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A CONVENIENT, RAPID AND NEW CATALYST OXIDATION METHOD WITH KClO₃/H₂SO₄/FeSO₄ FOR PREPARING ARYL AZO COMPOUNDS

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ABSTRACT: Using potassium chlorate, sulfuric acid and ferrous sulfate as a catalytic oxidation system to oxidize the aryl substituted semicarbazide to prepare azo compounds in one phase have been described first time in this paper. Fourteen azo compounds have been synthesized in excellent yields(>90%). This method only needs cheap reagents, simple instrument and short reaction time. A possible mechanism has been suggested.

It has been reported by us that carbodiazone compounds can be synthesized in good yield by two-phase dehydrogenation of aryl substituted carbazide (fig.1)^[1]. We also reported the synthesis of azo urea compounds using phase transfer catalyzed dehydrogenation of substituted semicarbazide compounds(fig.2)^[2].

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$ArNHNHCONHNHAr^{2.4.6-(1-C_4H_3)_3C_6H_2OH/K_3Fe(CN)_6/NaOH} \rightarrow ArN=NCON=NAr$

Figure 1

ArNHCONHNHC₆H₅ <u>Galvinow1/K₃Fe(CN)₆ / NaOH</u> ArNHCON=NC₆H₅ CH₂Cl₂ Figure 2

Now we report the use of a cheap catalytic oxidation system $KClO_3/H_2SO_4/FeSO_4$ in the synthesis of aryl azo compounds in one phase first time. Fourteen azo urea compounds have been prepared from the aryl substituted semicarbazides in excellent yield with very short reaction time. Eight (2a-2h) of them are new compounds.

EXPERIMENTAL SECTION

Melting points were determined with kofler micro melting point apparatus and were uncorrected. Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. Infrared spectra were recorded by using a SP3-300 spectrophotometer using KBr pellets. ¹HNMR spectra were measured in CDCl₃ or DMSO-D₆ using TMS as reference standard with a JEOL-Fx-90Q NMR spectrometer. Mass spectra were recorded on a KRTOS-AEI-MS50(U.K) spectrometer.

Scheme

$$\frac{\text{ArNHCONHNHC}_{6}\text{H}_{5}}{\text{I}} \xrightarrow{\text{KCIO}_{3}/\text{H}_{2}\text{SO}_{4}/\text{FeSO}_{4}}{\text{CH}_{3}\text{COCH}_{3}} \xrightarrow{\text{ArNHCON}=\text{NC}_{6}\text{H}_{5}}$$

General Procedure

1.0 Mmol of 1,4-disubstituted aryl semicarbazide compounds (1a-1n) was dissolved in 5-10 ml of acetone with heating. 1.0 Mmol KClO₃ in 5ml of 2N H_2SO_4 was added and the mixture was heated under gentle reflux. A catalytic amount of FeSO₄ (0.07 mmol) in 1 ml of water was added with heating and shaking. The color of solution changes to orange-red or deep-red rapidly. After 2.5 minutes, 30 ml cold water was added. Orange-red flocculent deposit was produced. The mixture was filtered and washed with water. The product was dried by heating at temperature below 56 °C in vacuum. The structure of products were identified by elemental analyses, IR, ¹H-NMR and MS spectra data.

Table	Color, m. p., Yield	of compounds		
Entry	Structure	Color	m.p.(°C)	Yield (%)
2a	p-FC ₆ H ₄ NHCON=NC ₆ H ₅	orange	105-107	91
2b	p-ClC ₆ H ₄ NHCON=NC ₆ H ₅	orange-red	139-140	98
2c	p-BrC ₆ H ₄ NHCON=NC ₆ H ₅	orange-red	137-138	96
2d	p-IC ₆ H ₄ NHCON=NC ₆ H ₅	orange-red	132-134	93
2e	o-ClC ₆ H ₄ NHCON=NC ₆ H ₅	orange	80-82	92
2f	o-BrC ₆ H ₄ NHCON=NC ₆ H ₅	red	69-71	91
2g	m-ClC ₆ H ₄ NHCON=NC ₆ H ₅	red	86-87	94
2h	m-BrC ₆ H ₄ NHCON=NC ₆ H ₅	orange	93-95	98
2i	o-MeC ₆ H ₄ NHCON=NC ₆ H ₅	orange-red	103-105	91
2j	m-MeC ₆ H ₄ NHCON=NC ₆ H ₅	orange	68-7 0	95
2k	p-MeC ₆ H ₄ NHCON=NC ₆ H ₅	orange-red	105-107	92
21	2,3-Me ₂ C ₆ H ₃ NHCON=NC ₆ H ₅	brown-red	121-123	91
2m	2,6-Me ₂ C ₆ H ₃ NHCON=NC ₆ H ₅	yellow	118-119	98
2n	p-EtOC ₆ H ₄ NHCON=NC ₆ H ₅	orange-red	128-129	96

These compounds are stable. There is no change after keeping for long time. All compounds gave satisfactory spectroscopic and analytical data.

2a: IR(KBr)v: 3340, 3030, 1710, 1600, 1500, 1415 cm⁻¹; ¹H-NMR δ : 7.05-8.02 (m, 9H, ArH), 8.41 (s, 1H, NH); Anal. Calcd. for C₁₃H₁₀N₃OF: C, 64.19; H, 4.14; N, 17.28. Found: C, 64.02; H, 4.39; N, 17.33.

2b: IR(KBr))v: 3320, 3050, 1680, 1585, 1485, 1440cm⁻¹; ¹H-NMR δ : 7.22-7.98 (m, 9H, ArH), 8.64 (s, 1H, NH); MS (m/z): 259 (M⁺), 154, 126(100), 105; Anal. Calcd for C₁₃H₁₀N₃OCI: C, 60.13; H, 3.88; N, 16.18. Found: C, 60.32; H, 3.96; N, 16.15.

2c: IR(KBr)v: 3325, 3040, 1680, 1585, 1490, 1440cm⁻¹; ¹H-NMR δ : 7.24-7.96 (m, 9H, ArH), 8.54 (s, 1H, NH); MS (m/z): 304(M⁺), 199, 171(100), 105, 90. Anal. Calcd for C₁₃H₁₀N₃OBr C, 51.49; H, 3.33; N,13.86. Found: C, 51.69; H, 3.50; N, 14.02.

2d: IR(KBr))v: 3300, 3030, 1680, 1580, 1485, 1440cm⁻¹; ¹H-NMR δ : 7.26-8.02 (m, 9H, ArH), 8.56 (s, 1H, NH); MS (m/z): 351(M⁺), 246, 218(100), 105, 90. Anal. Calcd for C₁₃H₁₀N₃OI, C, 44.47; H, 2.87; N, 11.97. Found: C, 44.66; H, 2.71; N, 11.86.

2e: IR(KBr)v: 3340, 3040, 1700, 1595, 1480, 1420cm⁻¹; ¹H-NMR δ : 7.16-8.62 (m, 9H, ArH), 8.55 (dd, 1H, NH); Anal. Calcd for C₁₃H₁₀N₃OCl: C, 60.13; H, 3.88; N, 16.18. Found: C, 60.25; H, 3.89; N, 15.91.

2f: IR(KBr)v: 3280, 3040, 1680, 1580, 1500, 1435cm⁻¹; ¹H-NMR δ : 7.10-8.60 (m, 9H, ArH), 8.56 (dd, 1H, NH) Anal. Calcd for C₁₃H₁₀N₃OBr C, 51.49; H, 3.33; N, 13.86. Found: C, 51.54; H, 3.28; N, 14.10.

2g: IR(KBr)v: 3260, 3020, 1680, 1600, 1485, 1430cm⁻¹; ¹H-NMR δ : 7.12-8.16 (m, 9H, ArH), 8.60 (dd, 1H, NH); Anal. Calcd for C₁₃H₁₀N₃OCl: C, 60.13; H, 3.88; N, 16.18; Found: C, 60.37; H, 3.69; N, 16.31.

2h: IR(KBr)v: 3320, 3030, 1700, 1595, 1500, 1430cm⁻¹; ¹H-NMR δ : 7.09-8.12 (m, 9H, ArH), 8.57 (dd, 1H, NH); Anal. Calcd for C₁₃H₁₀N₃OBr C, 51.49; H, 3.33; N, 13.86. Found: C, 51.71; H, 3.52; N, 13.96.

2k: IR (KBr)v: 3175, 3042, 2950, 1675, 1580, 1420cm⁻¹; ¹H-NMR δ: 2.24 (s, 3H), 7.06-8.02 (m, 9H, ArH), 8.16 (s, 1H, NH); Anal. Calcd for C₁₄H₁₃N₃O: C, 70.29; H, 5.44; N, 17.57. Found: C, 70.13; H, 5.29; N, 17.81.

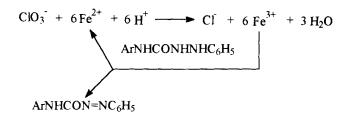
2m: IR (KBr)v: 3243, 3045, 2990, 2915, 1685, 1580, 1485, 920cm⁻¹; ¹H-NMR δ : 2.22 (s, 6H), 7.34-7.98 (m, 8H), 8.23 (s, 1H); Anal. Calcd for C₁₅H₁₅N₃O: C, 71.15; H, 5.93; N, 16.60. Found: C, 71,36; H, 5.75; N, 16.49.

RESULTS AND DISCUSSION

Azo compounds have been widely utilized as dyes and analytical reagents. These compounds can also be used in material of non-linear optics, material of optics information storing in laser dish, and dyes with oil solubility in photochromy in modern technology.^{3,4} The preparation of azo compounds have been described in many literatures.^{5,6} However, the reports of the preparation of azo compounds which the -N=N- of these compounds are connected to a carbonyl group on one side and an aryl group on the other are very few.

In this paper, a convenient, rapid and new catalyst oxidation method with $KClO_3/H_2SO_4/FeSO_4$ for preparing azo urea compounds in one phase have been established, with cheap reagents, mild reaction condition, single experiment short reaction time, obvious phenomenon and high yield. The products were separated easily.

According to the fact of the oxidation reaction, a possible mechanism of the reaction is suggested as following:



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