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Note

A Simple, Efficient and New Method for Preparing *N*-Aryl-2-Phenyldiazenecarboxamide

Cailan Wang* (王彩蘭), Yulu Wang (王玉爐), Xiaoyang Wang (王曉陽),
Jianping Li (李建平) and Hong Wang (王 紅)
Department of Chemistry, Henan Normal University, Xinxiang, 453002, China

Using ferric chloride to oxidize aryl substituted semicarbazide for preparing azo compounds has been described for the first time in this paper. Nine azo compounds have been synthesized in a good to excellent yield (≥88%). This method only needs cheap reagents, simple instruments and a short reaction time.

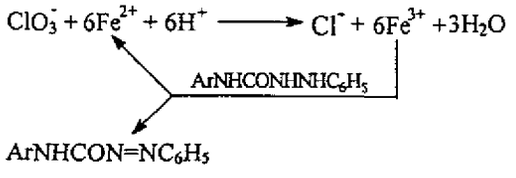
INTRODUCTION

Azo compounds are widely utilized as dyes and analytical reagents. They can also be used as materials for nonlinear optics and for storage of optical information in laser disk.[1] Recently, many noteworthy studies have shown that azobenzene derivatives possess excellent optical memory and photoelectric properties.[2] The preparation of ordinary azo compounds has been described in many references.[3,4] However, those compounds generally bear alkyl or aryl groups on both sides of the azo linkage (-N=N-). Here we report a new synthesis method using ferric chloride to oxidize aryl substituted semicarbazide for preparing a new type of azo compounds in which one side of the azo group is connected to a carbonyl group.

RESULTS AND DISCUSSION

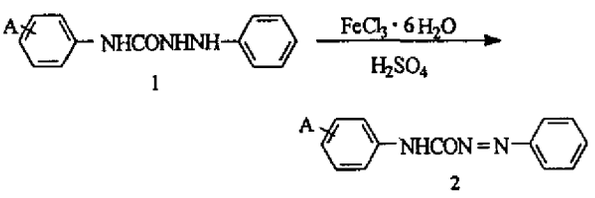
It has been first reported by us that azo urea compounds can be synthesized in good yield using phase transfer catalyzed dehydrogenation of substituted semicarbazide compounds.[5] We also reported the method of using potassium chlorate, sulfuric acid and ferrous sulfate as a catalytic oxidation system to oxidize the aryl substituted semicarbazide to prepare azo compounds in one phase.[6] In this latest experiment, we found the oxidizing reaction did not occur before the addition of ferrous sulfate. According to the phenomenon of the oxidation reaction, a possible mechanism has been suggested.

Scheme I



In order to prove the correctness of this mechanism, ferric chloride was used as an oxidizer in acid medium to substitute for the oxidation system of $KClO_3/H_2SO_4/FeSO_4$ for oxidizing the aryl substituted semicarbazide. Nine azo ureas have been synthesized in good yield under mild conditions. We describe this simple, rapid and efficient method in this paper.

Scheme II



a) A = H b) A = *p*-F c) A = *p*-I
d) A = *o*-Cl e) A = *m*-Cl f) A = *p*-Cl
g) A = *o*-Br h) A = *m*-Br i) A = *p*-Br

EXPERIMENTAL SECTION

Melting points were determined with a Kofler micro melting point apparatus and are uncorrected. IR spectra were recorded on a SP3-300 spectrophotometer in KBr. ^1H NMR spectra were measured on a JEOL-Fx-90Q spectrometer using TMS as internal standard and $CDCl_3$ as solvent. MS spectra were taken on a KRATOS-AEI-MS50 (U.K) spectrometer. Elemental Analyses were performed on a Carlo-Erba 1102 elemental analyzer.

General Procedure for the Preparation of *N*-Aryl-2-phenyl Diazenecarboxamide 2a-2i

1,4-Disubstituted aryl semicarbazides (**1a-1i**) were prepared using standard methods.[7,8]

1.0 Mmol of 1,4-disubstituted aryl simicarbazide compounds (**1a-1i**) in 10-15 mL of acetone was placed in a two-necked flask equipped with mechanical stirrer. 2.0 Mmol $FeCl_3 \cdot 6H_2O$ in 5 mL of 2N H_2SO_4 aqueous solution was added and the mixture was heated under gentle reflux. The color of the solution changed to orange-red or deep-red rapidly. After 2-4 minutes, 30 mL cold water was added. An orange-red flocculent deposit was produced. The mixture was filtered and washed with water. The product was dried by heating at temperature below 50 °C in vacuum. The structure of products were identified by elemental analyses, IR, ^{1}H NMR and MS spectra data.

***N*-Phenyl-2-phenyldiazenecarboxamide 2a**

Red tabular; yield 97%; mp 110-112 °C. IR ν_{max} (KBr) 3240 (m, NH), 3060 (w, ArH), 1695 (s, C=O), 1595, 1550 (m, ArH), 1435 (m, N=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.12-7.96 (m, 10H, ArH), 8.38 (s, 1H, NH); EI/MS *m/z* (%): 225 (M^+, 16.6); Anal. calcd. for $C_{13}H_{11}N_3O$: C, 69.31; H, 4.92; N, 18.66. Found: C, 69.12; H, 4.76; N, 18.94.

***N*-(4-Fluorophenyl)-2-phenyldiazenecarboxamide 2b**

Yellow tabular; yield 90%; mp 106-107 °C. IR ν_{max} (KBr) 3340 (m, NH), 3045 (w, ArH), 1705 (s, C=O), 1590, 1545 (m, ArH), 1425 (m, N=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.07-8.05 (m, 9H, ArH), 8.42 (s, 1H, NH); EI/MS *m/z* (%): 243 (M^+, 14.6); Anal. calcd. for $C_{13}H_{10}N_3OF$: C, 64.19; H, 4.14; N, 17.28. Found: C, 64.06; H, 4.37; N, 17.43.

***N*-(4-Iodophenyl)-2-phenyldiazenecarboxamide 2c**

Orange-red needles; yield 89%; mp 134-135 °C. IR ν_{max} (KBr) 3300 (m, NH), 3050 (w, ArH), 1680 (s, C=O), 1590, 1540 (m, ArH), 1440 (m, N=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.26-8.02 (m, 9H, ArH), 8.55 (s, 1H, NH); EI/MS *m/z* (%): 351 (M^+, 6.2); Anal. calcd. for $C_{13}H_{10}N_3OI$: C, 44.47; H, 2.87; N, 11.97. Found: C, 44.36; H, 2.68; N, 11.79.

***N*-(2-Chlorophenyl)-2-phenyldiazenecarboxamide 2d**

Orange-red tabular; yield 88%; mp 83-84 °C. IR ν_{max} (KBr) 3340 (m, NH), 3055 (w, ArH), 1700 (s, C=O), 1595, 1550 (m, ArH), 1425 (m, N=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.12-8.56 (m, 9H, ArH), 8.72 (s, 1H, NH); EI/MS *m/z* (%): 259 (M^+, 9.66); Anal. calcd. for $C_{13}H_{10}N_3OCl$: C, 60.13; H, 3.88; N, 16.18. Found: C, 60.29; H, 3.73; N, 15.96.

***N*-(3-Chlorophenyl)-2-phenyldiazenecarboxamide 2e**

Red tabular; yield 95%; mp 87-88 °C. IR ν_{max} (KBr) 3260 (m, NH), 3030 (w, ArH), 1685 (s, C=O), 1600, 1490 (m, ArH), 1430 (m, N=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.10-8.22 (m, 9H, ArH), 8.68 (s, 1H, NH); Anal. calcd. for $C_{13}H_{10}N_3OCl$: C, 60.13; H, 3.88; N, 16.18. Found: C, 60.34; H, 3.96; N, 16.35.

***N*-(4-Chlorophenyl)-2-phenyldiazenecarboxamide 2f**

Red needles; yield 94%; mp 141-142 °C. IR ν_{max} (KBr) 3320 (m, NH), 3050 (w, ArH), 1680 (s, C=O), 1585, 1490 (m, ArH), 1440 (m, N=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.18-8.06 (m, 9H, ArH), 8.62 (s, 1H, NH); EI/MS *m/z* (%): 259 (M^+, 18.7); Anal. calcd. for $C_{13}H_{10}N_3OCl$: C, 60.13; H, 3.88; N, 16.18. Found: C, 59.97; H, 3.68; N, 16.03.

***N*-(2-Bromophenyl)-2-phenyldiazenecarboxamide 2g**

Red tabular; yield 95%; mp 72-73 °C. IR ν_{max} (KBr) 3280 (m, NH), 3040 (w, ArH), 1680 (s, C=O), 1580, 1500 (m, ArH), 1435 (m, N=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.10-8.36 (m, 9H, ArH), 8.56 (s, 1H, NH); Anal. calcd. for $C_{13}H_{10}N_3OBr$: C, 51.49; H, 3.33; N, 13.86. Found: C, 51.38; H, 3.14; N, 13.69.

***N*-(3-Bromophenyl)-2-phenyldiazenecarboxamide 2h**

Orange tabular; yield 92%; mp 94-95 °C. IR ν_{max} (KBr) 3320 (m, NH), 3030 (w, ArH), 1700 (s, C=O), 1590, 1500 (m, ArH), 1430 (m, N=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.06-8.10 (m, 9H, ArH), 8.62 (s, 1H, NH); EI/MS *m/z* (%): 304 (M^+, 10.2); Anal. calcd. for $C_{13}H_{10}N_3OBr$: C, 51.49; H, 3.33; N, 13.86. Found: C, 51.68; H, 3.50; N, 13.97.

***N*-(4-Bromophenyl)-2-phenyldiazenecarboxamide 2i**

Red needles; yield 94%; mp 147-148 °C. IR ν_{max} (KBr) 3325 (m, NH), 3040 (w, ArH), 1680 (s, C=O), 1580, 1490 (m, ArH), 1450 (m, N=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.26-7.90 (m, 9H, ArH), 8.68 (s, 1H, NH); EI/MS *m/z* (%): 304 (M^+, 11.1); Anal. calcd. for $C_{13}H_{10}N_3OBr$: C, 51.49; H, 3.33; N, 13.86. Found: C, 51.24; H, 3.57; N, 13.84.

ACKNOWLEDGMENT

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Key Words

Substituted semicarbazide; Ferric chloride; *N*-aryl-2-phenyldiazenecarboxamide.

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Amendment

Wu, Ming-Jung, *Synthesis and Biological Activities of Aryl Propargyl Sulfone* JCCS Vol *45*, 783-788, Table 1, should be corrected as below.

Table 1. Inhibition of *in vitro* Human Tumor Cell Growth by **5**, **7**, **19**, **23**, **26**, **29** and **32** (IC_{50}, μg/mL)[a]

Compound	Colo 205	HepG2	HA22T	SK-BR-3	Molt-4
5	57.32	---	65.91	70.00	9.45
7	5.63	5.40	---	7.18	0.78
19	>100	---	>100	>100	>100
23	52.13	---	7.65	6.35	3.01
26	48.28	---	47.13	10.00	2.57
29	6.20	---	5.58	5.21	3.22
32	8.44	---	4.62	5.39	1.96

[a] Relative potency of growth inhibition of cancer cell line was graded by concentration required for 50% inhibition.