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Nucleophilic Substitution in Arylazo Phenols—a Simple Route for Preparing Chlorosubstituted Azobenzenes

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ABSTRACT

The reaction of arylazo phenols **6–11**, *arylazo resorcinols* **20**, **25**, *and arylazo phloroglucinols* **26** *with* $POCl_3$ *in dimethylformamide yields chlorosubstituted arylazo benzenes* **13–18**, **21**, **23**, *respectively, in moderate to high yields. Replacement of the OH-group by Cl is favoured by acceptor substituents in the aryl fragments* ortho- *and/or* para-*linked to the azo group.*

If arylazo compounds derived from resorcinol are used, the substitution reaction proceeds in a stepwise manner, giving rise to the formation of o-*hydroxy*-p-*chlorosubstituted azo compounds* **20** *primarily and then of the dichlorosubstituted azo compounds* **23**.

INTRODUCTION

Halogensubstituted azobenzenes are of interest as starting materials in the preparation of modified azobenzene derivatives which are not readily available by alternative methods. Thus, the bromosubstituted aminoazobenzenes **1** can, for example, be converted by reaction with cyanides into

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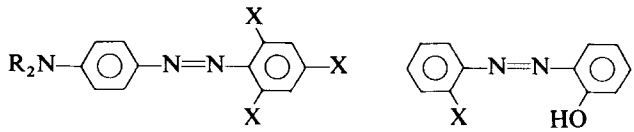
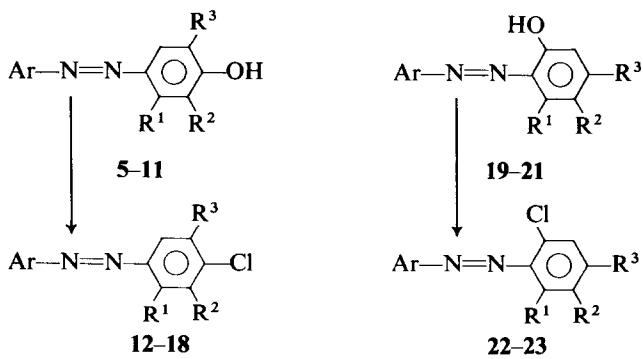


1 X = Br
2 X = CN
3 X = Cl
4 X = OH

Scheme 1

deeply coloured cyanosubstituted aminoazobenzenes **2**[1] which are useful as disperse dyes for polyester fibres.[2] In a similar manner, chlorosubstituted azophenols **3** can be converted into versatile complex ligands **4** by their reaction with alkaline hydroxides[3] (Scheme 1).

Remarkably, in both cases, the replacement of the halogen by the appropriate nucleophile does not take place very easily, and requires the assistance of a heavy metal catalyst such as Cu^{2+}. The reaction occurs only at the halogen atom which is ortho to the azo moiety.[4] Both the amino and hydroxy groups present in the azobenzene derivatives **1** and **3**, respectively, probably exhibit a deactivating influence on the nucleophilic substitution, which has been shown[5] to be activated by electron-attracting groups in the ortho- or para-positions to the leaving group. On the basis of this, halogensubstituted azobenzenes which do not contain such deactivating donor groups must therefore be better starting materials for nucleophilic substitution reactions giving rise to functionalized azobenzene derivatives.



5–11

12–18

19–21

22–23

		R^1	R^2	R^3
5	12	benzo		H
6	13	H	H	H
7	14	H	NO_2	H
8	15	H	$COOCH_3$	H
9	16	H	C_6H_5—N=N	H
10	17	H	C_6H_5—N=N	R^2
11	18	Cl	H	H

		R^1	R^2	R^3
19	22	benzo		H
20	23	H	H	Cl
21		Cl	H	Cl

Scheme 2

Such halogensubstituted azobenzenes are, however, rather scarce, since they cannot be prepared, as is the case for most other azobenzenes, by coupling simple aromatic halogen derivatives, because of the absence of appropriate activating groups for the coupling reaction.

Recently we have found,[6] however, a simple route for preparing halogensubstituted arylazo compounds which are free of donor groups in their molecular framework. These compounds are derivatives of 2- or 4-chloronaphthalene and have the general structures **12** and **22**. They can be prepared by the reaction of the readily available arylazo naphthols **5** and **19**, respectively, with $POCl_3$ in the presence of dimethylformamide (Scheme 2). In continuation of these studies, we have attempted to prepare halogen-substituted arylazo benzene derivatives using the same procedure, but starting from arylazo phenols. The results of these investigations are described here.

RESULTS AND DISCUSSION

Nucleophilic substitution of phenolic hydroxyl groups by chlorine in arylazo phenols

1. 4-Arylazosubstituted phenols

Analogous to the preparation of halogenated arylazo naphthalenes **12** and **22**,[6] the reaction of the arylazo phenols **6** with $POCl_3$ in the presence of dimethylformamide at about 100°C gives rise to the formation of the arylazo chlorobenzenes **13** (Scheme 2). In Table 1, the examples studied and the results obtained are listed.

It must be pointed out that the substitution reaction requires a much longer heating time than is necessary in the case of the arylazo naphthols **5** and **19** for complete exchange of the hydroxy group by chlorine, provided that the substitution pattern in the aryl moiety is the same as in the arylazonaphthols and that no further electron-accepting groups are present in the phenolic part of the arylazo intermediates.

However, where such electron-accepting groups are present, a much easier substitution reaction takes place. Thus, the nitrosubstituted arylazo phenols **7**, the carbomethoxysubstituted arylazo phenols **8**, and the phenylazo-substituted arylazo phenols **9** and **10**, which all contain electron-accepting groups in the ortho position to the exchanged hydroxy group, can be transformed into the appropriated arylazosubstituted chlorobenzenes **14–17** respectively, in a distinctly shorter reaction time, provided that identical conditions are chosen for the exchange reaction. As regards the

TABLE 1
Conversion of 4-Arylazo Phenols **6–11** into 4-Arylazo Chlorobenzenes **13–18** by Reaction with $POCl_3$/DMF

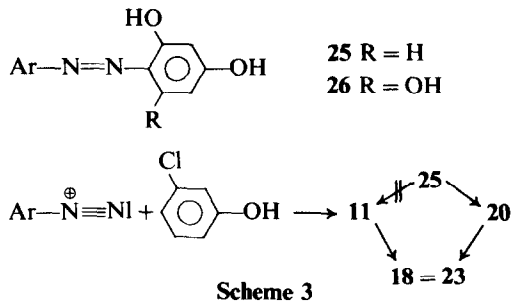
Educt	*Product*	*Ar*	*Reaction time (h)*	*Yield (%)*
6a	**13a**	C_6H_5	5	80
6b	**13b**	4-Cl—C_6H_4	5	85
6c	**13c**	4-Br—C_6H_4	5	85
6d	**13d**	4-CH_3—C_6H_4	6	60
6e	**13e**	3-NO_2—C_6H_4	5	72
6f	**13f**	2-NO_2—4-Cl—C_6H_3	3	68
7a	**14a**	C_6H_5	1·5	90
7b	**14b**	4-Cl—C_6H_4	1	85
7c	**14c**	4-NO_2—C_6H_4	1	60
7d	**14d**	2,4(NO_2)—C_6H_3	1	55
7f	**14f**	2-CN—4-NO_2—C_6H_3	1	61
8a	**15a**	4-NO_2—C_6H_4	1	59
8b	**15b**	2,4(NO_2)—C_6H_3	1	51
8c	**15c**	2-CN—4-NO_2—C_6H_3	1	61
9a	**16a**	C_6H_5	40 min	82
10a	**17a**	C_6H_5	10 min	72
11a	**18a**	4-Br—C_6H_4	3	60
11b	**18b**	4-NO_2—C_6H_4	2	80
20a	**23 (18c)**	C_6H_5	4	50

meta-chlorosubstituted arylazo phenols **11**, no activating effect could be observed in the course of the exchange reaction.

2. *Arylazosubstituted resorcinols*

Interesting behaviour with respect to the exchange of the hydroxy group by chlorine was observed with the readily available[7] arylazosubstituted resorcinols **25** (Scheme 3). These compounds contain two hydroxy groups and each of them is differently bonded in relation to the activating arylazo moiety. If these arylazosubstituted resorcinols **25** are allowed to react with $POCl_3$ in the presence of dimethylformamide in the usual manner, only one of the hydroxy group is replaced by chlorine after a relatively short reaction time. The second hydroxy group is, however, replaced if a much longer reaction time is employed.

To confirm which of the hydroxy groups is replaced first, the initially formed products were isolated and characterized in several cases. The first reaction product exhibits, and exemplified with the arylazo derivative **20a**, only one band in the IR spectrum at about 3450 cm^{-1}, which indicates,[8] also taking into account the data for the isomeric 4-arylazo phenol **11**, the presence of a hydroxy group ortho-linked to the arylazo moiety.



Scheme 3

Furthermore, **20a** can be converted into a fluorescent boron complex by reaction with boron triacetate according to the method described for similar arylazo phenols.[9]

3. Arylazosubstituted phloroglucinols

With arylazosubstituted phloroglucinols **26**, an OH–Cl exchange is also possible. As in the 2,4,6-trishydroxysubstituted azobenzene **26a**, this exchange is possible only with two of the three phenolic groups, even when the reactants are heated with $POCl_3$ under standard conditions for a very long time.

In accord with the previous findings for the arylazo resorcinols **25**, we postulate the structure of the resulting 2-arylazophenol as corresponding to formula **21**. In Table 2, the results of the transformations of arylsubstituted chlorphenols **11** or **20**, resorcinols **25** and phlorogluncinols **26** into 2,4-dichlorosubstituted arylazobenzenes **18**, **21** or **23**, respectively, are listed.

The UV/VIS absorption spectral data of all chlorosubstituted compounds are shown in Table 3. The results of the elementary analysis of the chlorosubstituted arylazobenzenes are summarised in Table 4.

TABLE 2

2,4-Dichlorosubstituted Arylazo Benzenes **18**, **21** or **23**, Respectively, Prepared by Reaction of Arylsubstituted Chlorophenols **11** or **20**, Resorcinols **25** or Phloroglucinols **26** with $POCl_3$/DMF

Educt	*Product*	*Ar*	*Reaction time (h)*	*Yield (%)*
25a	**23a/18c**	C_6H_5	4	50
20b	**23b/18a**	4-Br—C_6H_4	3	60
11b	**23b/18b**	4-Br—C_6H_4	3	82
20c	**18b/23c**	4-NO_2—C_6H_4	2	80
11c	**23c/18c**	4-NO_2—C_6H_4	2	78
20d	**18d/23d**	2,6$(Br)_2$—4-NO_2—C_6H_2	3	40
26a	**21a**	4-Cl—C_6H_4	3	75
26b	**21b**	4-Br—C_6H_4	3	78
26c	**21c**	4-NO_2—C_6H_4	2	72

TABLE 3
Melting Points and UV/VIS-Absorption Spectral Data (in Dimethylformamide) of the Chlorosubstituted Compounds **13–18**, **21** and **23**

No.	*Ar*	*MP* (°C) (*Lit.*)	λ_{max} (*nm*) (*log* ε)
13a	C_6H_5	93 (93)	326 (4·26) 442 (2·89) 357 (3·97)
13b	4-Cl—C_6H_4	188 (188)	336 (4·29) 444 (2·92)
13c	4-Br—C_6H_4	193–194 (195)	336 (4·27) 443 (2·92)
13d	4-CH_3—C_6H_4	149–150 (149)	329 (4·26) 442 (2·90)
13e	3-NO_2—C_6H_4	117 (149)	275 (4·04) 327 (4·25) 440 (2·81)
13f	2-NO_2—4-Cl—C_6H_3	121	336 (4·26) 444 (2·88)
14a	C_6H_5	83 (84)	337 (4·15) 412 (3·99) 457 (2·96)
14b	4-Cl—C_6H_4	151 (153)	327 (4·17) 432 (3·12)
14c	4-NO_2—C_6H_4	193 (198)	350 (4·35) 464 (2·98)
14d	2,4-(NO_2)—C_6H_3	185 (185)	343 (4·05) 428 (3·10)
14e	2-CN—4-NO_2—C_6H_3	193–195	346 (4·10) 439 (2·98)
15a	4-NO_2—C_6H_4	147–148 (147–148)	332 (4·08) 421 (2·95)
15b	2,4-(NO_2)—C_6H_3	162	348 (4·12) 432 (3·01)
15c	2-CN—4-NO_2—C_6H_3	175–179	352 (4·11) 441 (3·06)
16a	C_6H_5	122	331 (4·54) 448 (3·11)
17a	C_6H_5	181	335 (4·36) 431 (3·42) 602 (2·54)
23a/18c	C_6H_5	106	334 (3·97) 443 (2·71)
18a	4-Br—C_6H_4	138	349 (4·32) 468 (2·89)
18b	4-NO_2—C_6H_4	122–123	344 (4·23) 442 (2·97)
23d/18d	2,6-($Br)_2$—4-NO_2—C_6H_2	124	322 (3·99) 356 (3·92) 475 (3·14) 607 (2·45)
21a	4-Cl—C_6H_4	168	317 (4·32) 441 (3·05)
21b	4-Br—C_6H_4	172	315 (4·29) 439 (3·02)
21c	4-NO_2—C_6H_4	159	322 (4·31) 446 (3·07)

s: inflexion.

Although not all compounds prepared by the method described here are new, each representative could be prepared very simply from readily available arylazo phenol precursors. Hence, versatile starting materials for the preparation of modified arylazo benzenes, such as amino- or mercapto substituted arylazo benzenes, are available. Further work in this respect is in progress and will be reported at a later date.

EXPERIMENTAL

All melting points are uncorrected. The absorption spectra were measured in dimethylformamide at a concentration of 1×10^{-5} mol/l using an M40 UV–VIS spectrophotometer (VEB Carl Zeiss, Jena, Germany).

TABLE 4

Elemental Analysis Data for the Chlorosubstituted Compounds **13–18**, **21** and **23**

No.	*Formula*	*Molecular weight*	*C*	*H*	*N*	*Cl*
			Calculated (found)			
13a	$C_{12}H_9ClN_2$	216·5	66·50	4·28	12·73	16·12
			(66·51)	(4·16)	(12·93)	(16·40)
13b	$C_{12}H_8Cl_2N_2$	251	56·92	3·24	11·28	27·85
			(57·37)	(3·19)	(11·16)	(28·29)
13c	$C_{12}H_8BrClN_2$	295·5	48·80	2·91	9·79	12·10
			(48·73)	(2·71)	(9·48)	(12·01)
13d	$C_{13}H_{11}ClN_2$	230·5	66·93	4·63	12·28	15·12
			(67·68)	(4·77)	(12·12)	(15·40)
13e	$C_{12}H_8ClN_3O_2$	261·5	55·70	3·12	16·58	13·42
			(55·07)	(3·06)	(16·06)	(13·58)
13f	$C_{12}H_7Cl_2N_3O_2$	296	49·18	2·59	13·87	23·34
			(48·65)	(2·36)	(14·19)	(23·99)
14a	$C_{12}H_8ClN_3O_2$	261·5	55·19	3·40	16·02	13·67
			(55·07)	(3·06)	(16·06)	(13·58)
14b	$C_{12}H_7Cl_2N_3$	296	48·43	2·78	14·27	24·87
			(48·65)	(2·36)	(14·19)	(23·99)
14c	$C_{12}H_7ClN_4O_4$	306·5	47·53	2·40	18·03	11·47
			(46·98)	(2·28)	(18·27)	(11·58)
14d	$C_{12}H_6ClN_5O_6$	351·5	41·24	1·61	19·98	9·80
			(40·97)	(1·71)	(19·91)	(10·10)
14e	$C_{13}H_6ClN_5O_4$	331·5	47·62	1·75	21·64	11·51
			(47·06)	(1·81)	(21·12)	(10·71)
15a	$C_{14}H_{10}ClN_3O_4$	319·5	52·06	3·19	13·15	10·51
			(52·58)	(3·13)	(13·15)	(11·11)
15b	$C_{14}H_{10}ClN_4O_6$	365·5	46·34	2·45	15·40	9·42
			(46·09)	(2·47)	(15·36)	(9·74)
15c	$C_{15}H_{10}ClN_4O_4$	345·5	52·33	2·59	16·31	10·15
			(52·24)	(2·61)	(16·26)	(10·30)
16a	$C_{18}H_{13}ClN_4$	320·5	67·84	3·96	17·36	11·60
			(67·39)	(4·06)	(17·47)	(11·08)
17a	$C_{24}H_{17}ClN_6$	424·5	67·35	4·12	19·63	8·45
			(67·84)	(4·00)	(19·79)	(8·36)
23a/18c	$C_{12}H_8Cl_2N_2$	251	57·92	3·19	11·24	27·22
			(57·37)	(3·19)	(11·16)	(28·29)
18a	$C_{12}H_7BrCl_2N_2$	330	43·08	2·00	8·13	20·00
			(43·64)	(2·12)	(8·48)	(21·52)
18b	$C_{12}H_7Cl_2N_3O_2$	296	49·10	2·68	14·01	23·66
			(48·65)	(2·36)	(14·19)	(23·99)
23d/18d	$C_{12}H_5Br_2Cl_2N_3O_2$	454	30·74	1·06	8·94	16·91
			(31·72)	(1·10)	(9·25)	(15·64)
21a	$C_{12}H_7Cl_3N_2O$	301·5	48·06	2·33	9·61	34·19
			(47·76)	(2·32)	(9·29)	(35·32)
21b	$C_{12}H_7BrCl_2N_2O$	346	41·61	2·02	8·09	20·52
			(41·81)	(2·01)	(8·07)	(20·53)
21c	$C_{12}H_7Cl_2N_3O_3$	312	56·15	2·24	13·46	22·75
			(45·85)	(2·34)	(13·56)	(22·85)

Hydroxy-arylazo compounds 6–11, 20, 25, 26

Hydroxy-arylazo compounds were synthesized by conventional coupling reactions of the corresponding diazonium salt with the coupling component and recrystallization of the products from methanol.[10]

Chloro-arylazo compounds 13–18, 21, 23

A solution of the appropriate hydroxy-arulazo compound (5 g) in dimethylformamide (70 ml) was added at 0–5°C to a mixture of equimolar amounts of $POCl_3$ and dimethylformamide (10 ml). The reaction mixture was heated on a steam bath and the reaction was monitored by TLC. The cooled solution was added to methanol (50 ml) and ice (50 g). The product was filtered and recrystallized from methanol.

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