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Synthesis of some Azo Compounds Derived from Substituted 4`-Aminosulfonanilides

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ABSTRACT

The synthesis of azo compounds (9-11) has been achieved by reaction of diazonium salts of substituted 4`-aminosulfonanilides with some aromatic amines or phenols 4-Nitroaniline (1) is served as a synthon for 2,6-dibromo-4-nitroaniline (6). The compounds (1 and 6) undergo sulfonylation with methane- and 4-toluene sulfonyl chloride to give the corresponding sulfonanilides (2, 3, 7). The nitro group in these compounds is reduced to amino group to produce compounds (4, 5, 8). These compounds are diazotised to the corresponding diazonium salts, which are coupled with different aromatic amines or phenols to produce the azo compounds (9-11). The structure of the synthesized compounds has been confirmed on the basis of physical and spectral measurements.

تحضير بعض مركبات الازو المشتقة من معوضات `4-أمينوسلفونانيليد

الملخص

تم تحضير عدد من مركبات الآزو (9-11) بتفاعل أملاح الدايازونيوم لمعوضات 4`-أمينو سلفونليد مع عدد من الأمينات الأروماتية أوالفينولات. استخدم المركب 4-نيتروأنيلين (1) كمادة أولية لتحضير 2و6-ثنائي برومو-4-نيتروأنيلين (6), ثم استخدما هذين المركبين في تحضير معوضات الميثان - و 4-تلوين سلفونانيليد المقابلة (7,3,2) بمفاعلتهما مع كلوريد الميثان- والـ 4-تلوين سلفونيل. أختزلت مجموعة النيترو في هذه المركبات لتحضير مركبات الأمينو(8,5,4), ومن ثم حولت هذه المركبات إلى أملاح الدايازونيوم المقابلة التي أجري لها اقترانا مع بعض الأمينات الأروماتية والفينولات لتكوين مركبات الآزو (9-11). شخصت المركبات المحضرة اعتمادا على الطرق الفيزياوية والطيفية.

INTRODUCTION

The azo dye compound (prontosil), (4-sulfonamido-2’,4’-diaminoazobenzene), is the first sulfonamide that is used in medicine, it can cause remarkable cures of streptococcal infections of mice and human (Domagk, 1935).

More than half of the dyes of commerce fall within the azo dyes (Shreve, 1967). Because of their color, the azo compounds are of tremendous importance as dyes and they grow so rapidly that they become the largest and most versatile of all classes of synthetic dyes. Also azo dyes constitute the largest single class of dyes in use and find broad application in textiles, paper, leather, gasoline additives, foodstuffs, and cosmetics (Straub et al., 1993). They may be yellow, orange, red, blue, or even green, depending upon the exact structure of the molecule. Various substituents on either component lead to a variety of colors and solubility characteristics (Gorvin, 1951, Orelup, 1974). Also the process of formation of azo dyes is considered as simple, rapid and sensitive method to assay microgram amounts of many organic compounds (Hovind, 1975; Bashir and Othman, 2002, 2003). On the other hand, some azo compounds are used as acid-base indicators, such as methyl red (Carey, 1996).

The azo compounds are commonly prepared by coupling diazotized primary aromatic amines (diazonium salt) with phenoles or aromatic amines at pH 7-8, (Vogel, 1964; Sandler, 1968). The diazonium ions are weak electrophiles but have sufficient reactivity to attack strongly activated aromatic rings (Carey, 1996). In the present study, we synthesized some azo compounds containing a sulfonamido moiety (Scheme 1), which may be used as dying agents for wool, cotton and synthetic fiber.

EXPERIMENTAL

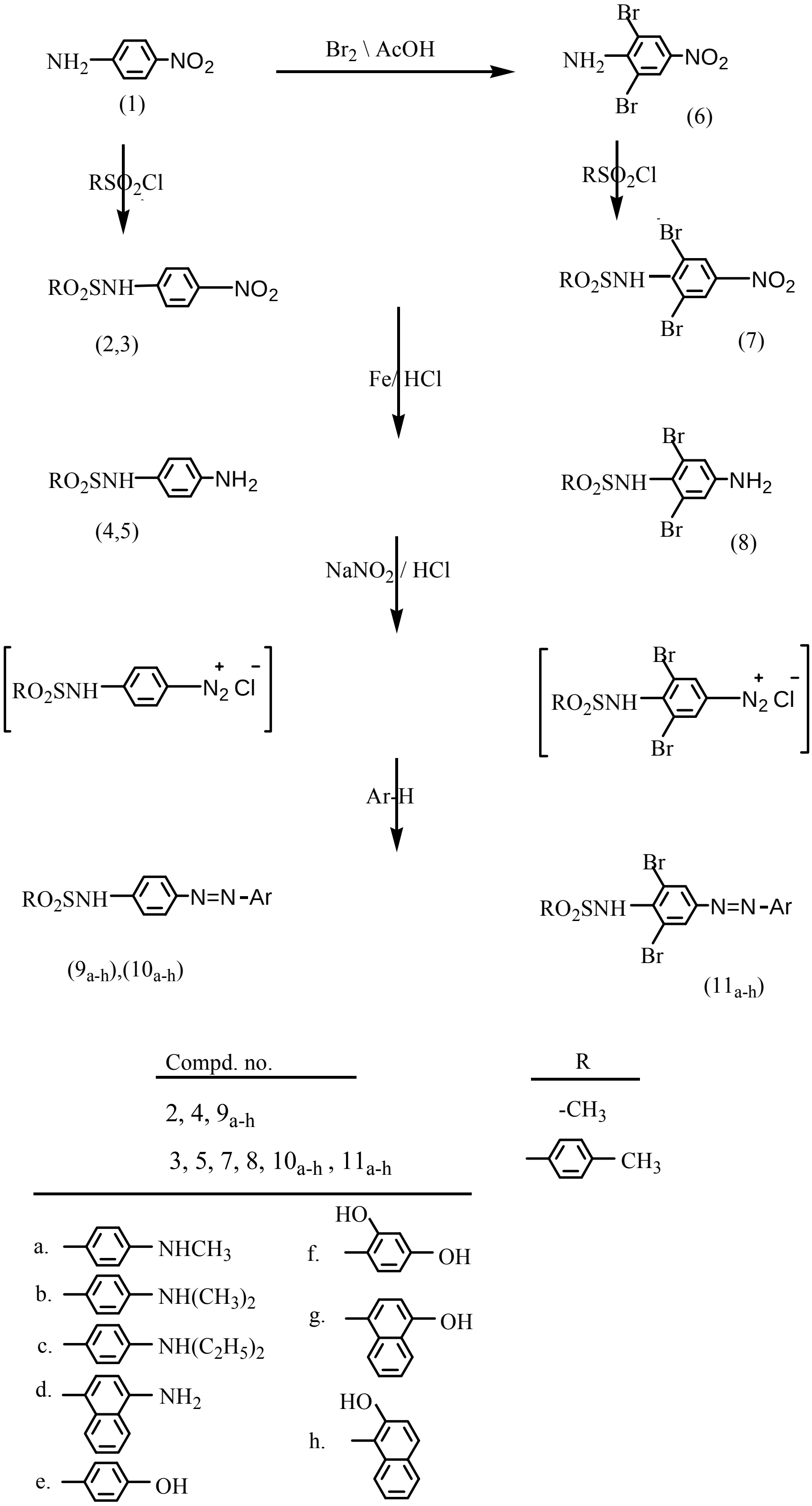
Melting points were determined on Gallenkamp melting point apparatus and were uncorrected. IR spectra were recorded on Pye-Unicam SP1100 spectrophotometer using KBr disc. UV spectra were recorded on Shimadzu (UV-160) UV-visible recording spectrophotometer.

2, 6-Dibromo-4-nitroaniline (6):

A solution of bromine (10.4g, 0.066 mole) in glacial acetic acid (24 ml) was added drop- wise to a stirred solution of 4-nitroaniline (1) (4.5g, 0.033 mole) in glacial acetic acid (40 ml) according to the previously reported method (Shepherd, 1947) to afford (80%) yield yellow crystals:m.p. 203-205^{o}C (Rep. 204-206 ^{o}C). IR (KBr), ν= 550 Cm^{-1} (C-Br), 1375 Cm^{-1} (NO_2), and 3400 cm^{-1} (N-H).

Preparation of substituted methane- and 4-toluene sulfonanilide (2,3,7):

To a magnetically stirred solution of substituted anilino compounds (1 and 6) (0.02 mole) and N-methylpiperidine (2.05 g, 0.02 mole) in dry THF (10 ml), a solution of methane- or 4-toluene sulfonylchloride (0.02 mole) in dry THF (20 ml) was added. The procedure was completed according to the previously reported method (Al-Iraqi, et. al., 2003) to produce yellow needles. The physical properties and the spectral data of compounds (2,3,7) were listed in Table (1).


(1)
Br2 \ AcOH
(6)
RSO2Cl
RSO2Cl
(2,3)
(7)
Fe/ HCl
(4,5)
(8)
NaNO2 / HCl
Ar-H
(9a-h),(10a-h)
(11a-h)
Compd. no.
R
2, 4, 9a-h
-CH3
3, 5, 7, 8, 10a-h , 11a-h
CH3
a. NHCH3
b. NH(CH3)2
c. NH(C2H5)2
d. NH2
e. OH
f. HO OH
g. OH
h. HO

Scheme 1

Table 1: The physical properties and spectral data of the compounds[**](2-5 and 8-11).

Compd. No.	M.p. °C	Yield %	Color	UV (CH_3OH) λ(nm)	IR. (KBr), v (cm^{-1})						
					S=O	C=C	N=N	C-Br	N-H	NO_2	O-H
2	214-216	91	Faint Yellow	265*, 391	1340(sh)	6010(m)			3330(b)	1380(s)	
3	122-124	81	Faint yellow	238, 370*, 390	1325(sh)	1585(s)			3300 (w&b)	1385(s)	
4	181-183	96	Faint yellow	232,308*, 390,392	1300(s)	1505(s)			3420 (s&b)		
5	178-180	86	Faint yellow	238,307*, 389	1370(vs.)	1570(s)			3555(b)		
7**	208-210	83	Faint yellow	272,362*, 392	1333(s)	1600(s)		550(m)	3340(b)	1375 (m)	
8	200-202	80	Greenish yellow	239,250, 352*, 389	1340(vs.)	1605 (vs.)		542(s)	3405(b)		
9a	188-189	61	Silvery	234,330*, 390,392	1330(m)	1510(s)	1570(vs)		3420 (s&b)		
9b	173-176	76	Deep orange	235,325*, 390,392	1325(m)	1500(s)	1575(vs)		3405 (s&b)		
9c	171-173	75	Deep orange	239,327*, 390,392	1360(vs)	1525(s)	1575(s)		3425 (s&b)		
9d	179-181	87	Faint brown	332,335*, 390,392	1300(s)	1500(s)	1575(s)		3420(b),		
9e	189-192	88	Dark gray	230,303*, 389	1310(s)	1515(s)	1578(s)		3400(b)		3580(b)
9f	188-190	82	Faint orange	320*, 333, 384	1320(s)	1510(s)	1570(s)		3380(b)		3550(b)
9g	163-167	82	Purple	305*, 339, 389	1315(vs)	1520(s)	1600(s)		3370(b)		3600(b)
9h	208-210	77	Slivery	320*, 333, 384	1310(s)	1520(m)	1595(vs)		3365(b)		3595(b)
10a	180-184	92	Deep orange	240,320*, 389	1362(vs)	1585(s)	1600(s)		3350(b)		
10b	170-172	87	Purple	239,310*, 389,391	1370(vs)	1570(s)	1610(sh)		3470(b)		
10c	175-178	83	Reddish brown	235,300*, 389,396	1325(m)	1580(s)	1590(s)		3350(b)		
10d	148-150	84	Deep pink	241*, 280, 389	1300(w)	1580(sh)	1610(s)		3480(b)		
10e	190-193	81	Yellowish green	238*, 239, 316,374,391	1350(m)	1530(m)	1585(s)		3320(b)		3530(b)
10f	160-163	64	Deep orange	235*, 315, 387,420	1310(vs)	1530(s)	1580(m)		3460(b)		3650(b)
10g	170-172	84	Deep violet	303,345*, 390	1360(vs)	1560(s)	1590(sh)		3480(b)		3600(b)
10h	110-112	80	Reddish brown	242,266, 276*, 285	1315(vs)	1565(s)	1600(s)		3275(b)		3600(b)
11a	176-178	81	Reddish brown	230,255, 279*, 391	1350(s)	1530(s)	1590(s)	540(s)	3350(b)		
11b	188-190	81	Dark brown	235,350*, 389,450	1335(s)	1500(s)	1570(vs)	545(m)	3300(b)		
11c	195-197	85	Dark violet	232,360*, 390	1325(s)	1520(m)	1590(vs)	550(s)	3480(b)		
11d	218-220	85	Purple	245*, 388, 391	1350(s)	1510(m)	1595(vs)	540(w)	3250(b)		
11e	195-198	80	Purple	238,252, 261,354*, 390	1330(s)	1500(m)	1575 (s&b)	512(m)	3450(b)		3600(b)
11f	180 deco	78	Deep orange	233,251, 360*	1365(s)	1545(s)	1587(s)	543(s)	3370(b)		3540(b)
11g	195-198	82	Faint brown	242,345*, 389	1345(s)	1530(m)	1590(s)	545(s)	3345(b)		3535(b)
11h	110-112	80	Reddish brown	236*, 350, 389	1340(s)	1520(s)	1600(s)	550(m)	3350(b)		3530(b)

* UV band at λ max.

** Ref. Al-Iraqi, 2003.

Preparation of substituted amino compounds (4,5,8):(Wang, et al., 1998):

The nitro compound (2,3 or 7) (0.006 mole) was dissolved in ethanol (10 ml) followed by the addition of (18%) hydrochloric acid (0.4 ml) and iron powder (2 g, 0.036 mole). The mixture was heated under reflux for 1.5 hrs. The black powder in the reaction mixture was removed by hot filtration and the filtrate was diluted with cold water (~20 ml) at which a yellow precipitate was formed. The precipitate was separated by filtration, washed with water, dried and recrystallized from ethanol. The physical properties and the spectral data were listed in Table (1).

Preparation of azo compounds (9- 11):

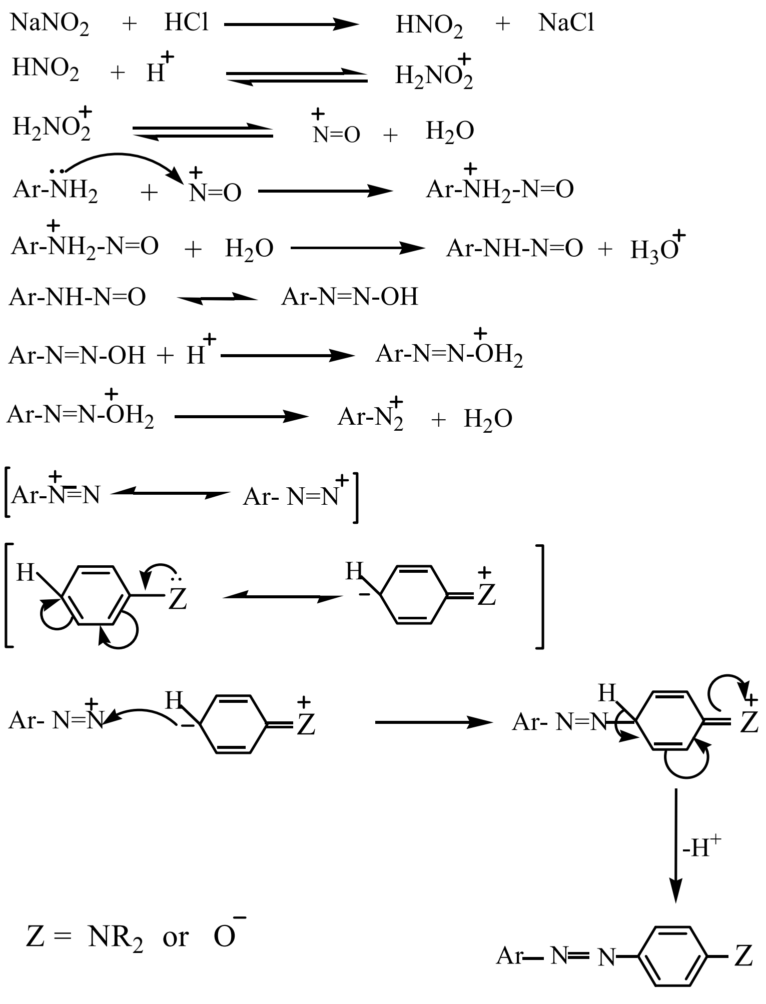
General procedure:

To a cold and stirred solution containing concentrated HCl (5 ml) and crushed ice (5 g), compound (4,5 or 8) (0.0057 mole) was slowly added. The mixture was cooled to 0 ^{o}C in an ice bath and a cold solution of sodium nitrite (0.44 g, 0.0063 mole) in water (4 ml) was added drop-wise with stirring while the temperature was maintained between 0 and 5 ^{o}C. The resulting solution was stirred at 0 to 5 ^{o}C for another 15 min.. Urea (0.1 g) was added to decompose excess sodium nitrite, consequently an aromatic amine or phenol (the phenol was dissolved in 5 ml. of 10% sodium hydroxide solution before addition) (0.012 mole) was added at 0 ^{o}C with stirring, at which a brilliant colored precipitate was formed immediately after the addition of the first drop of amine or phenol solution. After stirring at 0 ^{o}C for 1 hr., the mixture was filtered off and the precipitate washed with cold water, dried and recrystallized from ethanol-water. The physical properties and the spectral data of compounds (9-11) were listed in Table (1).

RESULTS AND DISCUSSION

The typical way of synthesizing aromatic azo compounds is by coupling of aromatic diazonium salts with phenols or aromatic amines, according to the route shown in Scheme 1. The 2,6-dibromo-4-nitroaniline (6) is prepared by bromination of 4-nitroaniline using a solution of bromine in acetic acid, through electrophilic aromatic substitution. The bromination process is performed before sulfonylation to ensure that the bromination takes place at two ortho positions. The sulfonylation of amino compounds (1 and 6) is performed by treatment of these compounds with methanesulfonyl chloride and 4-toluenesulfonyl chloride in dry THF in presence of N-methylpiperidine. The structure of compounds (2,3) is elucidated through the physical properties and the spectral data (Table 1). The IR spectra of these compounds show strong absorption bands at 1325-1340 cm^{-1}, which are attributed to the S=O stretching frequency, in addition to the general absorption bands at 1380-1385 cm^{-1} for the unsymmetrical stretching of NO_2 group, 3300 cm^{-1} due to N-H bond stretching (Parikh, 1974). The ultraviolet absorptions of these compounds occur at 238-391 nm. Then the nitro group in these compounds is reduced, by iron in acidic medium, to amino group to synthesize the compounds (4, 5, 8). The structure of these compounds is supported by the infrared spectroscopy, which revealed the absence of the characteristic frequency of NO_2 group and the appearance of the absorption bands at 3355-3420 Cm^{-1} which to the N-H stretching. The ultraviolet absorptions of these compounds occur at 232-392 nm which are attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

The amino compounds (4,5,8) are converted to diazonium salts by the reaction with sodium nitrite in acidic medium (HCl solution). These diazonium salts are coupled with different aromatic amines and phenols to give the azo compounds (9-11). The amino and hydroxy groups are considered as strong electron donating groups that increase the electronic density at the para-positions of the aromatic amines and phenols, and consequently give good positions for the electrophilic attack of the diazonium ion (Scheme 2). The structure of these compounds is supported by the infrared spectra, which show a characteristic frequency at 1570-1610 Cm^{-1} for the N=N bond stretching, in addition to the general absorption bands at 1300-1370 cm^{-1} for S=O stretching frequency and 3250-3480 and 3530-3600 Cm^{-1} due to N-H and O-H bond stretching respectively. The UV absorption spectra of these compounds show absorption bands at 230-450 nm, which are attributed to the π → π* and n → π* transitions. The suggested mechanism of diazotization and the coupling reaction (Saunders and Allen, 1985) are shown in Scheme 2.



Scheme 2

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