Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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To cite this article: Cai-lan Wang, Yu-lu Wang, Xiao-yang Wang, Jian-ping Li, Dong-lan Ma & Hong Wang (1997) A Convenient, Rapid and New Catalyst Oxidation Method with $KClO_3/H_2SO_4/FeSO_4$ for Preparing Aryl Azo Compounds, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:21, 3723-3728, DOI: 10.1080/00397919708007294

To link to this article: http://dx.doi.org/10.1080/00397919708007294

SYNTHETIC COMMUNICATIONS, 27(21), 3723-3728 (1997)

A CONVENIENT, RAPID AND NEW CATALYST OXIDATION METHOD WITH $KClO_3/H_2SO_4/FeSO_4$ 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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$$ArNHNHCONHNHAr \xrightarrow{2.4.6\text{-}(t\text{-}C_4H_9)_3C_6H_2OH/K_3Fe(CN)_6/NaOH} ArN{=}NCON{=}NAr$$

Figure 1

$$ArNHCONHNHC_6H_5 \xrightarrow[CH_2Cl_2]{Galvinoxyl/K_3Fe(CN)_6/NaOH} ArNHCON{=}NC_6H_5$$

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. ^{1}HNMR spectra were measured in $CDCl_3$ or DMSO-D_6 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

$$\underset{1}{ArNHCONHNHC_6H_5} \xrightarrow[CH_3COCH_3]{KClO_3/H_2SO_4/FeSO_4} \underset{2}{ArNHCON{=}NC_6H_5}$$

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 $KClO_3$ in 5ml of 2N H_2SO_4 was added and the mixture was heated under gentle reflux. A catalytic amount of $FeSO_4$ (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℃ 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.(℃)	Yield (%)
2a	p-$FC_6H_4NHCON{=}NC_6H_5$	orange	105-107	91
2b	p-$ClC_6H_4NHCON{=}NC_6H_5$	orange-red	139-140	98
2c	p-$BrC_6H_4NHCON{=}NC_6H_5$	orange-red	137-138	96
2d	p-$IC_6H_4NHCON{=}NC_6H_5$	orange-red	132-134	93
2e	o-$ClC_6H_4NHCON{=}NC_6H_5$	orange	80-82	92
2f	o-$BrC_6H_4NHCON{=}NC_6H_5$	red	69-71	91
2g	m-$ClC_6H_4NHCON{=}NC_6H_5$	red	86-87	94
2h	m-$BrC_6H_4NHCON{=}NC_6H_5$	orange	93-95	98
2i	o-$MeC_6H_4NHCON{=}NC_6H_5$	orange-red	103-105	91
2j	m-$MeC_6H_4NHCON{=}NC_6H_5$	orange	68-70	95
2k	p-$MeC_6H_4NHCON{=}NC_6H_5$	orange-red	105-107	92
2l	2,3-$Me_2C_6H_3NHCON{=}NC_6H_5$	brown-red	121-123	91
2m	2,6-$Me_2C_6H_3NHCON{=}NC_6H_5$	yellow	118-119	98
2n	p-$EtOC_6H_4NHCON{=}NC_6H_5$	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}; ^{1}H-NMR δ: 7.05-8.02 (m, 9H, ArH), 8.41 (s, 1H, NH); Anal. Calcd. for $C_{13}H_{10}N_3OF$: 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}; ^{1}H-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 $C_{13}H_{10}N_3OCl$: 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}; ^{1}H-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 $C_{13}H_{10}N_3OBr$ 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}; ^{1}H-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 $C_{13}H_{10}N_3OI$, 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}; ^{1}H-NMR δ: 7.16-8.62 (m, 9H, ArH), 8.55 (dd, 1H, NH); Anal. Calcd for $C_{13}H_{10}N_3OCl$: 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}; ^{1}H-NMR δ: 7.10-8.60 (m, 9H, ArH), 8.56 (dd, 1H, NH) Anal. Calcd for $C_{13}H_{10}N_3OBr$ 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}; ^{1}H-NMR δ: 7.12-8.16 (m, 9H, ArH), 8.60 (dd, 1H, NH); Anal. Calcd for $C_{13}H_{10}N_3OCl$: 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}; ^{1}H-NMR δ: 7.09-8.12 (m, 9H, ArH), 8.57 (dd, 1H, NH); Anal. Calcd for $C_{13}H_{10}N_3OBr$ 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}; ^{1}H-NMR δ: 2.24 (s, 3H), 7.06-8.02 (m, 9H, ArH), 8.16 (s, 1H, NH); Anal. Calcd for $C_{14}H_{13}N_3O$: C, 70.29; H, 5.44; N, 17.57. Found: C, 70.13; H, 5.29; N, 17.81.

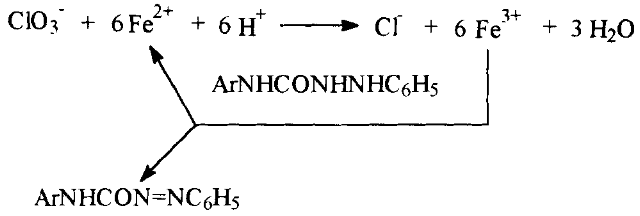
2m: IR (KBr)v: 3243, 3045, 2990, 2915, 1685, 1580, 1485, 920cm^{-1}; ^{1}H-NMR δ: 2.22 (s, 6H), 7.34-7.98 (m, 8H), 8.23 (s, 1H); Anal. Calcd for $C_{15}H_{15}N_3O$: C, 71.15; H, 5.93; N, 16.60. Found: C, 71,36; H, 5.75; N, 16.49.

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:



Acknowledgments: This study was supported by a grant from National Natural Science Foundation of China.

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(Received in The Netherlands 20 May 1997)