Synthesis of new type azo compounds by 4-hydroxy-2,2,6,6-tertamethyl-1-piperidinlyoxyl as the phase transfer dehydrogenation catalyst

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Use of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinlyoxyl as the phase transfer dehydrogenation catalyst to prepare azo compounds is reported for the first time. Eight N,N-diaryl diazenecarboxamides have been synthesized in high yields under mild conditions. A possible mechanism has been suggested involving a nitroxide free radical which acts on substituted semicarbazides to form azo compounds.

It is well known that 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinlyoxyl is a stable nitroxyl radical. It can be used as antioxidants and spin labeled compounds to mark protein, biomembrane and nucleic acid, etc. Furthermore, as an efficient inhibitor, it can prevent olefin polymerizing by free radical. However, use of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinlyoxyl 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, etc. Generally, azo compounds are synthesized by diazo coupling or oxidizing hydrazines using N-bromosuccinimide (NBS) and pyridine, fuming nitric acid or nitrogen dioxide. From our experience, N-bromosuccinimide-pyridine is an efficient oxidant, which has been reported by us. Fuming nitric acid and nitrogen dioxide do not proceed to completion, and with compounds containing phenyl groups, aromatic nitration can be a competing process.

In the present work, a new reaction of two phase transfer catalyzed dehydrogenation of aryl substituted semicarbazides has been studied and eight of new type azo compounds have been synthesized in (cf. Scheme I) excellent yields (90.0–98.8%) under mild condition. The reaction is completed within 5–10 min. The structures of these azo compounds were established by IR, 1H NMR, mass spectral data and elemental analyses.

Keeping the fact in view that when 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinlyoxyl was not added to the reaction system, there was no obvious change in colour, a possible mechanism was suggested. The nitroxide free radical acts on substituted semicarbazides and produces the corresponding N,N-diaryl diazenecarboxamide and hydroxyamino in dichloromethane phase. The hydroxyamino changes to nitroxide anion in sodium hydroxide solution. Finally the nitroxide anion becomes nitroxyl free radical by passing an electron to potassium ferricyanide (cf. Scheme II).

Experimental Section

General. Melting points are uncorrected. IR spectra were recorded on an SP3-300 spectrophotometer in KBr, and 1H NMR spectra on a JEOL-Ex-90Q spectrometer using TMS as internal standard. Elemental analyses (C, H, N) were carried out on a Carlo-Erba 1102 elemental analyzer. Mass spectra were recorded on a KRTOS-AEI-MS 50 (U.K).

Preparation of azo compounds 2a-h from substituted semicarbazides: General procedure. The substituted semicarbazide 1 (1 mmole) and a trace of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinlyoxyl as the phase transfer catalyst has not been reported so far.

2a: yellow needles, yield 93.0%, mp 107-08°C; IR
(KBr): 3340, 3020, 1710, 1600, 1500, 1420 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 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\(_3\)O: C, 64.19; H, 4.14; N, 17.28%. Found: C, 64.28; H, 4.18; N, 17.20%.

**N-(2-Cl-Phenyl)-2-phenyldiazenecarboxamide 2b:**
Orange-red tubular, yield 90.0%, mp 82-84°C; IR (KBr): 3340, 3060, 1700, 1590, 1480, 1420 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.14-8.60 (m, 9H, Ar-H), 9.04 (s, 1H, NH). Anal. Calcd for C\(_{13}\)H\(_{10}\)N\(_3\)OCl: C, 60.13; H, 3.88; N, 16.18%. Found: C, 60.21; H, 3.90; N, 16.15%.

**N-(3-Cl-Phenyl)-2-phenyldiazenecarboxamide 2c:**
Deep-red tubular; yield 98.0%, mp 84-86°C; IR (KBr): 3260, 3030, 1680, 1600, 1430 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.10-8.60 (m, 9H, Ar-H), 9.06 9s, 1H, NH). Anal. Calcd for C\(_{13}\)H\(_{10}\)N\(_3\)OCl: C, 60.13; H, 3.88; N, 16.18%. Found: C, 60.34; H, 3.92; N, 16.10%.

\(N\)-(4-Cl-Phenyl)-2-phenyldiazenecarboxamide 2d:
Red tubular, yield 95.0%, mp 140-42°C; IR (KBr): 3320, 3050, 1680, 1600, 1585, 1440 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 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\(_3\)OCl: C, 60.13; H, 3.88; N, 16.18%. Found: C, 60.59; H, 3.90; N, 15.95%.

**N-(2-Br-Phenyl)-2-phenyldiazenecarboxamide 2e:**
Deep-red tubular yield 94.5%, mp 70-72°C; IR (KBr): 3280, 3040, 1680, 1580, 1500, 1435 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.10-8.60 (m, 9H, Ar-H), 9.04 (s, 1H, NH). Anal. Calcd for C\(_{13}\)H\(_{10}\)N\(_3\)OBr: C, 51.49; H, 3.33; N, 13.86%. Found: C, 51.79; H, 3.36; N, 13.94%.

**N-(3-Br-Phenyl)-2-phenyldiazenecarboxamide 2f:**
Yellow-red needles, yield 98.5%, mp 94-96°C; IR (KBr): 3320, 3030, 1700, 1580, 1500, 1430 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.08-8.57 (m, 9H, Ar-H), 9.05 (s, 1H, NH). Anal. Calcd for C\(_{13}\)H\(_{10}\)N\(_3\)OBr: C, 51.49; H,
3.33; N, 13.86%.  Found: C, 51.60; H, 3.46; N, 13.84%.

**N-(4-Br-Phenyl)-2-phenyl diazene carboxamide**

2g: Red-tubular, yield 97.5%, mp 139-141°C; IR (KBr) : 3325, 3040, 1680, 1580, 1490, 1450 cm$^{-1}$; $^1$H NMR (CDCl$_3$) : $\delta$ 7.08-8.57 (m, 9H, Ar-H), 9.05 (s, 1H, NH); MS: m/z 305 (M+2) 303 (M$^+$), 200, 198, 172, 170, 105, 90, 77. Anal. Calcd for C$_{13}$H$_{10}$N$_3$OBr: C, 51.49; H, 3.33; N, 13.86%.  Found: C, 51.60; H, 3.46; N, 13.84%.

**N-(4-I-Phenyl)-2-phenyl diazene carboxamide**

2h: Orange-red tubular; yield 98.5%, mp 94-96°C; IR (KBr) : 3300, 3020, 1680, 1580, 1485, 1440 cm$^{-1}$; $^1$H NMR (CDCl$_3$) : $\delta$ 7.26-8.00 (m, 9H, Ar-H), 8.57 (s, 1H, NH); MS: m/z 351 (M$^+$), 246, 218, 105, 90, 77. Anal. Calcd for C$_{13}$H$_{10}$N$_3$OI: C, 44.47; H, 2.87; N, 11.97%.  Found: C, 44.87; H, 2.92; N, 11.69%.

**Reference**