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Heterocyclic monoazo dyes derived from 2-(*p*-aminophenyl)oxazolo-[4,5-*b*]pyridine and 7-(*p*-aminophenyl)- 4*H*-[1,3,4]thiadiazolo-[2,3-*c*][1,2,4]triazin-4-one

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2-(*p*-Aminophenyl)oxazolo [4,5-*b*]pyridine (**1**; y = O) has been diazotized and coupled with aniline, *N*, *N*-diethylaniline and phenol giving the monoazo dyes **2**. These compounds are quaternized to give the cationic dyes **9** and **10**. 4-Amino-6- methyl-1,2,4-triazine-3(2*H*)-thion-5-one **4** is reacted with *p*-aminobenzoic acid in polyphosphoric acid to afford 7-(*p*-aminophenyl)-3-methyl-4*H*-[1,3,4]thiadiazolo[2,3-*c*][1,2,4] triazin-4-one **3**. A series of monoazo dyes has been obtained using aniline, *N*, *N*-diethylaniline and phenol as coupling components and diazotized **3** as diazo compound.

The synthesis and properties of azo dyes obtained by coupling of the diazonium salts of 2-(*meta* and *para*-aminophenyl)imidazo [4,5-*b*]pyridines[1] (**1**, y = NH) and 2-(*meta* and *para*-aminophenyl oxazolo [4,5-*b*]pyridines[2] (**1** y = O) to obtain the corresponding azo dyes **2** have been already described.

The main synthetic route to 4*H*-[1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-5-one **3** was achieved through ring closure of **4** with a number of acids. Phosphorus oxychloride[3] and sulphuric acid[4] have been used as dehydrating agents. But these reactions fail when the acid used is aminobenzoic acid. Other synthetic methods for [1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazine have also been reported[5,6].

In this paper we wish to report the preparation of dyes derived from oxazolo[4,5-*b*]pyridine, a convenient synthesis of **3** using polyphosphoric acid and coupling of diazonium salt of **3** with aniline,*N*, *N* diethylaniline and phenol to obtain the coupling products as dyestuff.

Results and Discussion

2-(*p*-Aminophenyl)oxazolo[4,5 -*b*]pyridine (**1**, y = O) was prepared by condensing *p*-aminobenzoic acid with 2-amino-3-hydroxypyridine in polyphosphoric acid (85% phosphorus pentoxide)[7,8]. the diazotization of **1** was carried out by the usual procedure using sodium nitrite and hydrochloric acid and the coupling was done in moderatly acidic meidum in the presence of sodium acetate. Phenol, aniline and *N*, *N*-diethylaniline were used as coupling components to obtain the corresponding dyes (**5** and **6**). Compound **5** was acetylated and **6** (*R* = H) benzoylated to give the corresponding acetyl and benzoyl derivatives respectively (**7** and **8**). The UV spectra of **5**-**8** were directly compared and showed a close resemblance of the two patterns apart from the general hypsochromic shift. This hypsochromic shift is due to electron withdrawing nature of the carbonyl group and is expected.

The quaternary salts **9** and **10** were obtained by refluxing the dyes **7** and **8**, with an excess of methyl iodide. In the quaternized dyes (**9**, **10**) it would be expected that the pyridine nitrogen atom is the preferred site of reaction with alkyl halides. ^{1}H NMR spectroscopy confirmed this. The chemical shifts of methylene (δ 3.30) methyl (δ 1.1) protons remained the same in dyes **6**(R^2-Et) and **10** (R^2 = Et) clearly indicating that the nitrogen atom of the *N*, *N*- diethylamino group remains unchanged. Furthermore, in the ^{1}H NMR spectra of **9** and **10** the signal due to methyl group linked to the pyridine nitrogen is clearly detected (δ 4.5 ppm). All the above signals are consistent with

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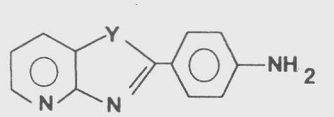

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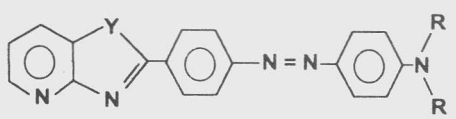

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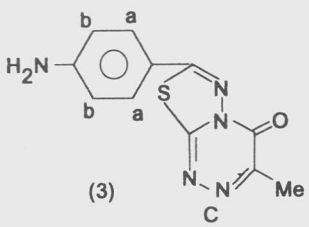

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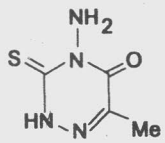

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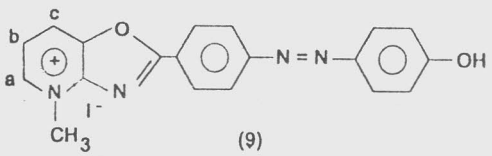

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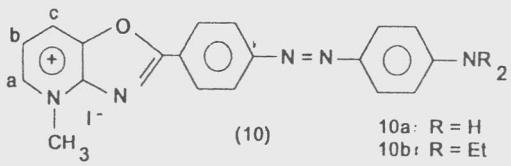

(10)

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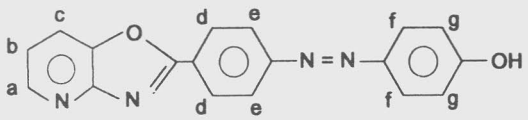
10b: R = Et



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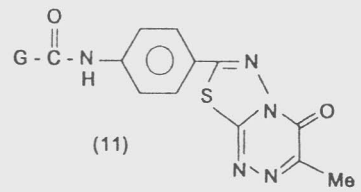
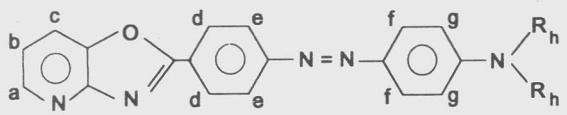


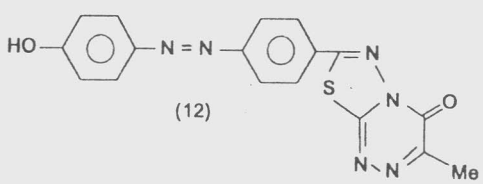
(11)

11a: G = Me
11b: G = Ph



(6)

6a: R = H
6a: R = Et



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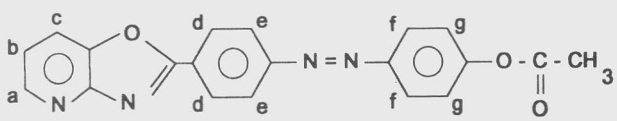

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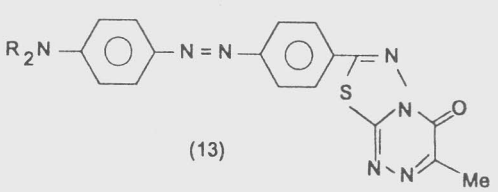
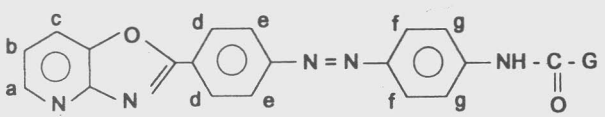


(13)

13a: R = H
13b: R = CH3



(8)

8a: G = Me
8b: G = Ph

those usually observed in pyridinium salts. This is supported by the general downfield shifts of the heteroaromatic protons Ha (δ 8.80 , 1H, doublet), Hb (δ 7.75, 1H, apparent triplet) and Hc (δ 8.65, 1H doublet) which are consistent with those observed for α-, β and δ-protrons in pyrimidinuim salt[9].

The IR spectrum of **10a** (R_2 = H) clearly showed a doublet at 3350 cm^{-1} which was assigned to NH_2 indicating that the amino group in **10a** (R_2 = H) had been retained intact. A comparison of the electronic spectra of **7** and **8** with those of **9** and **10** clearly showed a general bathochromic shift. These data together with mass spectra confirmed the structure assigned to the cationic dyes.

4-amino-6-methyl-1,2,4-triazine-3 (*H*)-thion-5-one **4**[10] was reacted with *p*-aminobenzoic acid in polyphosphoric acid (85% phosphorus pentoxide). The mixture was stirred at 160°C for 6 hr to afford

3. Acetylation and benzoylation of **3** were carried out with acetyl chloride and benzoyl chloride to give **11** (G = CH_3 or Ph).

Diazotization of **3** was carried out by the usual procedure and the resultant diazenium salt coupled with phenol, aniline and *N*, *N* diethylaniline to give the corresponding dyes (**12**, **13**). The spectroscopic data of these dyes were in accord with their structures assigned.

Experimental Section

General. Melting points are uncorrected and were obtained on a Koflar Hazbank Richert type 7841 melting points apparatus. IR spectra were obtained on a 4300 Schimadzu spectrometer. ^{1}H NMR spectra were recorded on a Varian 50 A spectrometer using TMS as internal reference (chemical shifts are reported in δ, ppm). Mass spectra were scanned on a Varian Mat CH-7 instrument at 70 eV.

Diazotization and coupling of 2-(*p*-amino-phenyl)oxazolo[4,5-*b*] pyridine 1. General procedure. Compound **1** (1.055g, 0.005 mole) was dissolved in glacial acetic acid (100 mL) and few drops of conc. hydrochloric acid were added. The reaction mixture was cooled to –5°. To this mixture a solution of sodium nitrite in water (10 mL) was slowly added. During the addition the temperature was kept just below 0°C. To this mixture an appropriate coupling component (0.005 mole) in acetic acid (10 mL) was added. The reaction mixture was stirred for 3 hr at room temperature and then a saturated solution of sodium acetate was added. The resultant solid was filtered, washed with water and crystallized from an appropriate solvent to afford the corresponding azo dye.

The azo dyes thus prepared are given below: **5** (89%), m.p. 300° (deocmp) (from water-ethanol); ^{1}H NMR (DMSO-d_6) 6.8-7 (d, 2H, H_g) 7.3 (q. 1H, H_b), 7.7-7.9 (m, 6H, H_d, H_e, 8.3 (m, 2H, H_a, H_c,) phenolic OH is probably hiden under aromatic protons; IR (KBr): 3550 (OH) 1590, 1500, 1350, 1770, 950 880 cm^{-1}; MS: m/z 316 (M^+, 16%), 315 (59.5.%), 286 (4%), 208 (4%), 191 (33%), 137 (9.5%), 91 (100%),, UV (EtOH): 380 nm.

6a (52%), m.p. 235° from DMSO-water, ^{1}H NMR: 6 (s, 2H, NH_2) exchangeable with D_2O), 6.6-6.8 (d, 2H, H_g), 7.2-7.3 (q, 1H, H_b), 7.7-7.6 (m, 6H, H_d, H_e, H_f), 8.6 (m, 2H, H_a, H_c), IR (KBr): 3300° (–NH_2), 1600, 1500, 1410, 1280, 1110, cm^{-1}; MS, m/z 316; UV (EtOH): 395 nm.

6b (38%), m.p. 252-53°, ^{1}H NMR (DMSPO-d_6): 1(t, 6H, 2CH_3), 3.3 (q, 4H, 2CH_2), 6.4-6.5 (d, 2H, H_g), 7-7.1 (q, 1H, H_b), 7.6 -7.7 (m, 6H, H_d, H_e, H_f, 8.17, (m, 2H, H_a, H_c); IR (KBr): 1590, 1520, 1420, 1150 830 cm^{-1}; MS: m/z 371 (M^+, 100%), 356 (48%), 341 (7%), 192 (7%), 146 (931%). 131 (37%), 117 (15%), 64 (22%); UV (EtOH): 480 nm.

Acetylation of 5. Compound **5** (1g. 0.0031 mole) was placed in a round bottomed flask and acetyl chloride (in excess) added to it dropwise. The reaction mixture was refluxed for 30 min and cooled to room temperature. The resultant solid was filtered, washed with water and crystallized from EtOH-H_2O (76%), to give **7a**, m.p. 238-40°), ^{1}H NMR (DMSO-d_6). 2.6 (S, 3H, CH_3), 8.91 (m, 11H, aromatic proton): IR (KBr); 1680, 1662, 1550 1315, 838,820 cm^{-1}, MS: m/z 358 (M^+, 97%), 315 (100%), 19(20%), 135(10.2%). 76(8.2%), 42(42%), UV (EtOH): 360 nm.

Acetylation of 6a. Compound **6a** (1g, 003 mole) was placed in a round bottomed flask and acetyl chloride (in excess) added to it slowly. The reaction mixture was refluxed for 30 min and cooled to room temperature. The resultant solid was filtered, washed with water and crystallized from EtOH-H_2O to afford **8a** (72%), m.p. 280°; ^{1}H NMR (DMSO-d_6). 2.1 (s, 3H, CH_3), 7.3 (q.1H, H_b, 7.7-8.2 (m, 8H, H_d, H_e, H_t, H_g), 8.4 (m.2H, H_a, H_c), 10.2 (5,1H, NH, exchangeable with D_2O); IR (KBr); 3400, 1680, 1605, 980 cm^{-1}; MS: m/z 415 (M^+ , 0.5%) 314 (26.3%), 299 (63%), 271(5%), 22(5%), 190(100%), 176(5%), 166(10%), UV (EtOH): 365 nm.

Benzoylation of 6a. Compound **6a** (1g; 0.003 mole) was dissolved in pyridine (25 mL) and benzoyl chloride (in excess) added to it dropwise. The reaction mixture was stirred for 3hr at room temperature. the excess solvent was removed by distillation in vacuum. The precipetated solid was filtered, washed with water and crystallized from DMSO-H_2O to afford **8b** (65%), m.p. 250. 52°, ^{1}H NMR (DMSO -d_6): 7.4-8.6 (aromatic protons), 10.6 (s, 1H, NH, exchangeable with D_2O); IR (KBr): 3400, 1664; 1602, 15.5, 1480, 980, 880, 800 cm^{-1}; MS: m/z 419 (M^+,10.5%) 314 (26.3%), 299 (63%), 271(5%), 222(5%), 207(371%),

190(100%), 166(10%), 137(26%); UV (EtOH): 365.

Preparation of cationic dyes: General procedure. The cationic dyes were obtained by refluxing the appropriate dye (**5**, **6a**, or **6b**) with an excess of methyl iodide for 20 hr. The crude material was washed with ether and crystallized from an appropriate solvent to afford the corresponding quaternary salt.

9 (70%), m.p. 235-36°; ^{1}H NMR (DMSO-d_6): 4.5 (s, 3H, N^+-CH_3), 7.1-9.2 (aromatic protons); IR (KBr): 3535, 1650, 1606, 1537, 1423, 1269, 1132, 757, cm^{-1}; MS. m/z 329 (M^+, 1.5%) 319 (1%), 315(65%), 247(38%), 218(31%), 205(95%), 136(85%), 121(46%), 103(12%), 96(100%), 62(85%), UV (EtOH): 398 nm.

10a (67%), m.p. 215°; ^{1}H NMR (DMSO-d_6): 4.4 (s, 3H, $-N^+-CH_3$), 6.3 (s, 2H, NH_2), 6.8-8.8 (aromatic protons); IR (KBr): 3350, 1650 1596, 1541, 1425, 1271, 1132, 856, 757 cm^{-1}; UV: 382 nm.

10b (68%), m.p. 214 (from butyl alcohol-pet. ether); ^{1}H NMR (DNSO-d_6): 1 (t, 6H, $2CH_3$), 4.45 (s, 3H, $-N^+-CH_3$) 6.9-8.8 (aromatic protons); IR (KBr): 1600, 1550, 1400, 1280, 1110 cm^{-1}; UV (EtOH): 477nm.

7-(*p*-Aminophenyl)-3-methyl-4*H*-[1, 3, 4]thiadiazolo [2,3-c][1,2,4]-triazin-4-one 3. Compound **4** (1.57 g, 0.001 mole), *p*-aminobenzoic acid (1.37 g, 0.001 mole) and polyphosphoric acid (40 g, 85%) were mixed. The mixture was heated at 160°C for 6 hr, and transferred to a beaker containing water (200 mL). The *p*H of this solution was then adjusted to **3** by addition of sodium hydroxide. The precipitated solid was filtered and crystallized from EtOH to afford the title compound (77%), m.p. 256°; ^{1}H NMR (DMSO-d_6): 2.5 (s, 3H, CH_3), 3.5(3,2H, NH_2) 6.7(d, 2H, H_a) 7.7 (d, 2H, H_b); IR (KBr): 3530, 1680, 1600, 1400, 1180 cm^{-1}; MS: m/z 259 (M^+, 5.1%) 256(76%), 227(26%), 216(6.6%), 160 (15%) 134 (100%), 116(32%), 91(11%), 67(11%), 28(64%), UV (EtOH): 366 nm.

Acetylation of 3. Compound **3** (1g; 0.0038 mole) was dissolved in acetic acid (50 mL). To this solution acetyl chloride (in excess) was added dropwise, and the reaction mixture refluxed for 30 min and then poured into water. The precipitated solid was filtered off to afford **11a** (67%), m.p. 290-292°; ^{1}H NMR (DMSO-d_6): 2 (s, 3H, CH_3) 2.4 (s, 3H, CH_3) 7.5-7.7 (m, 4H, H_a, H_b 10.2 (s, 1H, NH, exchangeable with D_2O); IR (KBr): 1680, 1602, 1510, 1489, 1200, 830 cm^{-1} , MS: m/z 302(M^+, trace), 300(27%), 260(50%), 229(27%), 135(86%), 116(100%), 70(89%), 44(45%), UV (EtOH): 336 nm.

Benzoylation of 3. Compound **3** (1g; 0.0038 mole) was dissolved in pyridine (50 mL) and benzoyl chloride (in excess) added to it dropwise. The reaction mixture was stirred for 2hr. The volume of pyridine was reduced by distillation in vacuum. The residue was poured into water and the precipitated solid filtered off, washed with water and dried to afford **11b** (67%), m.p. 280-81°; ^{1}H NMR (DMSO-d_6): 2.3 (s, 3H, CH_3) 7.2-7.4 (m, 9H, C_6H_4 and C_6H_5), 10.25 (8, 1H, NH); IR (KBr): 3420, 1720, 1630, 1595, 1405, 1320, 1190, 830 cm^{-1}; MS: m/z 363(M^+, trace), 362 (5.1%), 290(2%), 216(3%), 118(3.7%), 101(100%), 75(45%), 49(1.3%), 28(5.1%); UV (EtOH): 325 nm.

Diazotization and coupling of 7-(*p*-aminophenyl-3-methyl-4*H*-[1, 3, 4]thiadiazolo[2,3-c][1,2,4]triazin-4 one 3: General procedure. Compound **3** (0.518 g, 0.005 mole) was dissolved in glacial acetic acid (100 mL) and to this mixture few drops of concentrated hydrochloric acid were added. The reaction mixture was cooled down to −5°C. To this mixture a solution of sodium nitrite (0.395g, 0.005 mole) in water (10mL)] was added slowly. During the addition to water the temperature was kept just below 0°C. To this mixture an appropriate coupling compound (0.005 mole) in acetic acid (10 mL) was added dropwise. The reaction mixture was stirred for 3hr at room temperature and then saturated solution of sodium acetate added to it. The precipitated solid was filtered, washed with water and crystallized from an appropriate solvent to afford the corresponding azo dye. The azo dyes thus prepared are given below:

12 (57%), m.p. 240° (from DMSO-H_2O); ^{1}H NMR (DMSO-d_6): 2.9(s, 3H, CH_3), 6.8-7.8 (m, 9H, aromatic protons and phenolic OH); IR (KBr): 3357, 1681, 1602, 1485, 1409, 1139, 844 cm^{-1}; MS: m/z 364(M^+ , trace), 359(7.7%), 292(3.8%), 279(7.7%), 222(3.8%), 216(38%), 132(15%),

113(49%), 98(30%), 90(100%), 62(30%), 42(46%); UV (EtOH): 388 nm.

13a (60%), m.p. 250-51° (from DMSO-H_2O); ^{1}H NMR (DMSO-d_6): 2.3 (s, 3H, CH_3), 6.2 (s, 2H, NH_2) 7.3-7.8 (m, 8H, aromatic proton; IR (KBr): 3490, 1680, 1602, 1490, 1480, 1120, 835 cm^{-1}; MS: m/z 363 (M^+ trace), 257 (5.9%), 256 (43%), 226(21%), 216(4.4%), 187(5.9%), 158(24%), 140(100%), 117(64%), 86(18%), 75(15%), UV (EtOH): 390nm.

13b, (72), m.p. 240° from MeOH-H_2O); ^{1}H NMR (DMSO-d_6): 1.1 (s, 6H, $2CH_3$), 2.3(s, 3H, CH_3), 7.2-8.1 (m, 8H, aromatic protons); MS. m/z 445 (m^+ , trace), 415 (60%), 399(31%), 276(14%), 261(20%), 146(100%), 138(21%), 133(31%)/ 129(%), 161(21%), 89(23%), 42(41%); UV (EtOH): 486 nm.

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