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An Efficient Solid-State Synthesis of N-Aryl-2-phenyldiazenecarboxamides

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Abstract: A new and efficient solid-state reaction using $K_3Fe(CN)_6$/KOH to oxidize diaryl semicarbazides for preparing azo compounds has been reported. Nine N-aryl-2-phenyl-diazenecarboxamides have been synthesized in excellent yields with simple instrument.

Keywords: Solid-state synthesis, diaryl semicarbazide, N-Aryl-2-phenyldiazenecarboxamide.

The subject of organic solid-state synthesis is a fascinating one. It has many advantages such as high efficiency and selectivity, easy separation and purification, mild reaction conditions, and environmental acceptability[1]. In recent years, this method has been widely used in a variety of organic reactions including substitution[2], condensation[3], oxidation-reduction[4], rearrangement[5] and elimination[6]. However, the solid state reaction using $K_3Fe(CN)_6$/KOH to oxidize substituted semicarbazides has not been reported. Recently, we found that this method can more easily synthesize N-aryl-2-phenyldiazenecarboxamides.

Azo compounds have been widely utilized as dyes and analytical reagents. They can also be used as materials for non-linear optics and for storage optical information in laser disks[7]. The research of synthesizing azo compounds has received much attention over the years. However, all the reactions were carried out in solution until now.

As an extension to our previous work, we now report a convenient solid-state reaction of using $K_3Fe(CN)_6$/KOH to oxidize substituted semicarbazides **1** for the synthesis of N-aryl-2-phenyldiazenecarboxamides **2**. This method can overcome some disadvantages discussed in the literature, such as having to use large amount of solvent and expensive reagents[8], having to use a heating and stirring apparatus, and tedious work of preparing the oxidant-system[9]. It requires only inexpensive reagents, simple instruments, and a short reaction time under room temperature. Nine N-aryl-2-phenyldiazenecarboxamides have been synthesized in excellent yields.

$$\underset{\mathbf{1}}{ArNHCONHNHC_6H_5} \xrightarrow[\text{Solid state}]{K_3Fe(CN)_6/KOH} \underset{\mathbf{2}}{ArNHCON{=}NC_6H_5}$$

A mixture of **1** (1 mmol), $K_3Fe(CN)_6$ (2 mmol) and KOH (0.03 mmol) was ground

in an agate mortar. Within 3~4 min, the color of the mixture changed from orange-yellow to orange-red or deep red. Traced the reaction with TLC. After the reaction was completed, extracted the mixture with water and recrystallized the crude products with ethanol-water; dried in vacuum to yield the pure products. The structures of these products were characterized by elemental analysis, IR and ^{1}HNMR spectroscopy[10].

Table Date of physical property and yield of compounds **2a~2I**

product	Ar	m.p.(°C)	Lit[11] m.p.(°C)	Yield(%)	color
2a	C_6H_5	112-114	111-113	95	deep-red
2b	2-MeC_6H_4	101-103	102-104	91	orange-red
2c	3-MeC_6H_4	67-69	68-70	88	orange-red
2d	4-MeC_6H_4	105-107	105-106	87	orange-red
2e	4-$EtOC_6H_4$	124-126	126-127	89	orange-red
2f	2,3-$Me_2C_6H_3$	123-125	123-125	93	deep-red
2g	2,5-$Me_2C_6H_3$	120-122	119-121	96	yellow
2h	2,6-$Me_2C_6H_3$	116-118	117-119	94	orange-yellow
2i	3,4-$Me_2C_6H_3$	125-127	127-129	95	orange-red

In conclusion, the solid-state oxidation of substituted semicarbazides with $K_3Fe(CN)_6$/KOH is an efficient, mild and high yielding and environmental benign method for the synthesis of N-aryl-2-phenyldiazenecarboxamides.

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