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971

Phase Transfer Catalyzed Method to Prepare Symmetrical Azobenzenes from Anilines

 Xiao-Yang Wang^b(王曉陽), Yu-Lu Wang^{**}(王玉爐), Cai-Lan Wang^{*}(王彩闌), Jian-Ping Li^{*}(李建平), Hong Wang^{*}(王 紅) and Zi-Yi Zhang^{*b}(張自義) *Department of Chemistry, Henan Normal University, Xinxiang, 453002, China
^bDepartment of Chemistry, National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, 730000, China

Using free radical 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl as catalyst, the phase transfer catalyzed method of oxidation of anilines to symmetrical azobenzenes with a saturated solution of potassium ferricyanide in 2N aqueous potassium hydroxide and dichloromethane is described for the first time. The reaction has an intimate relation with Hammett substituent constants. This report offers an efficient and rapid method to prepare azobenzenes, and a possible mechanism is also suggested.

INTRODUCTION

Azobenzenes are useful synthetic intermediates.¹ They have been widely utilized as dyes and analytic reagents.² Azobenzene liquid crystal film has been used for optical-switching and image storage.^{3,4}

The oxidation of substituted semicarbazides to azo compounds with several reagents such as NBS (*N*-bromosuccinimide)/pyridine,⁵ KClO₃/H₂SO₄/FeSO₄,⁶ DMF-NO_X⁷ and 2,4,6-(t-C₄H₉)₃C₆H₂OH/K₃Fe(CN)₆/NaOH⁸ has been reported by us. The oxidation of substituted anilines to azobenzenes with a variety of reagents such as iodosobenzene diacetate,⁹ barium manganate,¹⁰ lead tetraacetate,¹¹ sodium hypochlorite¹² and manganese dioxide¹³ has also been reported. However, some of these methods require tedious work to prepare oxidants. At the same time, the oxidation of anilines with inorganic oxidants in aqueous solution is complicated by the poor solubility of anilines, and the yields are low.

The oxidation of an aromatic amine with potassium ferricyanide in the presence of KOH was first reported by Goldstein in 1973.¹⁴ Mesidine was oxidized by this oxidant in aqueous methanol at 45 °C for ten days to give the corresponding azobenzene. The oxidation of fluoroanilines to fluoroazobenezenes with this oxidant in refluxing aqueous ethanol was also reported by Leyva.¹⁵ However, from our experience, fluoroanilines can be oxidized to more complicated compounds by excessive potassium ferricyanide under 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 stirred for two hours

at room temperature; 4,4'-difluoroazobenzene was obtained in 34% yield with recovery of 4-fluoroaniline 47%. From our previous work,^{5,6,7,8} we considered the reaction might proceed by a free radical process. Accordingly, a trace of stable free radical 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl¹⁶ was added and 4,4'-difluoroazobenzene was obtained in 92% yield in two hours at room temperature. When we used this oxidation system to treat 4-chloroaniline, 4,4'-dichloroazobenzene was given only in very low yield (4%) because of its poor solubility in aqueous ethanol. Therefore, dichloromethane was used as the solvent and a saturated solution of potassium ferricyanide in 2N aqueous potassium hydroxide solution was used as the oxidant. To our surprise, 4,4'-dichloroazobenzene was obtained in 67% yield within 15 minutes at room temperature. Thus with 4hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl as catalyst, the phase transfer method 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. It used readily available reagents, unlike some of the literature preparations, 7^{13} which are required to make the oxidant. The generation of azobenzenes by a phase-transfer method is potentially of general interest, especially in industrial applications where the two phases may be recycled separately to improve efficiency.

RESULTS AND DISCUSSION

Eighteen symmetrical azobenzenes were prepared from the corresponding amines in satisfactory yields. Par-

Scheme I



ticularly the yields of azobenzene and 4,4'-difluoroazobenzene were over 90%. Even the oxidation of 1-naphthylamine gave 1-azonaphthalene in higher yield than that previously reported.¹³ The structures of these azobenzenes were established by UV, IR, ¹H NMR, mass spectral methods and elemental analysis. When this method was used to prepare nitroazobenzenes from nitroanilines, it failed. The possible reason was that the free radical could be captured by the nitro group.¹⁷

The ease of oxidation, as judged by the rate of color change of dichloromethane layer, showed that the amines with the electron donor groups seemed to react more rapidly than those with the electron withdrawing ones. It coincided with the Hammett substituent constants. The smaller the constants are, the more easily the reaction can go.

From this fact, we presumed that the reaction underwent an aromatic amine free radicals procedure. For the substituted aniline radicals, electron donor groups could make them stable, while electron withdrawing groups could make them unstable.²⁰ The more stable the aromatic amine free radicals were, the more facilely the azobenzenes were prepared. The yields obeyed this order (see Table 1). We tried to observe the aromatic amine free radicals by Electron Spin Resonance (ESR). Although we detected the instantaneous signs of radicals, we failed to record them because of their high instability.

From the phenomenon of the experiment, a possible mechanism of free radical oxidation²¹ is shown as Scheme II.

Scheme II



Firstly, 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl radical abstracted a hydrogen atom from substituted

R	yield (%)	m.p. °C	lit. m.p. °C ¹⁸	substituent constant $(\sigma)^{19}$	color and shape
н	91	67-68	68	0.000	red plates
2-CH3	79	54	55	-	red plates
3-CH3	82	53-54	54-55	-0.069	orange red prisms
4-CH3	89	143	144-155	-0.170	orange yellow plates
2-CH3O	64	143-145	143	-	yellow needles
4-CH3O	79	160-161	160	-0.268	scarlet needles
4-C2H5O	83	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-(CH3)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-C1	50	136	137	-	red plates
3-Ci	50	99	101	0.373	orange needles
4-C1	67	188	185	0.227	orange yellow needle:
4-Br	53	203-205	205	0.232	orange needles
4-1	49	235-236	235	0.276	orange red plates
l-naphthyl	27	188-189	190	-	brown needles

aniline, aromatic amine radical and hydroxyamine were formed. Secondly, the aromatic amine radicals coupled to generate symmetrical substituted hydrazobenzenes. Thirdly, N-O free radicals reacted on the substituted hydrazobenzenes to give the corresponding azobenzenes and hydroxyamine in dichloromethane phase. Fourthly, the hydroxyamine yielded to the nitroxide anion in potassium hydroxide solution. Finally, the nitroxide anion became a nitroxyl free radical by passing an electron to potassium ferricyanide.

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.

EXPERIMENTAL SECTION

Melting points were determined with a Kofler micro melting apparatus and were uncorrected. UV-visible spectra were taken in CHCl₃ 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-9OQ 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 spectra were observed on a Bruker ER 200D-SRC ESR apparatus.

General Procedure for the Preparation of Symmetrical Azobenzenes from Anilines

The substituted anilines (0.01 mol) and a trace amount of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl free 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 colour in the 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 was dried over anhydrous sodium sulfate. The solvent was concentrated after filtration of sodium sulfate. The resulting mixture was passed through a silica gel column using hexane or petroleum ether (b.p. 60-90 °C) as the eluent to get symmetrical azobenzenes.

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Key Words

Symmetrical substituted azobenzenes; Substituted anilines; Phase transfer; Radicals and radical reactions.

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Wang et al.

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