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Diazocoupling of 1-Phenyl-3-Trifluoromethyl-2-Pyrazolin-5-One. Synthesis of New Azopyrazolones Fast Dyes

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ABSTRACT. Diazocoupling of 1-phenyl-3-trifluoromethyl-2-pyrazolin-5-one (1) with different aryldiazonium salts yielded 4-[(aryl)diazenyl]-1-phenyl-3-trifluoromethyl-2-pyrazolin-5-ones (2) as coloured products. The new synthesized azo-dyes have been extensively employed on wool, silk, cotton and polyester textiles to give bright fast dyes ranges from yellow to deep violet colours, which are stable to laundry and exposure to sun light.

Introduction

It is well known that 5-pyrazolones are very important class of organic compounds due to their biological activities. In addition to their known bactericidal, fungicidal and herbicidal activities, they have, recently, hypothermic, antipyretic[1], antioxidant[2], antidepressant[3] and anti-inflammatory[4] activities.

On the other hand, it is well known that the most important commercial dyes are arylazopyrazolinones which are used as good fastness dyestuffs for wool, cotton, silk, leather, rubber and synthetic textiles. There are some azopyrazolones dyes with efficient biological activity[5].

Experimental

Melting points reported are uncorrected. IR spectra were recorded on Perkin Elmer's Spectrum RXIFT-IR spectrophotometer (υ in cm^{-1}) using KBr Wafer technique. UV spectra were measured by Perkin Elmer Lambada 25 UV/Visible spectrometer in ethanolic solution (λ in nm). The NMR spectra were recorded on Bruker Avance DPX400 spectrometer, using TMS as internal standard (chemical shifts in δ values in ppm). Elemental analyses were preformed using Perkin Elmer 2400, series II micro-analyzer. Ethyl 4,4,4-trifluoroacetoacetate is an Aldrich product and used without further purification.

Synthesis of 1-phenyl-3-trifluoromethyl-2-pyrazolin-5-one (1)

A mixture of ethyl 4,4,4-trifluoroacetoacetate (9.2 g, 0.05 mol) and phenylhydrazine (5.5 g, 0.055 mol) was heated at 150-160°C for 3h. The solid residue was washed by diethyl ether (10 ml) and filtered. The solid product was crystallized from ethanol to give 10.1 g (89% yield) of pyrazolone (**1**) as white crystals. $C_{10}H_7F_3N_2O$ (228), m.p. 200-202°C; IR: 763, 1143 (CF_3), 1562, 1595 (C=C, C=N), 1746 (HC=), 3285 (OH enolic); ^{1}H-NMR ($CDCl_3$): δ 3.73 (s, 1H, OH), 5.89 (s, 1H, C_4-H), 7.27-7.82 (m, 5H, Ph-H); MS: m/e (abundance %): 228 (M^+, 17), 199 (8), 105 (22), 91 (15), 77 (100), 51 (87).

Diazocoupling of 1-phenyl-3-trifluoromethyl-2-pyrazolin-5-one (1): Synthesis of 4-arylazo-1-phenyl-3-trifluoromethyl-2-pyrazolin-5-ones (2a-i)

The desired aromatic amine (0.015 mol) was treated with conc. HCl (5 ml) and cooled at 5°C in ice-bath. An aqueous cold solution of sodium nitrite (0.017 mol in 10 ml water) was added to the prepared aromatic amine hydrochloride to give the desired aromatic diazonium chloride solution which is added drop-wise with stirring during 30 min to an ice-cold solution of 1-phenyl-3-trifluoromethyl-2-pyrazolin-5-one (**1**, 0.012 mol) in pyridine (50 ml). After complete addition, the coloured precipitant was filtered, washed with water (3 x 25 ml), dried and crystallized from ethanol to give the coloured azopyrazolones (**2a-i**) crystals. The results are listed in Tables 1 and 2.

Table 1. The physical data of 4-arylazo-1-phenyl-3-trifluoromethyl-2-pyrazolin-5-ones (2a-i)

Compound	m.p °C	Colour (Yield %)	Mol. formula (M wt)	Analysis % calcd/found C	H	N
2a	180-182	orange (82)	$C_{16}H_{10}BrF_3N_4O$ (411.17)	46.74 46.53	2.45 2.41	13.63 13.39
2b	225-227	deep orange (93)	$C_{16}H_{11}F_3N_4O_2$ (348.28)	55.18 55.04	3.18 3.11	16.09 15.97
2c	155-157	Orange (58)	$C_{17}H_{14}F_3N_4O_2$ (362.31)	56.36 56.21	3.62 3.55	15.46 15.40
2d	167-169	Orange (84)	$C_{18}H_{13}F_3N_4O_2$ (374.32)	57.76 57.68	3.50 3.44	14.97 14.89
2e	296-298	Orange (92)	$C_{17}H_{11}F_4N_4O_3$ (376.29)	54.26 54.13	2.95 2.91	14.89 14.77
2f	169-171	Violet (73)	$C_{20}H_{20}F_4N_5O$ (403.40)	59.55 59.30	5.00 4.92	17.36 17.18
2g	178-180	Red (95)	$C_{23}H_{15}F_3N_4O$ (408.38)	64.70 64.59	3.70 3.60	13.72 13.61
2h	>300	Orange (68)	$C_{20}H_{13}F_3N_4O_4S$ (462.40)	51.95 51.90	2.83 2.77	12.12 12.06
2i	207-209	Red (62)	$C_{21}H_{17}F_3N_6O_2$ (442.39)	57.01 56.89	3.87 3.80	19.00 18.78

Table 2. Spectral data of 4-arylazo-1-phenyl-3-trifluoromethyl-2-pyrazolin-5-ones (2a-i).

Compound	IR (υ in cm^{-1}) CF_3	C=N(exo)	N=N C=C C=N (Pz)	C=O	NH OH	CH	NMR ($CDCl_3$, δ in ppm)
2a	790 1136	980 1179	1486 1546	1656	1285 3212	3048	7.25-7.90 (m, 9H, Ar-H), 15.09 (s, 1H, OH or NH).
2b	761 1139	986 1203	1488 1538	1648	1344 3229 3385	3059	6.91-7.89 (m, 9H, Ar-H), 9.06 (s, 1H, OH), 14.97 (bs, 1H, OH or NH).
2c	797 1138	992 1248	1491 1545	1655		2942 3049	3.85 (s, 3H, OCH_3), 6.97-7.95 (m, 9H, Ar-H), 14.22 (s, 1H, OH or NH).
2d	786 1139	987 1268	1495 1553	1677	1345 3326	3063 2920	2.57 (s, 3H, $COCH_3$), 7.29-8.12 (m, 9H, Ar-H), 14.48 (s, 1H, OH or NH).
2e	763 1141	985 1260	1496 1561	1668 1690	1428 3316	2826 3010	7.26-8.11 (m, 9H, Ar-H), 14.23 (s, 1H, COOH).
2f	810 1128	993 1269	1488 1555	1684	1346 1436	2972 3089	1.22 (t, 6H, 2 x CH_3), 3.42 (q, 4H, 2 x N-CH_2), 6.69 (s, 1H, C_4-H), 7.26-7.98 (m, 9H, Ar-H).
2g	760 1131	992 1292	1491 1547	1680		3015 3076	7.26-7.96 (m, 14H, Ar-H), 14.25 (bs, 1H, OH or NH).
2h	756 1133	986 1278	1570	1673	1351 1445 3440	3060	7.18-8.17 (m, 11H, Ar-H), 14.69 (s, 1H, OH or NH).
2i	726 827 1134	987 1286	1491 1567	1676		3055	2.62 (s, 3H, CH_3), 3.31 (s, 3H, N-CH_3), 7.36-8.06 (m, 10H, Ar-H), 14.53 (s, 1H, OH or NH).

General methods of dyeing

Method A: For arylazopyrazolones containing an acidic group (OH, COOH, SO_3H) such as **2b**, **2c** and **2h**.

Textile sample (2.0 g) was immersed in NaOH solution (5.0 %) for 30 min, then the sample was taken and immersed in the dyeing solution containing 0.5 g of arylazopyrazolone in 50.0 ml of NaOH (5.0 %). The mixture was left for 1h at 60°C. The solution was adjusted to pH 5 by adding glacial acetic acid with stirring for 15 min, then solution of 20.0 g of Na_2SO_3 in 250 ml water was added with stirring. The temperature of the mixture was raised to 90°C for 1h with stirring. Finally, the textile sample was taken, rinsed 3 times with 100 ml cold water and dried.

Method B: For arylazopyrazolones containing basic group (RNH, NH_2, R_2N-) *e.g.* **2f** and **2i**.

Textile sample (2.0 g) was immersed in acetic acid (50 %) for 30 min. The dyeing solution was prepared by dissolving 0.5 g of arylazopyrazolone in 2.0 ml conc. HCl and then diluted to 50 ml by adding acetic acid (50 %). The textile sample was taken and immersed in the dyeing solution for 30 min at room temperature and 30 min at 60°C, then sodium sulphate (10 g) was added with stirring. The temperature of the mixture was raised and kept at 90°C for 30 min. The textile sample was taken and rubbed, then immersed in Na_2CO_3 solution (30%) and kept at 60°C for 30 min. The sample was taken, rinsed with water (3 x 100 ml) and then with hot water and dried.

Method C: For neutral arylazopyrazolones *e.g.* **2a**, **2c**, **2d** and **2g**.

Textile sample (2.0 g) was immersed in the dyeing solution composed of arylazopyrazolone (0.5 g) in ethanol (50 ml). The mixture was refluxed with stirring for 2h. The sample was taken and kept at room temperature for drying, then washed by hot water (3 x 100 ml) and dried.

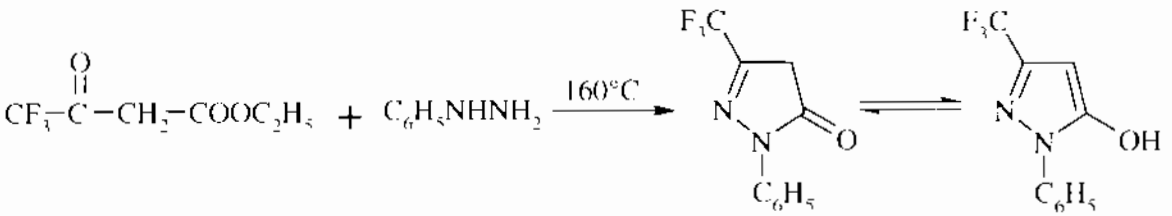
All dyed fabrics by 4-arylazopyrazolones (**2a-i**) are exposed to direct sunlight in open air for one month to give bright, fast and stable colour. The results are listed in Table 3.

Table 3. UV spectra and textile colour dyed by arylazopyrazolones (2a-i).

Compound	Method of dyeing	UV λ_{max} in nm	Fabric dyeing colour			
			wool	silk	cotton	polyester
2a	C	415, 270, 260, 235	yellow	yellow	pale yellow	yellow
2b	A	455, 245, 225	orange	orange	pale yellow	yellow
2c	C	450, 265, 235	yellow	yellow	pale yellow	yellow
2d	C	410, 255, 225, 210	yellow	yellow	pale yellow	yellow
2e	A	405, 225, 210	orange	orange	yellow	yellow
2f	B	545, 250, 235, 225, 215	violet	deep violet	pink	purple
2g	C	440, 259, 220, 210	yellow	yellow	orange	Yellow
2h	A	425, 250, 215	deep orange	red	pale orange	flesh
2i	B	455, 230, 210	yellow	orange	pale yellow	yellow

Results and Discussion

In continuation to our interest in pyrazolone chemistry[6-8], we have reported here the synthesis of some new intensively coloured 4-arylazo-1-phenyl-3-trifluoromethyl-2-pyrazolin-5-ones that might be used as commercial dyes. The key starting, 1-phenyl-3-trifluoromethyl-2-pyrazolin-5-one (**1**), was prepared by fusion of an equimolar amount of ethyl 4,4,4-trifluoroacetoacetate and phenylhydrazine.

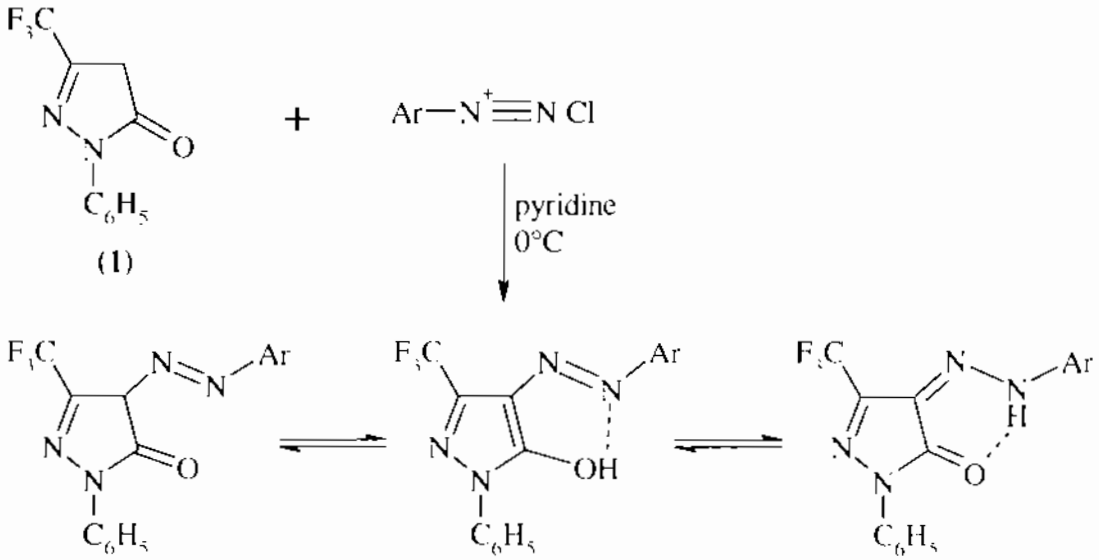


(1)

A cold solution of aryldiazonium chlorides which are prepared by treatment of sodium nitrite solution with the hydrochloride solution of primary aromatic amines, namely, 4-bromoaniline, 4-hydroxyaniline, 4-methoxyaniline, 4-aminoacetophenone, 4-aminobenzoic acid, 4-N,N-diethylaminoaniline, 4-aminobiphenyl, 1-amiuonaphthalene-4-sulphonic acid and antipyrine, are coupled with a cold solution of 1-phenyl-3-

trifluoromethyl-2-pyrazolin-5-one (**1**) in pyridine to give the corresponding water insoluble 4-arylazopyrazolones (**2a-i**) as coloured products ranges from orange to deep violet crystals.

The arylazopyrazolones (**2**) are existed in three tautomeric mixture[9], 4-arylazo-2-pyrazolin-5-ones (**2A**), 4-arylazo-5-hydroxypyrazoles (**2B**) and 5-oxo-2-pyrazolinyl-4-arylhydrazones (**2C**).



a) Ar = C_6H_4-Br,4-

b) Ar = C_6H_4-OH,4-

c) Ar = C_6H_4-OCH_3,4-

d) Ar = C_6H_4-$COCH_3$,4-

e) Ar = C_6H_4-COOH,4-

f) Ar = C_6H_4-$N(C_2H_5)_2$,4-

g) Ar = C_6H_4-C_6H_5,4-

h) Ar = 1-naphthyl-SO_3H,4-

i) Ar = 2,3-dimethyl-1-phenyl-5-oxo-pyrazol-3-in 4 yl

The structure of the new azopyrazolones (**2a-i**) have been established by elemental analysis, IR and NMR spectral data (Tables 1 and 2). Wool, silk, cotton and polyester textiles were subjected to arylazodyes (**2a-i**) solutions, dried, washed with water and detergents then exposed to direct sun light for one month give fast, stable and bright coloured textiles. Dyeing by acidic arylazodyes (**2b**, **2e**, **2h**) were done by their solution in NaOH solution (10%), while basic arylazodyes (**2f**, **2i**) in HCl solution (10%). The neutral insoluble arylazodyes either in NaOH or HCl solutions were done in hot ethanolic solution. The UV spectral data and textile coloures are listed in Table 3.

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ازدواج ديازو للمركب ١-فينيل-٣-تراي فلوروميثيل-٢-بيرازولين-٥-ون. تصنيع أصباغ آزوبيرازولونات السريعة

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جـــــدة - المملكة العربية السعودية

المستخلص. ازدواج ديازو للمركب ٣-تراي فلوروميثيل-١-فينيل-٢-بيـــرازولين-٥-ون مع الأمينات الأروماتية المختلفة والتي تحمل مجموعات بديلـــة حمـــضية أو قاعدية تنتج ٤-أريل آزو-٣-تراي فلوروميثيل-٢-بيرازولين-٥-ونات التـــي تـــم استخدامها بصورة واسعة على منسوجات الصوف والحريـــر والقطـــن والبوليـــستر وأعطت أصباغ سريعة وساطعة مع مدى من الألوان من الأصـــفر إلـــى البنفـــسجي الداكن، والتي كانت ثابتة عند الغسيل وعند التعرض لضوء الشمس لفترات طويلة.