

## A Simple and Rapid Method for Synthesis of N,2-Diaryl Diazenecarboxamides

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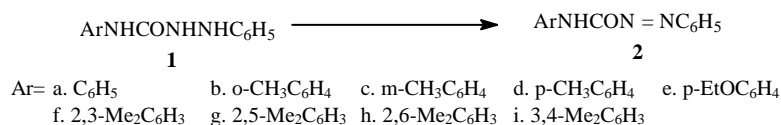
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**Abstract:** Using  $\text{Fe}_2(\text{SO}_4)_3/\text{H}_2\text{SO}_4$  as oxidant, nine N,2-diaryl diazenecarboxamides were synthesized from diaryl substituted semicarbazides in excellent yield under mild conditions for the first time. This method is simple, convenient and rapid.

**Keywords:** Oxidant; synthesis; semicarbazides; N,2-diaryl diazenecarboxamides.

It is well known that azo compounds have been widely utilized as analytic reagents and dyes. They can also be used in material of non-linear optics, material of optics information storing in laser disk, and dyes with oil solubility in photochromy in modern technology<sup>1</sup>. Recently, many noteworthy studies show that azo benzene derivatives possess very good optic remembering and photoelectric properties. Optical-switching and image storage can be made by azobenzene liquid crystal film<sup>2,3</sup>. The preparation of azo compounds have been described in many literatures<sup>4-6</sup>. In this paper, using  $\text{Fe}_2(\text{SO}_4)_3/\text{H}_2\text{SO}_4$  as oxidant, nine N,2-diaryl diazenecarboxamides were synthesized from diaryl substituted semicarbazides under mild conditions for the first time. This method is rapid, simple, convenient and suitable for base sensitive compounds.



To 1.0 mmol 1,4-diaryl substituted semicarbazides **1a-1i**<sup>7</sup> in 10~15 mL acetone, 2.0 mmol  $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$  in 5 mL 2mol/L  $\text{H}_2\text{SO}_4$  aqueous solution was added and the mixture was heated under gentle reflux. The color of solution changed to orange-red or deep-red rapidly. After 3~5 minutes, 30 mL cold water added. Orange-red or deep-red flocculent deposit was produced. The mixture was filtered and washed with water. The product was dried below 50°C in vacuum. The structure of products were identified by elemental analysis, IR and <sup>1</sup>HNMR spectra.

**Table 1.** m.p., color, yield and elemental analysis of compounds **2a-2i**

compd.	m.p. <sup>o</sup> C	color	yield(%)	Elemental analyses(found)		
				C	N	H
<b>2a</b>	111-113	deep-red	96.0	69.31(69.10)	18.66(19.01)	4.93(4.80)
<b>2b</b>	102-104	orange-red	89.2	70.29(70.02)	17.57(17.95)	5.44(5.21)
<b>2c</b>	68-70	orange-red	90.1	70.29(70.14)	17.57(17.89)	5.44(5.13)
<b>2d</b>	105-106	orange-red	88.7	70.29(70.09)	17.57(17.99)	5.44(5.62)
<b>2e</b>	126-127	orange-red	94.5	66.91(67.07)	15.61(16.06)	5.58(5.22)
<b>2f</b>	123-125	deep-red	93.0	71.15(70.98)	16.60(16.92)	5.93(5.56)
<b>2g</b>	119-121	yellow	96.5	71.15(70.89)	16.60(16.97)	5.93(5.62)
<b>2h</b>	117-119	orange-yellow	98.0	71.15(71.01)	16.60(16.89)	5.93(5.53)
<b>2i</b>	127-129	orange-red	95.4	71.15(71.06)	16.60(17.01)	5.93(5.48)

**Table 2.** IR and <sup>1</sup>HNMR spectra data of compounds **2a-2i**

compd.	IR(cm <sup>-1</sup> )			<sup>1</sup> HNMR ( ppm)		
	N-H	C=O	N=N	N-H	ArH	CH <sub>3</sub>
<b>2a</b>	3230	1690	1410	8.90 (s, 1H)	7.02-7.90 (m, 10H)	
<b>2b</b>	3200	1680	1405	8.25 (s, 1H)	7.02-8.03 (m, 9H)	2.25 (s, 3H)
<b>2c</b>	3350	1690	1415	8.20 (s, 1H)	6.84-8.02 (m, 9H)	2.26 (s, 3H)
<b>2d</b>	3180	1685	1410	8.16 (s, 1H)	7.04-8.04 (m, 9H)	2.24 (s, 3H)
<b>2e</b>	3310	1680	1410	8.24 (s, 1H)	6.85-8.00 (m, 9H)	1.26 (t, 3H) 3.85 (q, 2H)
<b>2f</b>	3190	1700	1430	8.22 (s, 1H)	7.03-8.02 (m, 8H)	2.23(s, 6H)
<b>2g</b>	3300	1680	1435	8.23 (s, 1H)	6.88-8.03 (m, 8H)	2.24 (s, 6H)
<b>2h</b>	3250	1685	1425	7.68 (s, 1H)	7.30-8.00 (m, 8H)	2.25 (s, 6H)
<b>2i</b>	3260	1695	1420	8.22 (s, 1H)	7.04-8.00 (m, 8H)	2.24 (s, 6H)

We have developed a convenient, rapid and simple method for preparing N, 2-diaryl diazenecarboxamides from diaryl substituted semicarbazides.

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#### References

1. X. J. Peng, J. Z. Yang, *Chin. Image Sci. and Practice*, **1988**, 4, 5.
2. D. Campbell, L. R. Dix, P. Rostron, *Dyes Pigm.*, **1995**, 29 (1), 77.
3. T. Ikeda, O. Tsutumi, *Science*, **1995**, 268, 1873.
4. Y. L. Wang, C. J. Ru, J. P. Li, H. Wang, D. L. Ma, *Synth. Commun.*, **1994**, 24, 1737.
5. W. Malinowski, J. Szadowski, *Pol. J. Appl. Chem.*, **1993**, 37, 127.
6. J. P. Li, J. Y. Wang, D. L. Ma, Y. L. Wang, *Chin. Chem. Lett.*, **1996**, 7(5), 393.
7. N. Rabjohn, Edited. *Org. Synth. Coll.*, Vol. IV., New York: John Wiley & Sons Inc., **1963**, p49.

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