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Xiao-Yang Wang [a] , Yu-Lu Wang [b] , Jian-Ping Li [b] & Zi-Yi Zhang [a]

[a] Department of Chemistry , Lanzhou University , Lanzhou, 730000, China

[b] Department of Chemistry , Henan Normal University , Xinxiang, 453002, China

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THE NEW SYNTHESIS OF AZO COMPOUNDS BY 4-HYDROXY-2,2,6,6-TERTRAMETHYL-1-PIPERIDINYLOXYL AS THE PHASES TRANSFER DEHYDROGENATION CATALYST

Xiao-Yang Wang[a], Yu-Lu Wang*[b], Jian-Ping Li[b], Zi-Yi Zhang[a]

[a]Department of Chemistry, Lanzhou University, Lanzhou, 730000, China
[b]Department of Chemistry, Henan Normal University, Xinxiang, 453002, China

Abstract: Using 4-hydroxy-2,2,6,6-tertramethyl-1-piperidinyloxyl as the phases transfer dehydrogenation catalyst to prepare azo compounds is reported first time, ten N, 2-diaryl diazenecarboxamides were synthesized in high yield under mild condition. A possible mechanism was suggested by a nitroxide free radical which acted on substituted semicarbazides to form azo compounds.

It is well known that 4-hydroxy-2,2,6,6-tertramethyl-1-piperidinyloxyl is a stable nitroxyl radical. It can be used as antioxidants[1,2] and spin labeled compounds to mark protein, biomembrance and nucleic acid[3,4] etc. Furthermore, as an efficient inhibitor, it can prevent olefin polymerizing[5] by free radical. However, using 4-hydroxy-2,2,6,6-tertramethyl-1-piperidinyloxyl as the phase transfer catalyst has not been reported so far.

Azo compounds have been widely utilized as dyes and analytical reagents. Optical-switch and image storage can be made by azobenzene liquid crystal film[6]

*To whom correspondence should be addressed.

etc.. Generally, azo compounds are synthesized by diazo coupling or oxidating hydrazine using N-bromosuccinimide (NBS) and pyridine, fuming nitric acid and nitrogen dioxide oxidations[7,8,9]. From our experience, N-bromosuccinimide-pyridine is an efficient oxidant, which had been reported by us[10]. Fuming nitric acid and nitrogen dioxide do not proceed to completion and, with compounds containing phenyl groups, aromatic nitration can be a completing process.

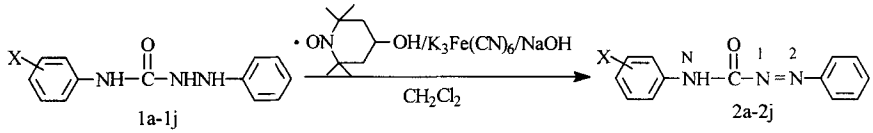
In this paper, a new reaction of two phases transfer catalyzed dehydrogenation of aryl substituted semicarbazides has been studied and ten of new type azo compounds have been synthesized in excellent yield (91.0~98.5%) under mild condition. This method only needs simple instruments and short reaction time (5~10 minutes). The structures of these azo compounds were established by IR, ^{1}H NMR, mass spectral data and elemental analysis.

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.).

Preparation of azo compounds 2a-2j from substituted semicarbazides. General procedure. The substituted semicarbazides 1a-1j (1mmol) and a trace of 4-hydroxy-2,2,6,6-tertramethyl-1-piperidinyloxyl free radical (1%mmol) were dissolved in dichloromethane (50mL) and shaken with the saturated solution of potassium ferricyanide in 2 normal aqueous sodium hydroxide (12mL). After 5-10 minutes, the color in organic phase changed from white to yellow-orange or

orange-red or deep-red. The dichloromethane layer was separated, and the water layer was extracted with dichloromethane four times. The dichloromethane layers were mixed together and washed with water until neutrality, then dried with anhydrous sodium sulfate overnight. The dichloromethane was distilled in water-bath after sodium sulfate removed. The products were recrystallized and dried below 50°.



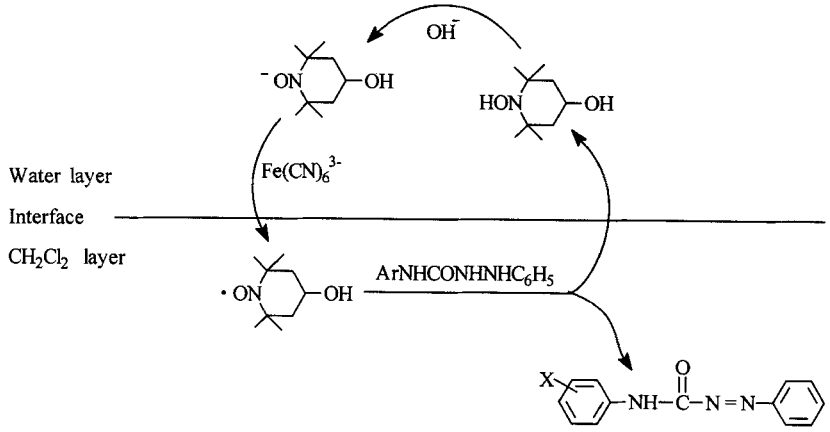
a: X=H b: X=2-Me c: X=3-Me d: X=4-Me e: X=4-EtO
f: X=2,3-Me_2 g: X=2,5-Me_2 h: X=2, 6-Me_2 i: X=4-F j: X=4-Cl

Scheme I

N,2-diphenyl diazenecarboxamide 2a: deep-red tabular; Yield: 95.0%; m.p. 109-111°; IR (KBr): 3230, 3060, 1680, 1600, 1500, 1420cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.03-7.80 (m, 10H, Ar-H), 8.90 (s, 1H, NH); MS: m/z 225 (M^+), 120, 105, 90, 77; Anal. calcd for $C_{13}H_{11}N_3O$: C, 69.31; H, 4.93; N, 18.66. Found: C, 69.21; H, 4.83; N, 18.50.

N-(2-methyl-phenyl)-2-phenyl diazenecarboxamide 2b: orange-red tabular; Yield: 91.0%; m.p. 103-104°; IR (KBr): 3240, 3060, 2995, 2850, 1670, 1590, 1480, 1420cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.27 (s, 3H, CH_3), 7.06-7.98 (m, 9H, Ar-H), 8.90 (s, 1H, NH); Anal. calcd for $C_{14}H_{13}N_3O$: C, 70.26; H, 5.48; N, 17.57. Found: C, 70.21; H, 5.39; N, 17.15.

N-(3-methyl-phenyl)-2-phenyl diazenecarboxamide 2c: orange-red tabular; Yield: 97.2%; m.p. 70-71°; IR (KBr): 3260, 3030, 2970, 2850, 1685, 1600, 1470, 1425cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.26 (s, 3H, CH_3), 6.80-8.02 (m, 9H, Ar-H), 8.25



Scheme II

(s, 1H, NH); Anal. calcd for $C_{14}H_{13}N_3O$: C, 70.26; H, 5.48; N, 17.57. Found: C, 70.34; H, 5.46; N, 17.41.

N-(4-methyl-phenyl)-2-phenyl diazenecarboxamide 2d: orange-red tabular; Yield: 95.5%; m.p. 103-104°; IR (KBr): 3320, 3050, 2990, 2850, 1685, 1600, 1580, 1440cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.26 (s, 3H, CH_3), 7.10-8.05 (m, 9H, Ar-H), 8.26 (s, 1H, NH); Anal. calcd for $C_{14}H_{13}N_3O$: C, 70.26; H, 5.48; N, 17.57. Found: C, 70.25; H, 5.40; N, 17.53.

N-(4-ethoxyl-phenyl)-2-phenyl diazenecarboxamide 2e: orange-red needle; Yield: 94.5%; m.p. 125-126°; IR (KBr): 3320, 3040, 2995, 2880, 1675, 1580, 1500, 1435cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.27 (t, 3H, CH_3), 3.90 (q, 2H, CH_2), 6.81-8.00 (m, 9H, Ar-H), 8.25 (s, 1H, NH); Anal. calcd for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61; N, 15.60. Found: C, 66.70; H, 5.60; N, 15.53.

N-(2,3-dimethyl-phenyl)-2-phenyl diazenecarboxamide 2f: brown-red tabular; Yield: 98.5%; m.p. 123-124°; IR (KBr): 3220, 3020, 2960, 2900, 1700, 1580, 1500, 1430cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.20 (s, 6H, $2CH_3$), 7.02-8.02 (m, 8H, Ar-

H), 8.21 (s, 1H, NH); Anal. calcd for $C_{15}H_{15}N_3O$: C, 71.11; H, 5.97; N, 16.60. Found: C, 71.10; H, 5.90; N, 16.53.

N-(2,5-dimethyl-phenyl)-2-phenyl diazenecarboxamide 2g: yellow tabular; Yield: 95.5%; m.p. 123-124°; IR (KBr): 3325, 3040, 2960, 2850, 1680, 1580, 1490, 1450cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.25 (s, 6H, $2CH_3$), 6.80-8.02 (m, 8H, Ar-H), 8.20 (s, 1H, NH); Anal. calcd for $C_{15}H_{15}N_3O$: C, 71.11; H, 5.97; N, 16.60. Found: C, 71.08; H, 5.95; N, 16.55.

N-(2,6-dimethyl-phenyl)-2-phenyl diazenecarboxamide 2h: orange-red tabular; Yield: 98.5%; m.p. 118-120°; IR (KBr): 3300, 3010, 2950, 2840, 1685, 1580, 1480, 1435cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 6H, $2CH_3$) 7.42-8.00 (m, 8H, Ar-H), 7.77 (s, 1H, NH); Anal. calcd for $C_{15}H_{15}N_3O$: C, 71.11; H, 5.97; N, 16.60. Found: C, 71.05; H, 5.93; N, 16.53.

N-(4-F-phenyl)-2-phenyl diazenecarboxamide 2i: yellow needle; Yield: 93.0%; m.p. 107-108°; IR (KBr): 3340, 3020, 1710, 1600, 1500, 1420cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.09-8.03 (m, 9H, Ar-H), 8.45 (s, 1H, NH); MS: m/z 243 (M^+), 138, 110, 105, 90, 77; Anal. calcd for $C_{13}H_{10}N_3OF$: C, 64.19; H, 4.14; N, 17.28. Found: C, 64.28; H, 4.18; N, 17.20.

N-(4-Cl-phenyl)-2-phenyl diazenecarboxamide 2j: red tabular; Yield: 95.0%; m.p. 140-142°; IR (KBr): 3320, 3050, 1680, 1600, 1585, 1440cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.20-8.05 (m, 9H, Ar-H), 8.60 (s, 1H, NH); MS: m/z 259 (M^+), 154, 126, 105, 90, 77; Anal. calcd for $C_{13}H_{10}N_3OCl$: C, 60.13; H, 3.88; N, 16.18. Found: C, 60.59; H, 3.90; N, 15.95.

Results and Discussion

According to the fact that when 4-hydroxy-2,2,6,6-tertramethyl-1-piperidinyloxyl was not added to the reaction system, there is no obvious changeable color, a

possible mechanism[11] was suggested: Firstly, nitroxide free radical acted on substituted semicarbazide and attained corresponding N,2-diaryl diazenecarboxamide and hydorxyamino in dichlormethane phase. Secondly, the hydorxyamino changed to nitroxide anion in sodium hydroxide solution. Finally the nitroxide anion became nitroxyl free radical by passing an electron to potassium ferricyanide.

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