Chinese Chemical Letters Vol. 10, No. 7, pp. 533–536, 1999

The Synthesis of Symmetrical Azobenzenes from Anilines by Phase Transfer Catalysis

Xiao Yang WANG[1], Yu Lu WANG[2]*, Jian Ping LI[2], Li Fang SUN[2], Zi Yi ZHANG[1]*

[1]Department of Chemistry, National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000
[2]Department of Chemistry, Henan Normal University, Xinxiang 453002

Abstract: Using galvinoxyl as catalyst, the phase transfer catalyzed method of oxidation of primary amines to symmetrical azobenzenes with a saturated solution of potassium ferricyanide in 2 mol/L aqueous potassium hydroxide and dichloromethane is described. The reaction has intimate relation with Hammett substituent constants. This report offers an efficient and rapid method to prepare azobenzenes and a possible mechanism is also suggested.

Keywords: Azobenzenes, anilines, galvinoxyl, phase transfer, radical reaction.

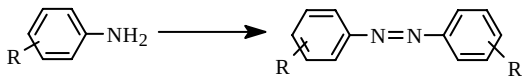
Azobenzenes have been widely utilized as dyes and analytical reagents[1]. They can also be used as material of non-linear optics, optic information storing material in laser disk and dyes with oil solubility in photochromy in modern technology[2,3].

The oxidation of substituted semicarbazides to azo compounds with several reagents such as NBS (N-bromosuccinimide)/pyridine[4], $KClO_3/H_2SO_4/FeSO_4$[5], DMF-NO_X[6] and 2,4,6-(t-C_4H_9)$_3C_6H_2OH/K_3Fe(CN)_6$/NaOH[7] has been reported by us. The oxidation of substituted anilines to azobenzenes with a variety of reagents such as phenyliodoacetate[8], sodium hypochlorite[9] and manganese dioxide[10] has also been reported. However the oxidation of anilines with inorganic oxidants in aqueous solution is complicated by the poor solubility of anilines.

The oxidation of an aromatic amine with potassium ferricyanide and KOH was first reported by Goldstein in 1973[11]. Mesidine was oxidized by this oxidant in methanol/water mixture at 45℃ for ten days to give the corresponding azobenzene. A second experiment on the oxidation of fluoroanilines to fluoroazobenezenes with this oxidant in ethanol/water mixture was reported by Leyva[12]. The mixture was refluxed for six to eight hours. However, from our experience, fluoroanilines can be oxidized to complicated compounds by the excessive potassium ferricyanide at high temperature for a long time. In order to prepare 4,4'-difluoroazobenzene from 4-fluoroaniline, we reduced the amount of the oxidant to a half and kept only two hours at room temperature, 4,4'-difluoroazobenzene was obtained in 38% yield and 4-fluoroaniline 45% recovered. From our previous work[4-7], we considered the reaction might proceed by a free radical

mechanism. Accordingly a trace of stable galvinoxyl was added and 4,4'-difluoroazobenzene (yield, 91%) was obtained in two hours at room temperature. When we used this oxidation system to treat the 4-chloroaniline, 4,4'-dichloroazobenzene was given only in low yield (6%) because of the poor solubility of 4,4'-dichloroazobenzene in ethanol/water. Therefore dichloromethane was used to replace ethanol and a saturated solution of potassium ferricyanide in 2 mol/L aqueous potassium hydroxide instead of the solid reagent. To our surprise, 4,4'-dichloroazobenzene was got (yield, 67%) within 15 minutes at room temperature. With galvinoxyl as catalyst, the reaction of phase transfer to prepare symmetrical azobenzenes from primary anilines in short time under mild conditions was established for the first time. This method was efficient, convenient and rapid.

Scheme 1



The substituted anilines (0.01 mol) and a trace amount of galvinoxyl radical (see **scheme I** were dissolved in dichloromethane (50 mL) and shaken with a saturated solution of potassium ferricyanide in 2 mol/L aqueous potassium hydroxide (50 mL). After 5-15 minutes, the color in organic phase changed to brown or deep-red. The dichloromethane layer was separated, and the water layer was extracted with dichloromethane four times. The dichloromethane layers were combined and washed with water until the washing was neutral. The organic solution were dried with anhydrous sodium sulfate. The solvent was removed in reduced pressure and the resulting mixture was passed through a silica gel column using hexane or petroleum ether (b.p. 60-90℃) as eluent to get symmetrical azobenzenes which were dried in vacuum.

Table The yield, m.p., lit. m.p., appearance of azobenzenes and Hammett substituent constants(σ)

R	yield(%)	m.p.℃	lit. m.p.℃[13]	substituent constant (σ)[14]	color and shape
H	93	67-68	68	0.000	red plates
2-CH_3	79	54	55	-	red plates
3-CH_3	83	53-54	54-55	-0.069	orange red prisms
4-CH_3	89	143	144-155	-0.170	orange yellow plates
2-CH_3O	65	143-145	143	-	yellow needles
4-CH_3O	79	160-161	160	-0.268	scarlet needles
4-C_2H_5O	84	155-156	157-159	-0.250	yellow plates
4-F	92	99-100	99	0.062	orange yellow plates
2-Cl	50	136	137	-	red plates
3-Cl	50	99	101	0.373	orange needles
4-Cl	67	188	185	0.227	yellow needles
4-Br	53	203-205	205	0.232	orange needles
4-I	49	236-235	235	0.276	orange red plates
α-naphthyl	28	188-189	190	-	brown needles

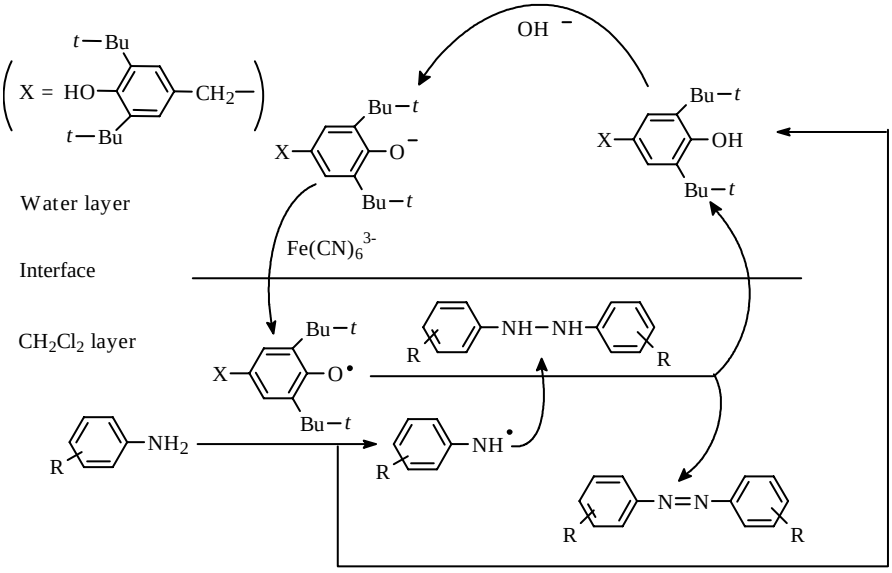
Fourteen symmetrical azobenzenes were prepared from corresponding amines in satisfied yield. Particularly the yields of azobenzene and 4,4'-difluoroazobenzene are over 90%, Even the oxidation of 1-naphthylamine gave 1-azonaphthalene in higher yield than that of the previously reported.[10] The structures of these azobenzenes were established by UV, IR, ^{1}H NMR, mass spectral methods and elemental analysis.

Results and Discussion

This ease of oxidation as judged by the rate of color change of dichloromethane layer shows only small difference, but the reaction has intimate relation with the Hammett substituent constants. Because the constants of the electron donor groups are always negative or smaller than that of the electron withdrawing groups, the amines with the former groups reacted more rapidly than those with the latter.

From the phenomenon of the experiment, a possible free radical oxidation[15] is shown as the following:

Scheme 2



Firstly galvinoxyl radical abstracted a hydrogen atom from substituted aniline, aromatic amine radical and galvinoxy phenol were formed. Secondly the aromatic amine radicals coupled to generate symmetrical substituted hydrazobenzenes. Thirdly galvinoxyl radicals acted on the substituted hydrazobenzenes to give the corresponding azobenzenes and galvinoxy phenol in dichloromethane phase. Fourthly the phenol yielded to the phenol anion in potassium hydroxide solution. Finally, the phenol anion became galvinoxyl radical by passing an electron to potassium ferricyanide.

From the possible mechanism above, the substituted aniline radicals belong to electron deficient systems, electron donor groups could make them stable, while electron

withdrawing groups could make them unstable[16]. The more stable the aniline radicals are, the more facilely the azobenzenes are prepared. The yields followed the order (see **Table**). We tried to observe the aromatic amine free radicals by Electron Spin Resonance. Although we found the instantaneous signs on the screen of the apparatus, we can not record them because of their high instability.

In order to prove the correctness of this mechanism, hydrazobenzene was treated by this oxidant, and azobenzene was also synthesized in good yield under mild conditions.

Acknowledgments

We are grateful for the financial support from the National Natural Science Foundation of China

References and notes

1. W. Russ, and H. Tappe, *Eur. Pat. Appl. EP*. 629, 667, **1994**.
2. Ikeda, and O. Tsutumi, *Science*. **1995**, *268*, 1873.
3. J. Peng, and J. Z. Yang, *Chin. Image Sci and Practive*, **1988**, *4*, 5.
4. Y. Wang, Y. L Wang, J. P. Li, C. L. Wang, and H. Wang, *Chinese Chemical Letters*, **1997**, *8*(6), 473.
5. L. Wang, Y. L.Wang, X. Y. Wang, J. P. Li, H. Wang, and D. L. Ma, *Synth. Commun*., **1997**, *27*(21), 3723.
6. L Wang, Y. L. Wang, X. Y. Wang, J. P. Li, D. L. Ma, and H. Wang, *Org. Prep. Proced. Int*., **1998**, *30*(1), 997.
7. L. Wang, C. J. Ru, J. P. Li, H. Wang, and D. L. Ma, *Synth. Commun*., **1994**, *24*(12), 1737.
8. Neu, *Ber Dtsh. Chem. Ges*. **1939**, *72*, 1505.
9. Burdon, C. J. Morton, and D. F. Thomas, *J. Chem. Soc*. **1965**, 2621.
10. H. Wheeler, D. and Gonzalez, *Tetrahedron*, **1964**, *20*, 189.
11. L. Goldstein, and E. McNelis, *J. Org. Chem*. **1973**, *38*, 183.
12. Elisa, M. Elena, M. Concepcion, and L. Socorro, *Tetrahedron Letters*, **1997**, *38*, 7847.
13. Heilbron, and H M. Bunbury, *Dictionary of Organic Compounds*, 5rd ed., published **1982** by Chapman and Hall.
14. H Jaffe, *Chem. Rev*. **1953**, *53*, 191.
15. Sykes, *A Guidebook to Mechanism in Orgnic Chemistry* (Bath press, New York),**1986**,p. 307.
16. P. Cheng, Y. Lu, and B. Liu, *Science in China (Series B)*, **1988**, *28*(2), 164.

Received 26 October 1998
Revised 15 April 1999