SHORT PAPER

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A rapid solid-state synthesis of diazenecarboxamide-azo compounds using ferric nitrate and sodium bisulfate as an oxidation system[†]

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A new and rapid solid-state method for the preparation *N*-aryl-2-phenyl-diazenecarboxamide azo compounds from aryl substituted semicarbazides is reported. With this method, nine diazenecarboxamide compounds have been synthesised in good to excellent yields (89–98%). In addition, this method has the advantages of mild reaction conditions, cheap reagents, simple methodology and short reaction times.

Keywords: *N*-aryl-2-phenyldiazenecarboxamides, ferric nitrate, sodium bisulfate, solid-state synthesis

Azo compounds have been widely utilised as dyes and analytical reagents,[1] photo-regulation materials of polypeptide function[2] and materials for non-linear optics and for storage optical information in laser disks.[3,4] Recent studies have shown that azobenzene derivatives possess excellent optical memory and photoelectric properties.[5,6] The development of new and efficient methods for the synthesis of novel azo compounds is a very important subject in organic synthesis.

N-aryl-2-phenyldiazenecarboxamides belong to a special kind of new azo compounds. We have developed several oxidation methods for preparing these by using various oxidation system, such as 2,4,6-(t-C_4H_9)$_3C_6H_2OH$/ $K_3Fe(CN)_6$/NaOH, Galvinoxyl/$K_3Fe(CN)_6$/NaOH phase transfer system,[7, 8] DMF-NO_2,[9,10] $(CH_2CO)_2NBr/C_5H_5N$ and $KClO_3/FeSO_4/H_2SO_4$ oxidising system under various conditions.[11,12] A number of *N*-aryl-2-phenyldiazenecarboxamide compounds have been prepared in good yields by these methods. However, a disadvantage of these methods is that the reaction must be carried out in rather dilute solution.[13] As a result, removal of the excess solvent is very tedious and environmentally unacceptable. This problem can be partly overcome by running the reaction in acetone, but the special heating and stirring apparatus needed for this procedure made the process even more tedious.

Solid-state synthesis has aroused interest in recent years since it possesses such advantages as high efficiency and selectivity, [14] easy separation and purification, mild reaction conditions,[15] and environmental acceptability.[16] In order to overcome the above disadvantages of solution synthesis for *N*-aryl-2-phenyl-diazenecarboxamide compounds, we report a convenient and rapid solid-state reaction of using ferric nitrate and sodium bisulfate as a new oxidation system to oxidise electron-donating aryl-substituted semicarbazides (**1**) for preparing this new-type azo compounds (**2**, Scheme 1). To the best our knowledge, oxidation of NHNH bonds by using this new oxidation system in solid-state has not been reported previously.

On the basis of our results, the method of using ferric nitrate and sodium bisulfate as an oxidation system for the oxidation of aryl substituted semicarbazides has proved to be very efficient and convenient. This reaction takes place smoothly at room temperature and only needs inexpensive reagents and simple instruments. In addition, this new method also has the advantage of a visual change, environmental friendly nature and short reaction time. On the other hand, we find that the oxidation process failed to proceed when the $Fe(NO_3)_3{\cdot}9H_2O$ was replaced with $FeCl_3{\cdot}6H_2O$ or $Fe_2(SO_4)_3{\cdot}9H_2O$ under similar reaction condition.

$$\underset{\mathbf{1}}{\mathrm{ArNHCONHNHPh}} \xrightarrow[\substack{NaHSO_4\cdot H_2O \\ \text{Solid State}}]{Fe(NO_3)_3\cdot 9H_2O} \underset{\mathbf{2}}{\mathrm{ArNHCON{=}NPh}}$$

a: Ar=2-MeC_6H_4 b: Ar=3-MeC_6H_4 c: Ar=4-MeC_6H_4
d: Ar=2,3-$Me_2C_6H_3$ e: Ar=2,5-$Me_2C_6H_3$ f: Ar=2,6-$Me_2C_6H_3$
g: Ar=3,4-$Me_2C_6H_3$ h: Ar=4-$EtOC_6H_4$ i: Ar= α - $C_{10}H_7$

Scheme 1

Nine *N*-aryl-2-phenyldiazenecarboxamides have been synthesised in excellent yields. Structures of these products were confirmed by their IR, ^{1}H NMR spectra and elemental analysis. In the IR spectrum of aryl substituted semicarbazides (**1**), there are three N–H absorptions in the region between 3020cm^{-1} and 3260cm^{-1}, while in that of the products (**2**), there is a single peak between 3150cm^{-1} and 3400cm^{-1} together with the characteristic absorption of N=N between 1410cm^{-1} and 1460cm^{-1}. In addition, other analytical data of the products, such as the melting points are also in accordance with what have been reported in the literature.

Experimental

Melting points were measured by a Kofler micro melting point apparatus. IR spectra were recorded in KBr disks using a FTS-40 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker FT-NMR Avance 400 spectrometer with $CDCl_3$ as solvent and TMS as internal standard. Chemical shifts are reported in δ units (ppm). Elemental analyses were performed on a PE-2400 CHN elemental analyzer.

General procedure for the preparation of N-aryl-2-phenyldiazenecarboxamides (**2a–i**): A mixture of aryl substituted semicarbazide **1** (1 mmol), ferric nitrate (2 mmol) and sodium bisulfate (1 mmol) was ground thoroughly in an agate mortar at room temperature. After 2–3 min, the colour of the solid mixture changed from white to light brown. Then, the reaction mixture was extracted in a small beaker (100 ml) with acetone (10 ml). Cold water (15 ml) was added to the acetone solution and the yellow, orange-yellow or orange-red flocculent products precipitated immediately. The products were isolated by filtration, and washed with water until the washings became neutral. Finally, the products were dried at temperature below 50°C in vacuum.

The physical and spectra data of compounds **2a-2i: 2a**: *N-(2-Methylphenyl)-2-phenyldiazenecarboxamide*: Orange-red tabular plates; Yield: 92%; m.p. 103–104°C; IR (KBr) ν: 3165, 3045, 2995, 1680, 1580, 1415cm^{-1}; ^{1}H NMR δ: 2.25 (s, 3H, CH_3), 7.02–8.04

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(m, 9H, ArH), 8.45 (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, 5.54; N, 17.69.

N-(3-Methylphenyl)-2-phenyldiazenecarboxamide (**2b**): Orange-red tabular plates; Yield: 89%; m.p. 68–69°C; IR (KBr) ν: 3360, 3045, 2990, 1685, 1586, 1425cm^{-1}; ^{1}H NMR δ: 2.26 (s, 3H, CH_3), 6.78–8.00 (m, 9H, ArH), 8.26 (s, 1H, NH); Anal. calcd. for $C_{14}H_{13}N_3O$: C, 70.29; H, 5.44; N,17.57. Found: C, 70.06; H, 5.63; N, 17.57.

N-(4-Methylphenyl)-2-phenyldiazenecarboxamide (**2c**): Orange-red tabular plates; Yield: 94%; m.p. 104–106°C; IR (KBr) ν: 3175, 3050, 2965, 1680, 1582, 1420cm^{-1}; ^{1}H NMR δ: 2.24 (s, 3H, CH_3), 7.08–8.02 (m, 9H, ArH), 8.18 (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, 5.52; N, 17.60.

N-(2,3-Dimethylphenyl)-2-phenyldiazenecarboxamide (**2d**): Orange-red tabular plates; Yield: 92%; m.p. 122–124°C; IR (KBr) ν: 3185, 3052, 2965, 2905, 1682, 1580, 1442cm^{-1}; ^{1}H NMR δ: 2.22 (s, 6H, $2CH_3$), 7.04–8.02 (m, 8H, ArH), 8.22 (s, 1H, NH); Anal. calcd. for $C_{15}H_{15}N_3O$: C, 71.15; H, 5.93; N,16.60. Found: C, 70.96; H, 5.81; N, 16.77.

N-(2,5-Dimethylphenyl)-2-phenyldiazenecarboxamide (**2e**): Yellow tabular plates; Yield: 94%; m.p. 121–122°C; IR (KBr) ν: 3245, 3048, 2965, 2900, 1675, 1575, 1440cm^{-1}; ^{1}H NMR δ: 2.24 (s, 6H, $2CH_3$), 6.86–8.02 (m, 8H, ArH), 8.20 (s, 1H, NH); Anal. calcd. for $C_{15}H_{15}N_3O$: C, 71.15; H, 5.93; N,16.60. Found: C, 71.36; H, 5.70; N, 16.82.

N-(2,6-Dimethylphenyl)-2-phenyldiazenecarboxamide (**2f**): Orange-red tabular; Yield: 98%; m.p. 118–119°C; IR (KBr) ν: 3240, 3045, 2990, 2910, 1680, 1580, 1430cm^{-1}; ^{1}H NMR δ: 2.24 (s, 6H, $2CH_3$), 7.42–8.00 (m, 8H, ArH), 8.16 (s, 1H, NH); Anal. calcd. for $C_{15}H_{15}N_3O$: C, 71.15; H, 5.93; N,16.60. Found: C, 71.06; H, 6.11; N, 16.65.

N-(3,4-Dimethylphenyl)-2-phenyldiazenecarboxamide (**2g**): Orange-yellow tabular; Yield: 96%; m.p. 126–128°C; IR (KBr) ν: 3250, 3060, 2965, 2905, 1685, 1585, 1440cm^{-1}; ^{1}H NMR δ: 2.20 (s, 6H, $2CH_3$), 7.02–8.02 (m, 8H, ArH), 8.22 (s, 1H, NH); Anal. calcd. for $C_{15}H_{15}N_3O$: C, 71.15; H, 5.93; N,16.60. Found: C, 71.29; H, 6.07; N, 16.82.

N-(4-Ethoxylphenyl)-2-phenyldiazenecarboxamide (**2h**): Orange-red tabular; Yield: 95%; m.p. 127–128°C; IR (KBr) ν: 3325, 3042, 2990, 2878, 1680, 1585, 1420cm^{-1}; ^{1}H NMR δ: 1.43 (t, 3H, CH_3), 4.05 (q, 2H, CH_2), 6.95–8.02 (m, 9H, ArH), 8.35 (s, 1H, NH); Anal. calcd. for $C_{15}H_{15}N_3O_2$: C, 66.91; H, 5.58; N,15.61. Found: C, 67.02; H, 5.45; N, 15.90.

N-(α-Naphthyl)-2-phenyldiazenecarboxamide (**2i**): Orange-red needle; Yield: 97%; m.p. 132–134°C; IR (KBr) ν: 3266, 3045, 1700, 1593, 1448cm^{-1}; ^{1}H NMR δ: 7.20–8.25 (m, 12H, ArH), 8.82 (s, 1H, NH); Anal. calcd. for $C_{17}H_{13}N_3O$: C, 74.18; H, 4.73; N,15.27. Found: C, 74.39; H, 4.56; N, 15.41.

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