Oxidation of arylaminomagnesium compounds by copper salts

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Oxidation of arylaminomagnesium compounds by cupric chloride has been investigated. A possible oxidation reaction mechanism is considered.

Keywords: amines, magnesium, copper, oxidations

Organomagnesium compounds are widely used in organic chemistry and the properties of these compounds merit thorough investigation. It is reported here that arylamino-magnesium compounds are oxidised by cupric chloride to give symmetrical azo compounds.

Azo compounds are useful compounds due to their applications in optical materials, molecular devices and their importance to theoretical studies,[1-8] so synthesis of azo compounds is a worthwhile investigation. Symmetrical azo compounds can be synthesised from primary aromatic amines using lead tetraacetate, potassium permanganate, potassium ferricyanide, sodium hypobromide, chromic acid anhydride, manganese dioxide, lead peroxide (see ref.9 and references therein) cetyltrimethylammonium dichromate[10] Galvinoxyl[11] or 2,4,6-tri-*tert*-butylphenol[12] was used as a phase transfer catalyst to prepare symmetrical azo compounds from primary amines. Recently, four-electron oxidative formation of aryl diazenes using a tantalum redox-active ligand complex was reported.[13] $CuCl_2 \cdot 2H_2O$ was used as oxidant for synthesis of symmetric azo compounds, but only azo-3,3'-phenanthrene was synthesised.[14] CuCl-catalysed aerobic oxidative reaction of primary aromatic amines was reported to give symmetric azo compounds, but yields were low in most cases.[15] There are many drawbacks in the literature methods as reagents may be expensive or toxic and yields may be low. We report here an efficient and interesting method for synthesis of symmetrical azo compounds from primary aromatic amines.

Results and discussion

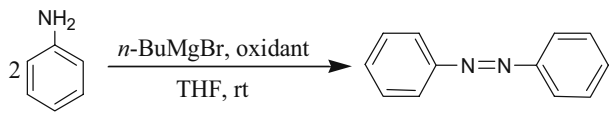
When phenylaminomagnesium bromide from reaction of equal equivalents of aniline and *n*-Bu MgBr is oxidised by $CuCl_2$ in THF, the product is azobenzene (1) instead of, 2-diphenylhydrazine (Table 1, Entry 3). 2-Diphenylhydrazine is an intermediate which is not stable and easily oxidised further to form azobenzene under the reaction condition (Scheme 1).

To improve yields, several reaction systems were investigated for the synthesis of azobenzene. Various copper or iron compounds were used as oxidants, and *n*-BuMgBr was used as the metalation reagent. The results are listed in Table 1. It is revealed that the reaction is efficient when the oxidant is $CuCl_2$ (2 equiv.) and 2 equiv. of *n*-BuMgBr are used; the isolated yield is then 95%.

To explore the scope of oxidation of arylaminomagnesium compounds by $CuCl_2$, more primary aromatic amines were used as substrates. The results are listed in Table 2. When substituents are in a *meta*- or *para*- position to the amino group, the yields of azo compounds are 89–91%. When substituents are in *ortho*- position to the amino group, the yields of azo compounds are 80–87%. It shows that steric hindrance has an effect on the formation of azo compounds.

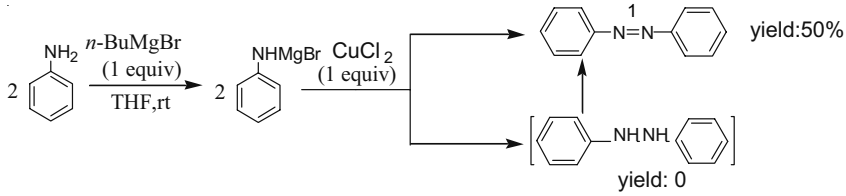
A possible mechanism for the reaction conditions in Table 2 is postulated as follows: *n*-BuMgBr acts as a metalation reagent and an arylaminomagnesium compound is formed when an amine reacts with one equivalent of *n*-BuMgBr.

Table 1 Optimisation of reaction systems in the synthesis of azobenzene[a]



Entry	Oxidant	*n*-Bu MgBr	Reaction time/h	Isolated yield/%
1	2 mmol $Fe(acac)_3$	2 mmol	72	Trace
2	2 mmol $Cu(acac)_2$	2 mmol	72	76
3	1 mmol $CuCl_2$	1 mmol	5	50
4	2 mmol $CuCl_2$	2 mmol	5	95

[a]Reaction conditions: To a solution of *n*-Bu MgBr in THF (8 mL), aniline (1 mmol) was added. After stirring for ½ h, oxidant was added to the reaction mixture which was then stirred at room temperature for the specified time. Product isolation was as in the Experimental section.



Scheme 1 Oxidation of phenylaminomagnesium bromide.

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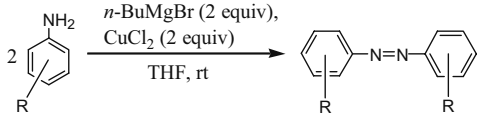
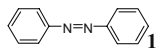
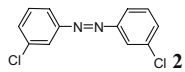
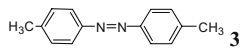
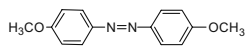
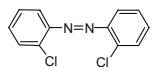
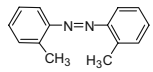
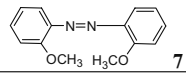
Table 2 Oxidation of arylaminomagnesium compounds by $CuCl_2$[a]



Entry	Substrate	Product	Isolated yield/%
1		 **1**	95
2		 **2**	90
3		 **3**	91
4		 **4**	89
5		 **5**	87
6		 **6**	86
7		 **7**	80

$CuCl_2$ then acts as an oxidant. The mechanism involves free radicals (Scheme 2). The reaction is initiated by the formation of ArNHNHAr and terminated by the oxidation of this intermediate.

In conclusion, oxidation arylaminomagnesium compounds by $CuCl_2$ is an efficient and interesting reaction system for the synthesis of symmetrical azo compounds from primary aromatic amines.

Experimental

General procedure for the oxidation of arylaminomagnesium compounds

To a solution of *n*-BuMgBr (2 mmol) in THF (8 mL), an amine (1 mmol) was added. After stirring for ½ h, $CuCl_2$ (2 mmol) was added to the reaction mixture and stirring continued at room temperature for 5 h. Then a little amount of silica gel was added, and the resulting mixture was evaporated to dryness. Purification was done by column chromatography on silica gel to give the azo compounds.

Azobenzene (**1**): M.p. 68–69 °C (Lit.[11] 67–68 °C). Orange red solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.51 (m, 6H), 7.92 (m, 4H). IR (KBr/cm^{-1}): 306, 1582, 1483, 1453, 1299, 1221, 927, 776, 690. Found: C, 78.89, H, 5.61, N, 15.41. Calcd for $C_{12}H_{12}N_2$, C, 79.12, H, 5.49, N, 15.38%.

3, 3'-Dichloroazobenzene (**2**): M.p. 102–104 °C (Lit.[11] 99 °C). Orange red solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.47 (m, 4H), 7.84 (m, 2H), 7.90 (s, 2H). IR (KBr/cm^{-1}): 3072, 1585, 1569, 1464, 1417, 1201, 1067, 887, 793, 684. Found: C, 57.51, H, 3.12, N, 11.28. Calcd for $C_{12}H_{10}Cl_2N_2$, C, 57.37, H, 3.19, N, 11.16%.

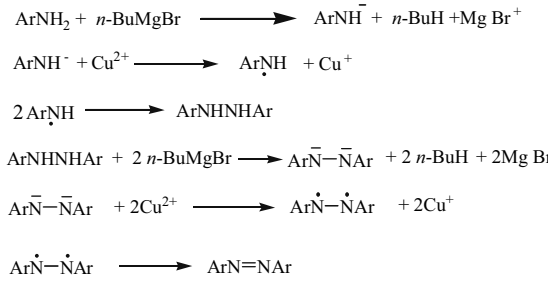
4, 4'-Dimethylazobenzene (**3**): M.p. 144–145 °C (Lit.[10] 144–145 °C). Orange yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.43 (s, 3H), 7.30 (d, J = 8 Hz, 2H), 7.80 (d, J = 8 Hz, 2H). IR (KBr/cm^{-1}): 3022, 2921, 1599, 1502, 1154, 825. Found: C, 79.81, H, 6.54, N, 13.25. Calcd for $C_{14}H_{16}N_2$, C, 80.00, H, 6.67, N, 13.33%.

4, 4'-Dimethoxyazobenzene (**4**): M.p. 153–154 °C (Lit.[10] 160 °C). Yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 3.89(s, 3H), 7.0 (dd, J_1 = 2 Hz, J_2 = 4.8 Hz, 2H), 7.88 (dd, J_1 = 2 Hz, J_2 = 4.8 Hz, 2H). IR (KBr/cm^{-1}): 3018, 2929, 1600, 1579, 1498, 1458, 1440, 1245, 1145, 1024, 843. Found: C, 69.22, H, 6.02, N, 11.45. Calcd for $C_{14}H_{16}N_2O_2$ C, 69.42, H, 5.79, N, 11.57%.

2, 2'-Dichloroazobenzene (**5**): M.p. 129–130 °C (Lit.[11] 136 °C). Orange red solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.36 (m, 2H), 7.44 (m, 2H), 7.56 (m, 2H), 7.78 (m, 2H). IR (KBr/cm^{-1}): 3087, 1582, 1466, 1442, 1254, 1060, 764, 726. Found: C, 57.58, H, 3.33, N, 10.92. Calcd for $C_{12}H_{10}Cl_2N_2$, C, 57.37, H, 3.19, N, 11.16%.

2, 2'-Dimethylazobenzene (**6**): M.p. 53–54 °C (Lit.[11] 54 °C). Orange red solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.74 (s, 3H), 7.24 (m, 1H), 7.33 (m, 2H), 7.63 (d, J = 7.6 Hz, 1H). IR (KBr/cm^{-1}): 3052, 2925, 1597, 1478, 1456, 1376, 1119, 1041, 771, 718. Found: C, 80.17, H, 6.44, N, 13.09. Calcd for $C_{14}H_{16}N_2$, C, 80.00, H, 6.67, N, 13.33%.

2,2'-Dimethoxyazobenzene (**7**): M.p. 150–151 °C, (Lit.[11] 143–145 °C). Orange red solid. ^{1}H NMR ($CDCl_3$, 400 MHz): 4.02 (s, 6H), 7.00 (t, J = 8 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 7.42 (m, 2H), 7.64 (m, 2H). IR (KBr/cm^{-1}): 3003, 2946, 1593, 1489, 1470, 1437, 1280, 1251, 1159, 765. Found: C, 69.54, H, 5.91, N, 11.49. Calcd for $C_{14}H_{16}N_2O_2$, C, 69.42, H, 5.79, N, 11.57%.



Scheme 2 Mechanism for oxidation of arylaminomagnesium compounds.

Received 25 October 2008; accepted 13 December 2008
Paper 08/0264 doi: 10.3184/030823409X401808
Published online: 24 February 2009

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