Synthesis of 9,9'-bisacridinediones

P Murugan & V T Ramakrishnan
Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India
Received 27 April 1998; accepted (revised) 28 March 2000

Reaction of octaketone 3 with ammonium acetate/methanol furnishes the 9,9'-bisacridinediones 4a-c. The bisxanthene 5, prepared from octaketone 3, on treatment with ammonium acetate/methanol gives 4a/4b.

The term "bicaridine" is considered to include compounds containing two acridine ring systems directly linked together. 9,9'-Bicaridine was first obtained by heating 10,10'-dimethyl-9,9'-bicaridinium iodide when methyl iodide was evolved. Mostly 9,9'-bicaridine was prepared from 9-chloroacridine with (i) Raney Nickel in methanol, (ii) with Pd/H in xylene and (iii) copper powder. Recently, irradiation of 10-methylcaridione has been reported, which yields 10,10'-dimethyl-9,9'-bicaridine.

In continuation of our work on laser dyes, we have synthesised 10,10'-bicaridines. We report herein the synthesis of 9,9'-bisacridinediones. Condensation of dimedone 1 and glutaraldehyde 2 in aq. ethanol in the presence of pyridine furnished the octaketone 3 (Scheme I) which was refluxed in acetic acid with ammonium acetate/amines to give the respective bisacridinediones 4a-c. The octaketone 3 was refluxed in acetic anhydride to give bixanthene 5, which was subsequently treated with ammonium acetate/methylvamine in acetic acid to get the respective bisacridinedione 4a/4b. The structure of the above compounds were established by their IR, $^1$H NMR and mass spectral data, and elemental analysis. Compound 5b was characterized by X-ray crystallography studies. The mass spectral fragmentation of compound 4a is depicted in Scheme II.

Experimental Section

General. Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer (258) spectrometer. $^1$H and $^{13}$C NMR spectra were taken using jeol GSX400 (400 MHz) spectrometer. Mass spectra were recorded on a Jeol mass spectrometer (JMS- DX 303 HF). Absorption spectra were taken using a Hitachi-320 spectrophotometer. Fluorescence spectra were recorded using LSB Perkin-Elmer fluorescence spectrophotometer.

1, 1, 3, 3-Tetraakis-(5,5-dimethylcyclohexane-1,3-dion-2-yl) propane 3. A 25% solution of glutaraldehyde in water (4.2 mL, 0.01 mole) was added to a solution of dimedone (6 g, 0.04 mole) in ethanol (25 mL). A few drops of pyridine were then added, and the mixture warmed until the solution became cloudy. After 25 min, the reaction mixture was diluted with water (50 mL) and allowed to stand overnight. The separated octaketone 3 was collected by filtration, dried and recrystallized from chloroform-pet. ether (1:1), yield 3.8 g (60%); mp 228 -30°C. Anal. Caled for C$_7$H$_{12}$O$_2$: C, 71.12; H, 8.38. Found: C, 71.48; H, 8.52%. IR (KBr): 1610 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$ 1.01 (bs), 1.95, 2.25 (2 m), 3.81 (t), 12.38 (s); $^{13}$C NMR (CDCl$_3$): $\delta$ 26.9, 29.9, 30.0, 31.4, 46.4, 47.2, 116.5, 189.8, 190.1.

1, 3-Bis [3, 3, 6, 6-tetramethyl-3, 4, 6, 7, 9, 10-hexahydro-1, 8 (2H, 5H) acridinedione-9-yl] propane 4a : General method. To the octaketone 3 (5 mmole) in acetic acid (15 mL) was added ammonium acetate (10 mmole, excess) and the mixture refluxed for 8 hr. The reaction mixture was cooled, the solid obtained was filtered, dried and recrystallized from chloroform-methanol (1:1) to obtain the bisacridinedione 4a, yield 57%; mp 356-358°C. Anal. Caled for C$_{57}$H$_{80}$N$_2$O$_2$: C, 75.72; H, 8.38; N, 4.49%. IR (KBr): 3340 (NH), 1635 (C=O), 1580 (C=C) cm$^{-1}$; UV (MeOH): $\lambda_{max}$ 376 nm; Flu (MeOH): 453 nm: $^1$H NMR (DMSO-d$_6$): $\delta$ 0.8-0.84 (m, 2H, CH$_2$-CH$_2$-); 0.94 (2s, 24H, gem-dimethyl), 1.01-1.11 (m, 4H, CH$_2$-CH$_2$-CH$_2$-), 1.96-2.1 (ABq, 8H J = 13Hz, C$_5$-CH$_2$); 2.15-2.3 (ABq, 8H, J = 14 Hz, C$_6$-CH$_2$); 3.67 (t, 2H, CH-CH$_2$); 8.85 (s, 2H, N-H); MS: m/z 315(20), 298(1), 287(5), 273(20), 272(80), 256(8), 231(8), 230(10), 216(19), 215(40), 188(10), 83(11). The bixanthene 5 was refluxed in acetic acid with ammonium acetate for 5 hr and cooled to obtain 4a in 50% yield.

1, 3-Bis [3, 3, 6, 10-pentamethyl-3, 4, 6, 7, 9, 10-hexahydro-1, 8 (2H, 5H) acridinedione-9-yl] propane
propane 4b: Yield 63%; mp 358-60°C. Anal. Calcd for C_{39}H_{54}N_{2}O_{4}: C, 76.18; H, 8.85; N, 4.96%. IR (KBr): 1649 (C=O), 1580 (C=C) cm\(^{-1}\); UV (MeOH): \(\lambda_{max}\) 380 nm; Flu (MeOH): \(\lambda_{max}\) 466 nm; \(^1\)H NMR (DMSO-d\(_6\)): \(\delta\) 0.76-0.78 (m, 2H, -CH\(_2\)-CH\(_2\)-CH\(_2\)-), 0.82-0.87 (m, 4H, -CH\(_2\)-CH\(_2\)-CH\(_2\)-), 0.92, 1.01 (2s, 24H, gemdimethyl), 2.1 (s, 8H, C\(_5\)-CH\(_2\)), 2.3, 2.61 (ABq, 8H J = 12Hz, C\(_5\)-CH\(_2\)), 3.2 (s, 6H, N-CH\(_3\)), 3.72 (t, 2H, CH-CH\(_2\)); MS: \(m/z\) 799 (80), 420 (2), 379 (20), 378 (100), 362 (8), 342 (8).

Scheme I

1,3-Bis-[10-(4-methoxyphenyl) -3, 4, 6, 6-tetramethyli- 3, 4, 6, 7, 9, 10-hexahydro-1,8 (2H, 5H) acridinedione-9-yl]propane 4c. To the octaketone 3 (1.6 moles) in acetic acid 15 mL was added p-anisidine (3.1 moles) and refluxed for 7 hr. The reaction mixture was cooled and poured into cold water (50 mL). The solid obtained was filtered, dried and recrystallized from chloroform-methanol (1:1) to give 4c, yield (57%); mp 218-20°C. Anal. Calcd for C\(_{57}\)H\(_{62}\)N\(_2\)O\(_6\): C, 76.67; H, 7.82; N, 3.50%. Found: C, 76.82; H, 7.88; N, 3.59%. IR (KBr): 1650 (C=O), 1578 (C=C) cm\(^{-1}\); UV (MeOH): \(\lambda_{max}\) 374 nm; Flu (MeOH): \(\lambda_{max}\) 456 nm; \(^1\)H NMR (DMSO-d\(_6\)): \(\delta\) 0.88 and 0.9 (2s, 24H, gemdimethyl), 1.01 (m, 2H, -CH\(_2\)-CH\(_2\)-CH\(_2\)-), \(J\) = 4Hz), 1.19 (bs, 4H, -CH\(_2\)-CH\(_2\)-CH\(_2\)-), 1.62-2.18 (ABq, 8H, C\(_5\)-CH\(_2\)), 2.0-2.2 (ABq, 8H, C\(_5\)-CH\(_2\)), 3.86 (s, 6H, OCH\(_3\)), 3.92 (bs, 2H, C\(_5\)-H), 7.09-7.31 (ABq, 8H, \(J\) = 6Hz, Ar-H); MS: \(m/z\) 799(80), 420(2), 379(20), 378(100), 362(8), 342(4).

1,3- Bis [3, 3, 6, 6-tetramethyl-1,2,3,4,5,6,7,8-octahydro-1,8-dioxoanthene-9-yl] propane 5. The octaketone 3 (1.6 moles) was refluxed in acetic anhydride (25 mL) for 10 hr. The reaction mixture was concentrated, and the solid 7 formed was filtered,
dried and recrystallized from chloroform to obtain the
xanthene 5, yield 72%, mp 248-50°C. Anal. Calcd for
C<sub>37</sub>H<sub>24</sub>O<sub>5</sub> C, 75.47; H, 8.21. Found: C, 75.68; H, 8.38%. IR (KBr) 1630 (C=O), 1570 (C=C) cm<sup>-1</sup>;
<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.89-0.97 (m, 2H-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.08 and 1.09 (2s, 24H, gem-dimethyl), 1.32-
1.4 (m,4H,-CH<sub>2</sub>-CH<sub>2</sub>-CH=), 2.2-2.27 (ABq, 8H, C<sub>2</sub>-
CH<sub>2</sub>; J = 14Hz), 2.32-2.42 (ABq, 8H, J = 15Hz C<sub>4</sub>
CH<sub>2</sub>), 3.67 (t, 2H,-CH=CH<sub>2</sub>-) <sup>1</sup>C NMR (CDCl<sub>3</sub>): δ 21.9, 25.3, 27.7, 29.1, 32.0, 34.4 40.8, 50.9, 115.1,
163.6, 196.8; MS: m/z 588(10), 315(21), 273(100),
217(17), 161(10), 133(20), 83(6).
Acknowledgement

The authors thank UGC (Special Assistance Programme) and DST New Delhi, for financial support, IIT, Madras for $^1$H NMR data and IICT, Hyderabad for MS.

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