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# THE IMPROVED METHOD OF OXIDATION OF 4-FLUOROANILINE TO 4-FLUOROAZOBENZENE

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**Abstract:** The improved method of oxidation of 4-fluoroaniline to 4-fluoroazobenzene with $K_3Fe(CN)_6$/KOH and 2,4,6-tri-tert-butylphenol as catalyst is described for the first time in this paper. This report offers an efficient and rapid method to prepare azobenzene and a possible mechanism is also suggested.

Fluoroazobenzenes are useful synthetic intermediates[1]. They have been widely utilized as dyes and analytic reagents[2], optical-switching and image storage can be made by azobenzene liquid crystal film[3,4].

The oxidation of substituted semicarbazides to azo compounds with several reagents such as NBS(N-Bromosuccinimide)/Pyridine[5], $KClO_3/H_2SO_4/FeSO_4$[6], DMF-$NO_X$[7] and 2,4,6-$(t\text{-}C_4H_9)_3C_6H_2OH/K_3Fe(CN)_6/NaOH$[8] has been reported by us. The oxidation of aromatic amines to azobenzenes with several reagents such as

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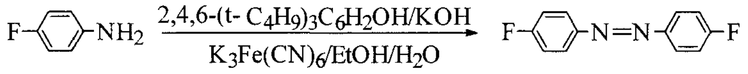
barium manganate[9], lead tetraacetate[10], sodium hypochlorite[11] and manganese dioxide[12] has also been reported. However the oxidation of fluoroanilines with inorganic oxidants in aqueous solution is complicated by the poor solubility of fluoroanilines.

The oxidation of an aromatic amine with potassium ferricyanide and KOH was first reported by Goldstein in 1973[13]. 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[14]. 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 this paper, the oxidation of 4-fluoroaniline to 4,4'-difluoroazobenzene with potassium ferricyanide, KOH and a trace of 2,4,6-tri-tert-butylphenol is reported for the first time. This method only needs two hours under room temperature.

## Experimental Section

Melting points were determined with a Kofler micro melting apparatus and were uncorrected. IR spectra were recorded on a SP3-300 spectrophotometer in KBr. $^1$H 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.).



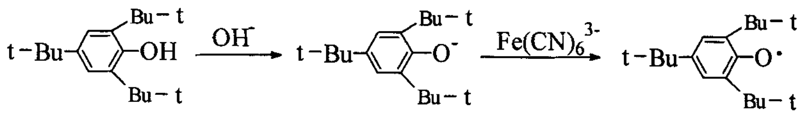
Yield: 93%

4-Fluoroaniline (0.01mol) and a trace of 2,4,6-tri-tert-butylphenol were added to a stirred ethanol/water (50/50) mixture. Then potassium hydroxide (0.03mol) and potassium ferricyanide (0.04mol) were added. The resulting mixture was kept under room temperature for two hours. After this time, the mixture was filtered to remove the remaining oxidant and extracted with $CH_2Cl_2$. The organic solution was washed four times with water and 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 as the solvent to get the 4-fluoroazobenzene (0.466mol) as a crystalline orange solid. Yield: 93%; m.p. 99-100°; IR (KBr): 3030, 1650, 1500, 1420cm$^{-1}$; $^1$H NMR ($CDCl_3$): δ 7.30-7.95(m, 8H, Ar-H); MS: m/z 218 ($M^+$), 123, 95; Anal. calcd for $C_{12}H_8N_2F_2$: C, 66.03; H, 3.69; N, 12.84. Found: C, 66.05; H, 3.66; N, 12.82. [Literature[15]: m.p. 98-99°; $^1$H-NMR( acetone-$d_6$): δ 7.96 (q, 4H, Ar-H), 7.34 (t, 4H, Ar-H); MS: m/z 218; $C_{12}H_8N_2F_2$, Found: C, 65.98; H, 3.66; N, 12.90].

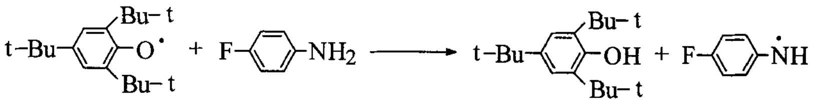
## Results and Discussion

From the fact of this experiment, a possible mechanism is shown as the following:

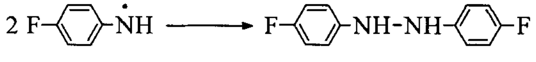
Firstly 2,4,6-tri-tert-butylphenol is changed to phenoxide anion by potassium hydroxide and a stable 2,4,6-tri-tert-butylphenol radical is produced by passing an electron to potassium ferricyanide.



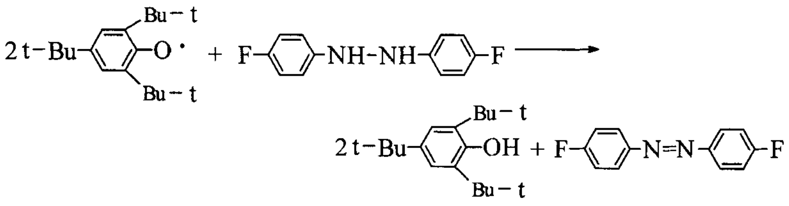
Secondly 2,4,6-tri-tert-butylphenol radical abstracts a hydrogen atom from 4-fluoroaniline and 4-fluoroaniline radical is formed.



Secondly the two 4-fluoroaniline radicals couple to generate 4,4'-difluorohydrazobenzene.



Finally the 2,4,6-tri-tert-butylphenol radicals act on the 4,4'-difluorohydrazobenzene to form the 4,4'-difluoroazobenzene[16] and the phenol radicals are changed to 2,4,6-tri-tert-butylphenols.



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