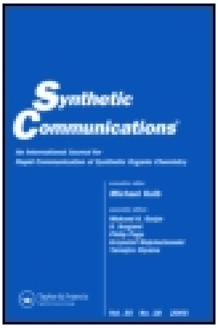

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THE PREPARATION OF SYMMETRICAL AZOBENZENES FROM ANILINES BY PHASE TRANSFER CATALYZED METHOD

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Abstract: Used Galvinoxyl as catalyst, the phase transfer catalyzed method of oxidation of primary amines to symmetrical azobenzenes with a saturated solution of potassium ferricyanide in 2N aqueous potassium hydroxide and dichloromethane is described for the first time in this paper. 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.

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 dish 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-$(t\text{-}C_4H_9)_3C_6H_2OH/K_3Fe(CN)_6/NaOH$[7] has been reported by

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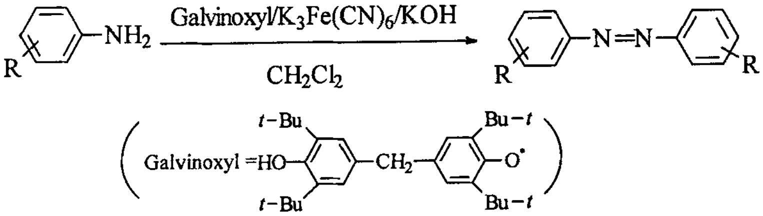
us. The oxidation of substituted anilines to azobenzenes with a variety of reagents such as phenyliodoacetate[8], sodium hypochlorite[9] and manganese dioxide[10] has also been reported. However the oxidation of anilines with inorganic oxidants in aqueous solution is complicated by the poor solubility 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 Elisa 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 under high temperature for long time. In order to prepare 4,4'-fluoroazobenzene from 4-fluoroaniline, we reduced the amount of the oxidant to a half and kept only two hours under room temperature, 4,4'-fluoroazobenzene (yield, 38%)and 4-fluoroaniline(yield, 45%) were both attained. From our work before[4-7], we considered the reaction might be completed by free radical procedure. Accordingly a trace of stable Galvinoxyl were added and 4,4'-difluoroazobenzene (yield, 91%) were obtained in two hours under room temperature. When we used this oxidation system to treat the 4-chloroaniline, 4,4'-dichloroazobenzene was given only small yield (6%) because of the poor solubility of 4,4'-dichloroazobenzene in ethanol/water. Therefor dichloromethane was taken place of ethanol and a saturated solution of potassium ferricyanide in 2N aqueous potassium hydroxide was instead of the solid state of them. To our surprise, 4,4'-dichloroazobenzene was got (yield, 67%) within 15 minutes under room temperature by this oxidation system. Thus Galvinoxyl as catalyst, the reaction of phase transfer to prepare symmetrical azobenzenes from primary anilines in short time under mild condition was established first time. This method was efficient, convenient and rapid.

Experimental Section

Melting points were determined with a Kofler micro melting apparatus and were uncorrected. UV-visible spectra were taken in $CHCl_3$ solution on a PE-LAMBDA spectrophotometer. IR spectra were recorded on a SP3-300 spectrophotometer in KBr. ^1H NMR spectra were measured on a JEOL-Fx-90Q spectrometer using TMS as internal standard. Elemental (C, H and N) analyses were carried out on a Carlo-Erba 1102 elemental analyzer. Mass spectra were recorded on KRTOS-AEI-MS 50 (U.K.). Electron Spin Resonance were observed on Bruker ER 200D-SRC ESR apparatus.



Scheme 1

The substituted anilines (0.01 mol) and a trace amount of Galvinoxyl radical were dissolved in dichloromethane (50 mL) and shaken with a saturated solution of potassium ferricyanide in 2N 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 a rotary evaporator and the resulting mixture was passed through a silica gel column using hexane or

Table 1. The yield, m.p., lit. m.p., appearance of azobenzenes and Hammett substituent constants (δ)

R	yield (%)	m.p.℃	lit. m.p.℃[13]	substituent constant (δ)[14]	color and shape
H	93	67-68	68	0.00	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	0.115	scarlet needles
4-C_2H_5O	84	155-156	157-159	-0.250	yellow plates
2,3-$(CH_3)_2$	76	109	110-111	-	orange needles
2,5-$(CH_3)_2$	79	115-117	119	-	yellow needles
2,6-$(CH_3)_2$	80	49	48	-	red plates
3,4-$(CH_3)_2$	84	142-144	140-141	-	red needles
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
a-naphthyl	28	188-189	190	-	brown needles

petroleum ether (b.p. 60-90℃) as the solvent to get symmetrical azobenzenes which were dried in vacuum.

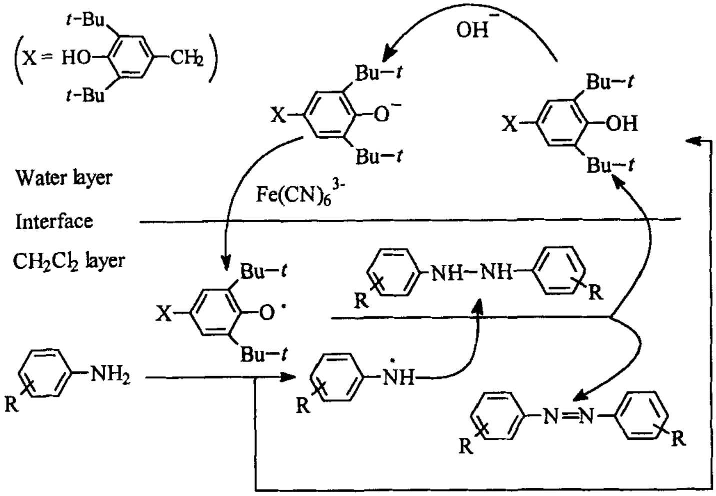
Results and Discussion

Eighteen symmetrical azobenzenes were prepared from corresponding amines in satisfied yield. Particularly the yields of azobenzene and 4,4'-difluoroazobenzene are over 90%, even the yield of the 1-azonaphthalene was 28%. The structures of these azobenzenes were established by UV, IR, ^1H NMR, mass spectral methods and elemental analysis.

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 and the yields were higher than those with the later.

From the fact, we presume the reaction undergo aromatic amine free radicals procedure. The substituted aniline radicals belong to electron deficient system, electron donor groups could make them stable, while electron withdrawing groups could make them unstable[15]. The more stable the substituted groups are, the more facilely the azobenzenes are prepared. The yields obeyed the order (see table 1). 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.

From the phenomenon of the experiment, a possible free radical oxidation[16] 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.

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References and notes

1. Russ, H. W.; Tappe, H. *Eur. Pat. Appl. EP.* 629, 667, **1994**.
2. Ikeda, T. and Tsutumi, O. *Science*. **1995**, 268, 1873.
3. Peng, X. J.; Yang, J. Z. *Chin. Image Sci and Practive*, **1988**, 4, 5.
4. Wang, Y. L.; Wang, X. Y.; Li, J. P.; Ma, D. L.; Wang ,H. *Synth. Commun.*, **1997**, 27(10), 1737-1742.
5. Wang, C. L.; Wang, Y. L.; Wang, X. Y.; Li, J. P.; Wang, H.; Ma, D. L.; *Synth. Commun.*, **1997**, 27(21), 3723-3728.
6. Wang, C. L.; Wang, Y. L.; Wang, X. Y.; Li, J. P.; Ma, D. L.; Wang, H. *Org. Prep. Proced. Int.*, **1998**, 30(1), 997-999.
7. Wang, Y. L.; Ru, C. J.; Li, J. P.; Wang, H.; Ma, D. L. *Synth. Commun.*, **1994**, 24(12), 1737-1742.
8. Neu, R. *Ber Dtsh. Chem. Ges.* **1939**, 72, 1505.
9. Burdon, J.; Morton, C. J.; Thomas, D. F. *J. Chem. Soc.* **1965**, 2621-2627.
10. Wheeler, O. H.; Gonzalez, D. *Tetrahedron*, **1964**, 20, 189-193.
11. Goldstein, S. L.; McNelis, E. *J. Org. Chem.* **1973**, 38, 183-185.
12. Elisa, L.; Elena, M.; Concepcion, M.; Socorro, L. *Tetrahedron Letters*, **1997**, 38, 7847-7848.
13. Heilbron Ian, Bunbury H M. *Dictionary of Organic Compounds*, the fifth edition, published 1982 by Chapman and Hall.
14. Jaffe, H. H. *Chem. Rev.* **1953**, 53, 191-261
15. Cheng, J. P.; Lu, Y.; Liu, B. *Science in China (Series B)*, **1988**, 28(2), 164-171.
16. Sykes, P. *A Guidebook to Mechanism in Orgnic Chemistry* (Bath press, New York),**1986**, 307.

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