

An Efficient Method for the Synthesis of Acyl-diazenes Using $\text{NaNO}_2/\text{NaHSO}_4 \cdot \text{H}_2\text{O}$

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Abstract: An efficient and convenient method for the synthesis of acyl-diazenes is reported. Ten acyl-diazenes have been synthesized from acylhydrazines in excellent yields under mild conditions. There are eight new substances among these compounds.

Keywords: Acyl-diazenes, acylhydrazines, $\text{NaNO}_2/\text{NaHSO}_4 \cdot \text{H}_2\text{O}$.

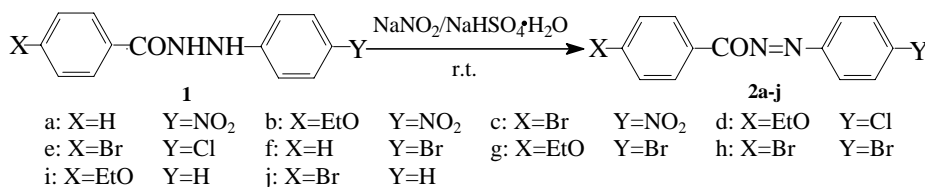
Azo compounds are widely utilized as analytic reagents and dyes¹, they can also be used in material of non-linear optics, material of optics information storing in laser disks, and dyes with oil solubility in photochromy in modern technology². Recently, many noteworthy studies have shown that some azo compounds possess excellent optical memory and photoelectric properties^{3,4}. For example, polymer scaffolds bearing azobenzene-potential are useful for optical information storage, azo-dye doped polyimide films are a kind of good photosensitive material^{5,6}.

Previously, the methods for the synthesis of azo compounds are versatile⁷⁻¹¹, but these methods have not been used to synthesize acyl-diazenes and most of them are deficient in some aspects. For example, tedious operation^{12,13}, expensive catalysts^{12,13}, strong acid or basic media^{8,11}. In order to overcome these limitations, we decided to develop a new reagent system.

$\text{NaNO}_2/\text{NaHSO}_4 \cdot \text{H}_2\text{O}/\text{SiO}_2$ is a known oxidation system for the rapid and selective oxidation of diaryl carbazides to corresponding carbazones¹⁴. In this oxidation system the presence of SiO_2 is crucial. Now we have synthesized ten acyl-diazenes by the similar method. During the course of experiments we found that the presence of SiO_2 is needless. If the reaction occurs with SiO_2 , the reaction period is not much shorter and higher yield is not obtained. The structures of the products were confirmed by IR, ¹HNMR and elemental analysis.

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Scheme



Experimental

Melting points were determined with a Kofler micro melting point apparatus and the thermometer was uncorrected. IR spectra were recorded on a SP3-300 spectro-photometer in KBr tablet. ¹HNMR spectra were measured on a FT-80A spectrometer using TMS as internal standard and CDCl₃ as solvent. Elemental analyses were performed on PE-2400 CHN elemental analyzer.

A mixture of acylhydrazine(1mmol), NaNO₂(4mmol) and NaHSO₄•H₂O(2mmol) in acetone(15mL) was stirred at room temperature for 55min (the end of the reaction was tested by TLC), orange red or deep red turbid solution came into being. The reaction mixture was filtrated, then cool water was poured to the filtrate slowly. 1 h later, the resulting precipitate was filtrated, washed with water and dried. The crude product was recrystallised and dried under vacuum.

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

compd. ^a	m.p. (°C)	lit. m.p. (°C)	yields (%)	elemental analysis (found)		
				C	H	N
2a ¹⁵	98-99.5	99-100	91.8	61.18(61.02)	3.55(3.23)	16.46(16.16)
2b	139-140.5		96.2	60.20(60.25)	4.38(4.22)	14.04(13.99)
2c	135-137		92.3	46.73(46.60)	2.41(2.28)	12.58(12.35)
2d	91-93		93.1	62.40(62.14)	4.54(4.31)	9.70(9.49)
2e	134-136		94.5	48.26(48.43)	2.49(2.27)	8.66(8.42)
2f ¹⁶	71-72.5	68	92.4	54.00(53.87)	3.14(2.91)	9.69(9.54)
2g	120-122		96.3	54.07(53.81)	3.93(3.62)	8.41(8.20)
2h	141.5-143		89.6	42.43(42.21)	2.19(2.23)	7.61(7.28)
2i	54-56		87.2	70.85(70.61)	5.55(5.24)	11.02(10.79)
2j	37-39		84.1	54.00(53.78)	3.14(2.90)	9.69(9.41)

a) Red or yellow tabular or needle crystal.

Table 2 IR and ^1H NMR spectra data of compounds 2a-j

Compd.	IR (cm^{-1})	^1H NMR(ppm)
2a	3110, 1703, 1612, 1597, 1525, 1510, 1450	7.55-8.46(m, 9H, ArH)
2b	3104, 2985, 2860, 1701, 1606, 1572, 1523, 1505, 1447	1.47(t, 3H, J=7.0Hz, CH_3), 4.15(q, 2H, J=7.0Hz, CH_2), 6.98-8.46(m, 8H, ArH)
2c	3010, 1704, 1610, 1587, 1530, 1503, 1437	7.70-8.46(m, 8H, ArH)
2d	3067, 2983, 2861, 1697, 1606, 1581, 1510, 1450	1.46(t, 3H, J=7.0Hz, CH_3), 4.12(q, 2H, J=7.0Hz, CH_2), 6.97-8.04(m, 8H, ArH)
2e	3094, 1706, 1611, 1587, 1503, 1422	7.54-7.96(m, 8H, ArH)
2f	3067, 1688, 1604, 1583, 1501, 1466	7.51-8.02(m, 9H, ArH)
2g	3079, 2986, 2870, 1702, 1607, 1574, 1502, 1454	1.46(t, 3H, J=7.0Hz, CH_3), 4.13(q, 2H, J=7.0Hz, CH_2), 6.93-8.06(m, 8H, ArH)
2h	3078, 1704, 1606, 1587, 1502, 1423	7.68-7.94(m, 8H, ArH)
2i	3062, 2984, 2857, 1698, 1605, 1579, 1504, 1455	1.45(t, 3H, J=7.0Hz, CH_3), 4.12(q, 2H, J=7.0Hz, CH_2), 6.92-8.06(m, 8H, ArH)
2j	3067, 1706, 1611, 1587, 1499, 1451	7.59-8.02(m, 9H, ArH)

In summary, the method for the oxidation of acylhydrazines with $\text{NaNO}_2/\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ is efficient and important. It has significant advantages such as operational simplicity, mild conditions and excellent yields.

Acknowledgments

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