

A Green and Facile Solid-state Synthesis Method for the Preparation of Diazenecarboxamide Azo Compounds with Potassium Ferricyanide and Sodium Hydroxide System

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Abstract: Eleven new-typed azo compounds were synthesized in good yields by dehydrogenating the corresponding aryl substituted semicarbazides using potassium ferricyanide and sodium hydroxide system under solid-state conditions.

Keywords: Diazenecarboxamides, azo compounds, potassium ferricyanide, solid-state synthesis.

It is well known that azo compounds are widely utilized as analytic reagents and dyes¹. They can also be used as the material of non-linear optics², and material of optics information storing in laser disks and oil-soluble dyes in photography in modern technology^{3,4}. Recently, many noteworthy studies have shown that some azo compounds possess excellent optical memory and photoelectric properties^{5,6}. For example, polymer scaffolds bearing azobenzene unit are useful for optical information storage⁷⁻⁹. Due to their great importance, the development of new and efficient methods for the synthesis of azo compounds have been attracted great interest in organic synthesis.

Oxidation of aryl substituted semicarbazides into the corresponding diazenecarboxamide azo compounds is an important transformation in synthetic organic chemistry and research of synthesizing this new-typed azo compound has received much attention over the years¹⁰⁻¹⁴. However, up to now the synthesis is usually carried out in solution and some of them have several disadvantages such as requiring large amounts of volatile or poisonous solvents, needing complicated heating and stirring apparatus, and forming undesirable side products. As an improvement to these solution phase reactions, herein we reported a facile and efficient solid-state method for the synthesis of diazenecarboxamides **2**, (**Scheme 1**) by using potassium ferricyanide and sodium hydroxide system at room temperature.

Base on our experimental results, the method of using potassium ferricyanide and sodium hydroxide as an oxidation system for the oxidation of aryl substituted semicarbazides **1** was proved to be very efficient and convenient. All the reactions were

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performed smoothly at room temperature. Furthermore, this method only requires simple instrument, cheap oxidant and easy work-up procedure. All of these benefits are in accordance with the requests of green production, saving-energy and high efficiency. With this method, eleven diazenecarboxamide azo compounds were synthesized in excellent yields (Shown in **Scheme 1**).

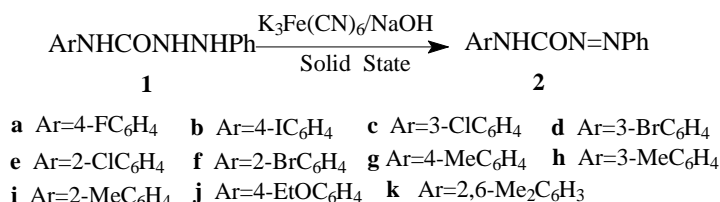
Table 1 Physical data and elemental analysis of **2a-k**

Compd.	m.p. ()	lit. ¹² m.p.	Yields	elemental analysis (found)			color
2a	107-108	105-107	91	64.19 (64.06)	4.14 (4.37)	17.28 (17.43)	yellow
2b	133-135	132-134	89	44.47 (44.36)	2.87 (2.86)	11.97 (11.79)	red
2c	86-87	86-87	95	60.13 (59.92)	3.88 (3.78)	16.18 (16.31)	deep-red
2d	94-95	93-95	89	51.49 (51.60)	3.33 (3.50)	13.86 (13.97)	yellow-red
2e	81-83	80-82	92	60.13 (60.29)	3.88 (3.73)	16.18 (15.96)	orange-red
2f	71-73	69-71	90	51.49 (51.66)	3.33 (3.47)	13.86 (13.99)	red
2g	105-107	105-107	92	70.29 (70.09)	5.44 (5.57)	17.57 (17.86)	orange-red
2h	68-69	68-70	89	70.29 (70.14)	5.44 (5.23)	17.57 (17.89)	orange-red
2i	101-103	103-105	91	70.29 (70.02)	5.44 (5.22)	17.57 (17.95)	orange-red
2j	126-128	128-129	90	66.91 (67.08)	5.58 (5.28)	15.61 (15.79)	orange-red
2k	117-118	118-119	98	71.15 (71.13)	5.93 (5.55)	16.60 (16.89)	orange-yellow

Table 2 IR and ¹H NMR spectral data of compounds **2a-k**

Compd.	IR (cm ⁻¹)	¹ H NMR (δppm)
2a	3340, 3045, 1705, 1590, 1545, 1425	7.07-8.05 (m, 9H, ArH), 8.42 (s, 1H, NH)
2b	3304, 3057, 1702, 1591, 1489, 1450	7.51-8.01 (m, 9H, ArH), 8.51 (s, 1H, NH)
2c	3260, 3030, 1685, 1590, 1490, 1435	7.10-8.10 (m, 9H, ArH), 8.55 (dd, 1H, J=2.0, 1.2Hz, NH)
2d	3320, 3030, 1700, 1590, 1500, 1430	7.12-8.04 (m, 9H, ArH), 8.55 (dd, 1H, J=2.0, 1.2Hz, NH)
2e	3330, 3047, 1705, 1596, 1480, 1435	7.18-8.03 (m, 9H, ArH), 8.50 (dd, 1H, J=2.0, 1.2Hz, NH)
2f	3290, 3040, 1695, 1580, 1506, 1440	7.17-8.05 (m, 9H, ArH), 8.49 (dd, 1H, J=2.0, 1.2Hz, NH)
2g	3180, 3051, 2990, 1685, 1600, 1580, 1420	2.24 (s, 3H, CH ₃), 7.06-8.02 (m, 9H, ArH), 8.16 (s, 1H, NH)
2h	3351, 3030, 2972, 1690, 1600, 1471, 1416	2.26 (s, 3H, CH ₃), 6.80-8.02 (m, 9H, ArH), 8.25 (s, 1H, NH)
2i	3175, 3050, 2995, 1680, 1590, 1480, 1415	2.27 (s, 3H, CH ₃), 7.06-7.98 (m, 9H, ArH), 8.90 (s, 1H, NH)
2j	3320, 3040, 2995, 2880, 1675, 1580, 1500, 1410	1.27 (t, 3H, J=8.0Hz, CH ₃), 3.90 (q, 2H, J=8.0Hz, CH ₂), 6.81-8.02 (m, 9H, ArH)
2k	3248, 3010, 2995, 2840, 1685, 1578, 1480, 1425	2.22 (s, 6H, 2CH ₃), 7.34-7.98 (m, 8H, ArH), 8.23 (s, 1H, NH)

Scheme 1



General Procedure

A mixture of **1** (1 mmol)¹⁵, potassium ferricyanide (2 mmol) and sodium hydroxide (0.03 mmol) was ground in an agate mortar (20 mL). Within 3-4 min, the color of the solid mixture changed from orange-yellow to orange-red or deep red. The reaction process was tested with TLC. After the reaction was completed, the reaction mixture was extracted with water and the crude products were recrystallized from ethanol-water, dried below 50 °C in vacuum. Range of yields 89% to 98%.

The oxidation process without sodium hydroxide was also studied. It has been found that under the neutral conditions the reaction was very sluggish and gave very poor yield even at much higher reaction temperature with a prolonged reaction time. It means that basic condition is indispensable for these oxidation reactions.

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