-1-carbaldehyde, acridine-2-carbaldehyde, acridine-3-carbaldehyde, and acridine-4-carbaldehyde have been synthesized for the first time.

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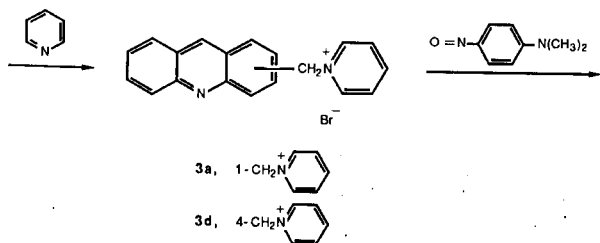
We required the previously unknown 1-, 2-, 3-, and 4-acridinecarbaldehydes **5a-d** for the synthesis of compounds suspected of existing in the heavy ends of coal-derived products.

The starting materials for this four-step synthesis were 1-, 2-, 3-, and 4-methylacridine **1a-d**. When compounds **1a-d** were brominated with *N*-bromosuccinimides (NBS) in carbon tetrachloride using a 100 Watt heat lamp for refluxing and irradiation, the corresponding 1-, 2-, 3-, and 4-bromomethylacridines **2a-d** were obtained. The reaction of the bromomethylacridines **2a-d** with pyridine in tetrahydrofuran (THF) at 0-5° afforded the corresponding acridinylmethylpyridinium bromides **3a-d**. Compounds **3a** and **3d** were isolated and purified to analytical purity; however compounds **3b** and **3c** decomposed at room temperature and it was not possible to characterize them thoroughly; therefore crude **3b** and **3c** were used for the preparation of **4b** and **4c** immediately. Compounds **3b** and **3c** were prepared as described for **3a**. When compounds **3a-d** were allowed to react with *p*-dimethylaminonitrosobenzene in aqueous ethanol containing sodium hydroxide, the corresponding *N'*-acridinylmethylidene-4-dimethylaminoaniline *N*-oxides **4a-d** were obtained. Hydrolytic cleavage of compounds **4a-d** with 1*N* hydrochloric acid provided 1-, 2-, 3-, and 4-acridinecarbaldehydes **5a-d**.

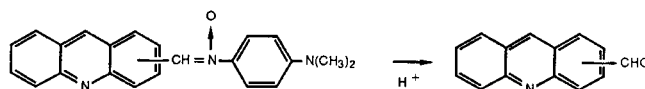


1a, 1-CH₃
1b, 2-CH₃
1c, 3-CH₃
1d, 4-CH₃

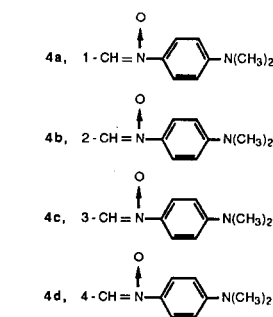
2a, 1-CH₂Br
2b, 2-CH₂Br
2c, 3-CH₂Br
2d, 4-CH₂Br



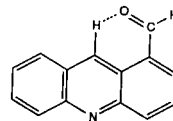
3a, 1-CH₂N⁺Py
3d, 4-CH₂N⁺Py



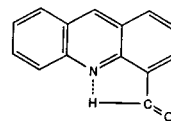
5a, 1-CHO
5b, 2-CHO
5c, 3-CHO
5d, 4-CHO



The nmr spectrum of 1-acridinecarbaldehyde (**5a**) indicates hydrogen bonding between H9 and the carbonyl oxygen atom shown below. Likewise the nmr spectrum of



4-acridinecarbaldehyde indicates hydrogen bonding between the aldehyde proton and the ring nitrogen as indicated below.



EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The ¹H nmr spectra were obtained on a Varian EM 360A spectrometer or on a JEOL FX-90Q Fourier Transform Spectrometer in deuteriochloroform with tetramethylsilane as the internal standard. The ir spectra were measured on a Beckman FT 1100 as potassium bromide discs. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona.

1-Methylacridine (**1a**) [3] and 3-Methylacridine (**1c**) [4].

Compounds **1a** and **1c** were obtained from the reaction of 3'-methylphenylaniline-2-carbaldehyde azide (3.8 g, 9.1 mmoles), glacial acetic acid (20 ml), and concentrated hydrochloric acid (8 ml) by the literature

method [4], and were separated by repeated crystallization from 90% hexanes. Compound **1c** precipitated first as yellow prisms in 40% yield (1.4 g), mp 124-125°, lit [4] mp 125-126°; ¹H nmr: δ 2.57 (s, 3H), 7.20-8.30 (m, 7H), 8.58 (s, 1H).

The more soluble **1a** crystallized next as pale yellow needles in 20% yield (0.7 mg), mp 87-89°, lit [3] mp 89°; ¹H nmr: δ 2.68 (s, 3H), 7.23-8.60 (m, 8H).

1-Bromomethylacridine (**2a**).

A mixture of **1a** (2.3 g, 11.7 mmoles) and *N*-bromosuccinimide (2.3 g, 12.9 mmoles) in carbon tetrachloride (100 ml) was refluxed with exposure to a tungsten lamp for 5 hours. After the mixture was cooled, the suspended succinimide was filtered. The filtrate was evaporated to dryness and the residual material was recrystallized from hexane as pale yellow needles, mp 153-155° dec, yield 2.2 g (68%); ¹H nmr: δ 4.92 (s, 2H), 7.21-8.34 (m, 7H), 8.95 (s, 1H).

Anal. Calcd. for C₁₄H₁₀BrN: C, 61.79; H, 3.70; N, 5.15; Br, 29.36. Found: C, 61.99; H, 3.87; N, 5.15; Br, 29.33.

2-Bromomethylacridine (**2b**).

Compound **2b** was obtained from the reaction of **1b** [4] (1.1 g, 5.8 mmoles) and NBS (1.2 g, 6.7 mmoles) after 3.5 hours irradiation as described for **2a**, as colorless prisms, mp 159-161° dec, yield 0.86 g (54%); ¹H nmr: δ 4.70 (s, 2H), 7.54-8.28 (m, 7H), 8.70 (s, 1H). This compound was used without further purification in the next step.

3-Bromomethylacridine (**2c**).

Compound **2c** was obtained from the reaction of **1c** (6.7 g, 3.5 mmoles) and NBS (6.8 g, 38 mmoles) upon irradiation for 3 hours as described for **2a** as pale yellow prisms from hexane-benzene (1:1) in 63% yield (5.9 g), mp 152-154° dec; ¹H nmr: δ 4.68 (s, 2H), 7.21-8.36 (m, 7H), 8.36 (s, 1H).

Anal. Calcd. for C₁₄H₁₀BrN: C, 61.79; H, 3.70; N, 5.15; Br, 29.36. Found: C, 61.65; H, 3.81; N, 5.12; Br, 29.19.

4-Bromomethylacridine (**2d**).

Compound **2d** was obtained from the photo reaction of **1d** [4] (8.6 g, 45 mmoles) and NBS (8.6 g, 48 mmoles) upon 3 hours irradiation as described for **2a** as pale yellow needles from hexane-benzene (1:2) mp 163-164°, lit [3] mp 164-165° in a yield of 54% (6.4 g); ¹H nmr: δ 5.02 (s, 2H), 7.28-8.47 (m, 7H), 9.08 (s, 1H).

1-Acridinylmethylpyridinium Bromide (**3a**).

Two ml of pyridine was added to a mixture of **2a** (1.7 g, 6.3 mmoles) in 35 ml of tetrahydrofuran (THF) (Fisher Scientific, used without purification), and the mixture was allowed to stand overnight at 0-5°. Compound **3a** precipitated and was filtered to afford pale yellow needles from THF (Fisher Scientific, used without purification), mp 218-222° dec, in 91% yield (2.0 g).

Anal. Calcd. for C₁₉H₁₅BrN₂: C, 64.97; H, 4.30; N, 7.98; Br, 22.75. Found: C, 64.95; H, 4.55; N, 7.89; Br, 22.89.

4-Acridinylmethylpyridinium Bromide (**3d**).

Compound **3d** was obtained from the reaction of **2d** (6.5 g, 24 mmoles) and pyridine (5 ml) in THF (Fisher Scientific, 250 ml, used without purification), in 79% yield (6.6 g) as a yellow powder from THF, mp 230-237° dec, lit [5] mp > 360°.

Anal. Calcd. for C₁₉H₁₅BrN₂: C, 64.97; H, 4.30; N, 7.98; Br, 22.75. Found: C, 65.05; H, 4.42; N, 7.83; Br, 22.61.

N'-(1-Acridinylmethylidene)-4-dimethylaminoaniline *N'*-Oxide (**4a**).

To a mixture of **3a** (0.9 g, 2.6 mmoles) in 30 ml of ethanol was added at room temperature with stirring 4-nitrosodimethylaniline (0.5 g, 3.3 mmoles), followed by 1*N* aqueous sodium hydroxide (15 ml). Stirring was continued for an hour at room temperature, then the mixture was cooled to 5° and diluted with 100 ml of water. The resulting reaction mixture was allowed to stand for 2 hours at 5°. The precipitate was filtered to

give yellow needles from toluene, mp 162-163° dec, in 56% yield (0.49 g).

Anal. Calcd. for C₂₂H₁₉N₃O: C, 77.40; H, 5.61; N, 12.31. Found: C, 77.66; H, 5.89; N, 12.06.

N'-(2-Acridinylmethylidene)-4-dimethylaminoaniline *N'*-Oxide (**4b**).

One ml of pyridine was added to a mixture of **2b** (0.85 g, 3 mmoles) in 10 ml of tetrahydrofuran (Fisher Scientific, used without purification), and the mixture was allowed to stand overnight at 0-5°. The resulting precipitate was quickly dissolved in 20 ml of ethanol, because the pyridinium salt gradually decomposed in the atmosphere. Aqueous sodium hydroxide (2*N*, 20 ml) and *N,N*-dimethyl-4-nitrosoaniline (0.6 g, 4 mmoles) were added to the mixture at room temperature with stirring. The resulting mixture was stirred for 30 minutes and then 70 ml of cold water was added. The mixture was allowed to stand at 0-5° overnight. The precipitated **4b** was filtered and purified to afford brick red needles from toluene, mp 208-210°, yield 0.38 g (36%).

Anal. Calcd. for C₂₂H₁₉N₃O: C, 77.40; H, 5.61; N, 12.31. Found: C, 77.17; H, 5.62; N, 12.07.

N'-(3-Acridinylmethylidene)-4-dimethylaminoaniline *N'*-Oxide (**4c**).

Compound **2c** (5.5 g, 20 mmoles) was dissolved in 80 ml of THF followed by the addition of 5 ml of pyridine which afforded the pyridinium salt **3c** as an unstable precipitate. The unstable **3c** was used immediately by adding 3.8 g (25 mmoles) of *N,N*-dimethyl-4-nitrosoaniline, 30 ml of 2*N* aqueous sodium hydroxide and 50 ml of absolute ethanol. There was obtained 2.4 g (34%) of deep orange prisms from toluene, mp 216-218° dec.

Anal. Calcd. for C₂₂H₁₉N₃O: C, 77.40; H, 5.61; N, 12.31. Found: C, 77.55; H, 5.63; N, 12.23.

N'-(4-Acridinylmethylidene)-4-dimethylaminoaniline *N'*-Oxide (**4d**).

Compound **4d** was obtained from the reaction of **3d** (6.2 g, 18 mmoles) and *N,N*-dimethyl-4-nitrosoaniline (4.5 g, 30 mmoles), 15 ml of 1*N* aqueous sodium hydroxide and 50 ml of ethanol as described for the synthesis of **4a**, yield 5.0 g (83%), as brick-red needles from toluene, mp 176-177°.

Anal. Calcd. for C₂₂H₁₉N₃O: C, 77.40; H, 5.61; N, 12.31. Found: C, 77.56; H, 5.69; N, 12.13.

1-Acridinecarbaldehyde (**5a**).

Thirty ml of 1*N* hydrochloric acid was added to **4a** (0.35 g, 1 mmole) with stirring at room temperature. After 5 minutes stirring it was cautiously neutralized with solid sodium bicarbonate and the precipitate was removed by filtration. It was dissolved in 5 ml of chloroform and placed on a column of alumina. Compound **5a** eluted first with benzene to afford pale green plates after recrystallization from 90% hexanes, mp 118-119°, (0.12 g, 55%); ¹H nmr: δ 7.42-8.61 (m, 7H), 10.23 (s, 1H), 10.36 (s, 1H); ir: ν 2731 (*H-C=O*), 1692 (*C=O*) cm⁻¹.

Anal. Calcd. for C₁₄H₉NO: C, 81.14; H, 4.38; N, 6.76. Found: C, 81.33; H, 4.58; N, 6.82.

2-Acridinecarbaldehyde (**5b**).

Compound **5b** was obtained from the hydrolysis of **4b** (100 mg, 0.3 mmole) with hydrochloric acid (1*N*, 10 ml) as described above, yield 26 mg (43%). There was obtained straw colored plates upon recrystallization from 90% hexanes, mp 196-198°; ¹H nmr: δ 7.37-8.54 (m, 7H), 8.91 (s, 1H), 10.19 (s, 1H); ir: ν 2840 (*H-C=O*), 1692 (*C=O*) cm⁻¹.

Anal. Calcd. for C₁₄H₉NO: C, 81.14; H, 4.38; N, 6.76. Found: C, 80.98; H, 4.44; N, 6.70.

3-Acridinecarbaldehyde (**5c**).

Compound **5c** was obtained from the hydrolysis of **4c** (200 mg, 0.59 mmole) with hydrochloric acid (2*N*, 50 ml) as described above, yield 97 mg (80%). There was obtained pale yellow needles upon recrystallization from 90% hexanes, mp 133-134°; ¹H nmr: δ 7.60-8.34 (m, 6H), 8.69 (m, 1H), 8.78 (s, 1H), 10.27 (s, 1H); ir: ν 2867 (*H-C=O*), 1692 (*C=O*) cm⁻¹.

Anal. Calcd. for C₁₄H₉NO: C, 81.14; H, 4.38; N, 6.76. Found: C, 80.91; H, 4.32; N, 6.65.

4-Acridinecarbaldehyde (**5d**).

Compound **5d** was obtained from the hydrolysis of **4d** (5.0 g, 15 mmoles) with hydrochloric acid (2*N*, 200 ml) as described above. There was obtained 0.1 g (3%) of yellow prisms upon recrystallization from 90% hexanes, mp 140-142°; ¹H nmr: δ 7.35-8.46 (m, 7H), 8.66 (s, 1H), 11.57 (s, 1H); ir: ν 2872 (H-C=O), 1687 (C=O) cm⁻¹.

Anal. Calcd. for C₁₄H₉NO: C, 81.14; H, 4.38; N, 6.76. Found: C, 81.04; H, 4.58; N, 6.85.

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REFERENCES AND NOTES

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