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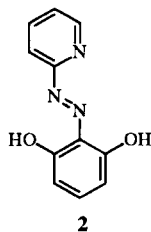
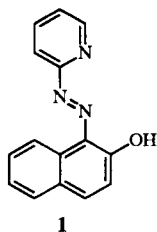
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The preparation of novel azo-dyes from *p*-aminophenylbenzacridinones is described. The structure of all the products was corroborated by ir, mass spectrometry and ¹H-nmr.

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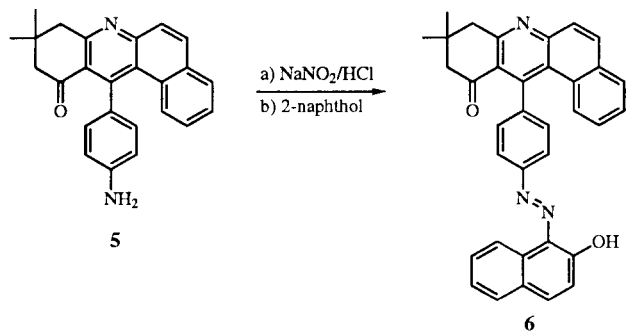
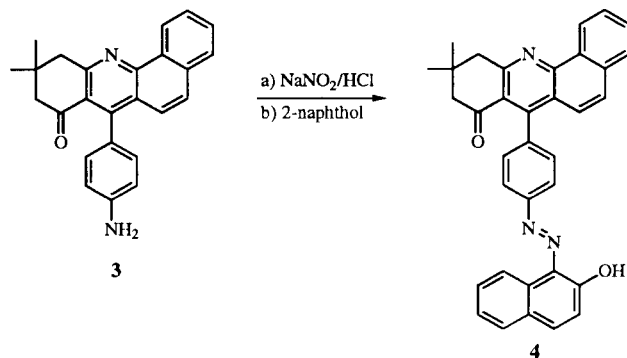
The role of heterocyclic compounds in the synthesis of azo dyes is well known. In addition to their wide utilization as diazo components [3] industrial applications go from fiber, mineral oils and plastic staining [4] to their use in laser devices and conversion solar energy systems [5]. Azo-heterocyclic compounds also are important in qualitative and quantitative analytical methods; 1-(2-pyridylazo)-2-naphthol **1** and 1-(2-pyridylazo)resorcinol **2** are two important examples of these compounds; in particular, metal-ion 1-(2-pyridoylazo)-2-naphthol complexes were studied since 1951 [6] and in 1955, it was reported that 1-(2-pyridylazo)resorcinol can be used as an indicator in direct titration with EDTA [7]. Likewise **1** has been used as chromogenic agent in the spectrophotometric determination of uranium [8,9].



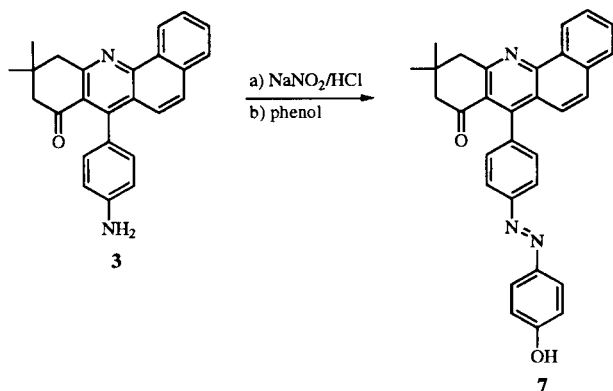
On other hand, as a part of a program directed toward the synthesis and spectral properties of heterocyclic derivatives we have explored the reactivity of benz[*a*] and benz[*c*]acridinones [10]. We describe in this report the synthesis of 1-(2-pyridylazo)-2-naphthol and 1-(2-pyridylazo)resorcinol analogs **4**, **6**, and **7** from 12-(*p*-aminophenyl)benz[*c*]acridinone **3** and 12-(*p*-aminophenyl) benz[*a*]acridinone **5**. Benzacridinones **3** and **5** have been prepared following reported procedures. The structures of these compounds were supported by ir, ¹H and ¹³C-nmr and mass spectral data that were similar to those reported [11].

In a typical procedure 12-(*p*-aminophenyl)benz[*c*]acridin-11-one **3** was diazotized with sodium nitrite and hydrochloric acid and then coupled with 2-naphthol to give **4** as a red-orange compound. Structural assignment

of **4** was made on spectroscopic grounds. The infrared spectrum of **4** displayed absorption at 3592, 1686 and 1386 cm⁻¹ that were assigned to -OH, C=O and N=N stretching, respectively. The presence of ions at *m/z* 521 (M⁺), and 115 (100%) in its mass spectrum was consistent with the existence of an N=N moiety in the framework of **4**. The ¹H-nmr spectrum of **4** showed typical signals for the acridine skeleton: one singlet (6H) at δ 1.2 for the methyl protons joined to C-7; two two-proton signals at δ 2.6 and δ 3.4 for methylene protons joined to C-8 and C-6, one broad signal at δ 5.8 for the hydrogen of phenolic -OH. The remaining aromatic protons in compound **4** appeared as unresolved multiplet at δ 6.8-9.5. All the above data agree with the structure of 12-[*p*-(2-naphthyl)-1-azo]phenyl]-10,10-dimethyl-8,9,10,11-tetrahydrobenz[*c*]acridin-11-one, **4**.



The diazotization and coupling of the 12-(*p*-aminophenyl)benz[*a*]acridin-11-one **5** with 2-naphthol, under similar conditions as for **3**, gave **6**. In the infrared spectra of **6** the appearance of bands at 3598, 1688 and 1537 cm^{-1} was consistent with the presence of hydroxyl, ketone carbonyl and azo group. In agreement with the suggested structure the ^1H -nmr spectra of compound **6** exhibited one proton broad signal at δ 4.76 which exchange upon introduction of deuterium oxide. One six-proton signal at δ 1.2 was assigned to the methyl protons of C-9. Two-proton signals at δ 3.3 and δ 2.6 were assigned to the methylene protons joined to C-8 and C-10. The remaining aromatic protons in compound **6** appeared as unresolved multiplet at δ 6.8-8.7. The mass spectrum of the compound showed the molecular ion at m/z 521 and the base peak at m/z 115 and its fragmentation is according to the assigned structure. All the above data agree with the structure of 12-[*p*-(2-naphtholyl-1-azo)phenyl]-9,9-dimethyl-8,9,10,11-tetrahydrobenz[*a*]acridin-11-one, **6**.



The general run of this reaction was tested when the 12-(*p*-aminophenyl)benz[*c*]acridin-11-one **3** and phenol were allowed to react according to the procedure described above and they afforded **7** as the only product. In agreement with the suggested structure the ir spectra (chloroform) of compound **7** exhibited a characteristically band for the phenolic-hydroxyl group at 3594 cm^{-1} together with a band at 1388 cm^{-1} assignable to the -N=N group. Its ^1H -nmr spectrum showed a singlet at δ 1.2 (6H) for the methyl protons joined to C-7 as well as two two-proton singlets at δ 2.60 and δ 3.75 that were assigned to the methylene protons joined to C-8 and C-6, respectively; one broad signal at δ 3.4 for the hydrogen of phenolic -OH. The remaining aromatic protons in compounds **7** appeared as unresolved multiplet at δ 6.9-9.6. All the above data agree with the structure of 7-[*p*-(hydroxyphenylazo)phenyl]-10,10-dimethyl-8,9,10,11-tetrahydrobenz[*c*]acridin-11-one, **7**.

Further studies of the use of these dyes as complexing agents are presently being carried out.

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded on a Nicolet FT-55X spectrophotometer. The ^1H and ^{13}C nmr spectra were determined on a Varian FT-200 instrument, all nmr spectra were obtained with the pulse sequence as part of the spectrometer's software and was determined in deuteriochloroform solution containing tetramethylsilane as the internal standard with chemical shifts (δ) expressed downfield from TMS. Mass spectra were obtained with a Jeol SX-100 mass spectrometer.

Synthesis of 12-[*p*-(2-Naphtholyl-1-azo)phenyl]-10,10-dimethyl-8,9,10,11-tetrahydrobenz[*c*]acridin-11-one, **4**.

General Procedure. Compound **3** and 2-Naphthol.

The amine **3** (0.310 g, 8.5×10^{-4} mole) was diazotized at pH 5-6, temperature of 0-5° and with a slight excess of nitrous acid during the procedure (starch/KI test). The 2-naphthol (0.120 g, 8.5×10^{-4} mole) was dissolved in aqueous sodium hydroxide (pH 8) with slight heating and then cooled to 0-5°. This solution was added to the stirred diazonium solution while maintaining the temperature at 4° for 1 hour. When the reaction was completed the mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with 10% aqueous sodium hydroxide solution until pH 7-8, dried over anhydrous sodium sulphate and the solvent removed in vacuum and the residue after crystallization from methylene chloride-hexane gave 0.410 g of **4** (93%), mp 243-245°; ir (neat): ν cm^{-1} 3592, 1686, 1545, 1386; ^1H -nmr (deuteriochloroform): δ 1.2 (s, 6H, 2 x CH_3), 2.6 (s, 2H, H-8), 3.4 (s, 2H, H-6), 5.8 (bs, 1H, -OH), 6.8-9.5 (m, 16H, Ar-H); ms: m/z 521 (M⁺), 115 (100%).

Anal. Calcd. for $\text{C}_{35}\text{H}_{27}\text{N}_3\text{O}_2$: C, 80.58; H, 5.22; N, 8.06. Found: C, 80.45; H, 5.18; N, 7.96.

Synthesis of 12-[*p*-(2-Naphtholyl-1-azo)phenyl]-9,9-dimethyl-8,9,10,11-tetrahydrobenz[*a*]acridin-11-one, **6**.

Compound **5** (0.1 g, 2.7×10^{-4} mole) and 2-naphthol (0.04 g, 2.7×10^{-4} mole) were allowed to react according to the procedure described above. Removal of the solvent under reduced pressure followed by recrystallization from methylene chloride-hexane gave 0.128 g (90%) of **6**, mp 270-272°; ir (neat): ν cm^{-1} 3598, 1688, 1537, 1383; ^1H -nmr (deuteriochloroform): δ 1.2 (s, 6H, 2 x CH_3), 2.6 (s, 2H, H-10), 3.3 (s, 2H, H-8), 4.76 (bs, 1H, -OH), 6.8-8.7 (m, 16H, Ar-H); ms: m/z 521 (M⁺), 115 (100%).

Anal. Calcd. for $\text{C}_{35}\text{H}_{27}\text{N}_3\text{O}_2$: C, 80.58; H, 5.22; N, 8.06. Found: C, 80.48; H, 5.20; N, 7.93.

Synthesis of 7-[*p*-(Hydroxyphenylazo)phenyl]-10,10-dimethyl-8,9,10,11-tetrahydrobenz[*c*]acridin-11-one, **7**.

Compound **3** (0.5 g, 1.35×10^{-3} mole) and phenol (0.13 g, 1.35×10^{-3} mole) were allowed to react according to the procedure described above. Removal of the solvent under reduced pressure followed by recrystallization from methylene chloride-hexane gave 0.28 g (44%) of **7**, mp 253-255°; ir (neat): ν cm^{-1} 3594, 1687, 1548, 1388; ^1H -nmr (deuteriochloroform): δ 1.2 (s, 6H, 2 x CH_3), 2.6 (s, 2H, H-8), 2.8 (s, 2H, H-6), 3.4 (bs, 1H, -OH), 6.9-9.6 (m, 14H, Ar-H); ms: m/z 471 (M⁺), 115 (100%).

Anal. Calcd. for $\text{C}_{31}\text{H}_{25}\text{N}_3\text{O}_2$: C, 78.95; H, 5.35; N, 8.92. Found: C, 78.90; H, 5.32; N, 8.87.

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