A New Method for the Synthesis of Acyl-diazenes Using $NaNO_2$-Ac_2O

Jian-Ping Li* (李建平), Ping Liu (劉　萍)
Wan-Xin Xue (薛萬新) and Yu-Lu Wang (王玉爐)
College of Chemistry & Environmental Science, Henan Normal University, Xinxiang, 453002, P. R. China
The Key Laboratory of Environmental Science and Technology of High Education of Henan Province,
Xinxiang, 453002, P. R. China

An efficient and convenient method for the synthesis of acyl-diazenes from acylhydrazines using $NaNO_2$-acetic anhydride as a novel oxidant agent is reported. The reaction gives excellent yields and the reaction time is not long.

Keywords: Acyl-diazenes; Acylhydrazines; $NaNO_2$-acetic anhydride.

INTRODUCTION

As we know, azo compounds have played an important role in many respects and have attracted great interest in organic synthesis. In previous data, the methods for the synthesis of azo compounds are versatile, such as two phases catalyzed dehydrogenation,[1] $KClO_3/H_2SO_4/FeSO_4$ oxidant reagents,[2] DMF-NO_X oxidant,[3] NBS(N-bromosuccinimide)/pyridine[4] and the solid state method,[5,6] but these methods haven't been used to synthesize acyl-diazenes, and most of them are deficient in some aspects, for example, tedious operation,[7,8] expensive catalysts,[7,8] strong acid or basic media.[2]

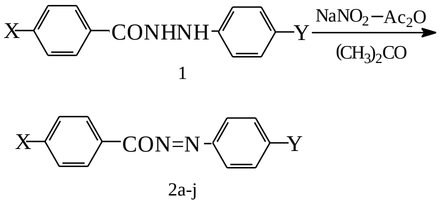
$NaNO_2$-Ac_2O is a known oxidation system for the rapid and selective oxidation of a variety of alcohols into their corresponding carbonyl compounds. Later, it has proved to be an efficient reagent which is used to synthesize α,β-unsaturated acyl azo compounds from α,β-unsaturated acylhydrazine.[9] The method has many advantages such as high efficiency and simple operation. Now we have synthesized acyl-diazenes by this method and believe that it is an important methodology in comparison to existing ones.

RESULTS AND DISCUSSION

It is well known that azo compounds are widely utilized as analytic reagents and dyes;[10] they can also be used in the material of non-linear optics, the material of optics information stored in laser disks, and in dyes with oil solubility in photochromy in modern technology.[11] Recently, many noteworthy studies have shown that some azo compounds possess excellent optical memory and photoelectric properties.[12,13] 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.[14,15] Therefore, the synthesis of azo compounds is important. Previously, there have been versatile methods of synthesizing azo compounds; they have their merits, but at the same time, they have drawbacks such as using expensive catalysts and tedious operation.

On the basis of these research results, we have been paying continuous attention to the synthesis of acyl-diazenes. We used a new reagent or reagent system to overcome the above limitations. During the course of experiments the method of using $NaNO_2$-Ac_2O as the oxidation system proved to be efficient and convenient.

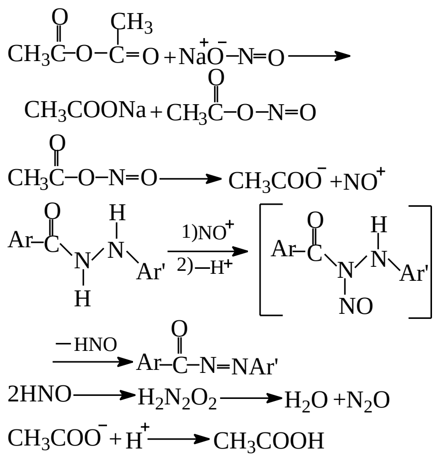
Scheme



a: X=H	Y=NO_2	b: X=EtO	Y=NO_2
c: X=Br	Y=NO_2	d: X=EtO	Y=Cl
e: X=Br	Y=Cl	f: X=H	Y=Br
g: X=EtO	Y=Br	h: X=Br	Y=Br
I: X=EtO	Y=H	j: X=Br	Y=H

In this paper, using $NaNO_2$-Ac_2O as an oxidation system, ten acyl-diazenes have been synthesized from acylhydrazines in excellent yields (75.6-93.9%) under mild conditions. This method does not need a long time and is easy to operate. It is efficient and convenient. In the reaction we have found there is no inevitable relationship between the yields

Possible reaction mechanism



and the effect of electron-withdrawing and -donating groups in the substrates. However, the substrates containing electron-withdrawing groups can make the reaction time shorter. The structures of the products were confirmed by IR, ^{1}H NMR and elemental analysis.

EXPERIMENTAL SECTION

Melting points were determined with a Kofler micro melting point apparatus and are uncorrected. IR spectra were recorded on a SP3-300 spectrophotometer in KBr. ^{1}H NMR spectra were measured on a FT-80A spectrometer using TMS as internal standard and $CDCl_3$ as solvent. Elemental analyses were performed on PE-2400 CHN elemental analyzer.

General Procedure for the Preparation acyl-diazenes (2a-2j)

A mixture of acylhydrazine (1 mmol), acetic anhydride (3 mmol) and $NaNO_2$ (3 mmol) in acetone (15 mL) was stirred at room temperature for 0.5-1 h; an orange red or deep red turbid solution came into being. The reaction mixture was filtrated, then cool water was poured to the filtered material slowly. 1 h later, the resulting precipitate was filtrated, washed with water and dried. The crude product was recrystallised and dried to yield the pure product.

1-Benzoyl-2-(*p*-nitrophenyl)diazene (2a)

Red tabular; Yield: 89.0%; mp 96-98 °C; IR (KBr) ν 3109, 1703, 1611, 1598, 1525, 1510, 1450 cm^{-1}; ^{1}H NMR δ 7.56-8.45 (m, 9H, ArH); Anal. Calcd. for $C_{13}H_9N_3O_3$: C, 61.18; H, 3.55; N, 16.46. Found: C, 61.02; H, 3.23; N, 16.16.

1-(*p*-Ethoxybenzoyl)-2-(*p*-nitrophenyl)diazene (2b)

Brown needles; Yield: 87.2%; mp 139-140.5 °C; IR (KBr) ν 3105, 2985, 2860, 1702, 1606, 1572, 1523, 1505, 1448 cm^{-1}; ^{1}H NMR δ 1.47 (t, 3H, CH_3), 4.15 (q, 2H, CH_2), 6.98-8.46 (m, 8H, ArH); Anal. Calcd. for $C_{15}H_{13}N_3O_4$: C, 60.20; H, 4.38; N, 14.04. Found: C, 60.25; H, 4.22; N, 13.99.

1-(*p*-Bromobenzoyl)-2-(*p*-nitrophenyl)diazene (2c)

Brown tabular; Yield: 93.9%; mp 134-136 °C; IR (KBr) ν 3010, 1705, 1610, 1587, 1530, 1503, 1438 cm^{-1}; ^{1}H NMR δ 7.71-8.47 (m, 8H, ArH); Anal. Calcd. for $C_{13}H_8BrN_3O_3$: C, 46.73; H, 2.41; N, 12.58. Found: C, 46.59; H, 2.30; N, 12.39.

1-(*p*-Ethoxybenzoyl)-2-(*p*-chlorophenyl)diazene (2d)

Brown tabular; Yield: 80.1%; mp 91-93 °C; IR (KBr) ν 3068, 2984, 2863, 1696, 1606, 1581, 1510, 1494, 1450 cm^{-1}; ^{1}H NMR δ 1.46 (t, 3H, CH_3), 4.12 (q, 2H, CH_2), 6.97-8.04 (m, 8H, ArH); Anal. Calcd. for $C_{15}H_{13}ClN_2O_2$: C, 62.40; H, 4.54; N, 9.70. Found: C, 62.12; H, 4.31; N, 9.49.

1-(*p*-Bromobenzoyl)-2-(*p*-chlorophenyl)diazene (2e)

Orange tabular; Yield: 84.9%; mp 135-137 °C; IR (KBr) ν 3094, 1706, 1610, 1587, 1503, 1422 cm^{-1}; ^{1}H NMR δ 7.54-7.96 (m, 8H, ArH); Anal. Calcd. for $C_{13}H_8BrClN_2O$: C, 48.26; H, 2.49; N, 8.66. Found: C, 48.47; H, 2.28; N, 8.41.

1-Benzoyl-2-(*p*-bromophenyl)diazene (2f)

Yellow powder; Yield: 90.3%; mp 71.5-73 °C; IR IR (KBr) ν 3067, 1687, 1604, 1583, 1487, 1466 cm^{-1}; ^{1}H NMR δ 7.51-8.02 (m, 9H, ArH); Anal. Calcd. for $C_{13}H_9BrN_2O$: C, 54.00; H, 3.14; N, 9.69. Found: C, 53.87; H, 2.91; N, 9.54.

1-(*p*-Ethoxybenzoyl)-2-(*p*-bromophenyl)diazene (2g)

Yellow tabular; Yield: 81.4%; mp 120.5-123 °C; IR (KBr) ν 3079, 2985, 2869, 1703, 1607, 1574, 1502, 1454 cm^{-1}; ^{1}H NMR δ 1.46 (t, 3H, CH_3), 4.13 (q, 2H, CH_2), 6.94-8.07 (m, 8H, ArH); Anal. Calcd. for $C_{15}H_{13}BrN_2O_2$: C, 54.07; H, 3.93; N, 8.41. Found: C, 53.78; H, 3.62; N, 8.19.

1-(*p*-Bromobenzoyl)-2-(*p*-bromophenyl)diazene (2h)

Orange tabular; Yield: 88.6%; mp 141.5-143 °C; IR (KBr) ν 3078, 1704, 1606, 1587, 1502, 1423 cm^{-1}; ^{1}H NMR δ 7.68-7.94 (m, 8H, ArH); Anal. Calcd. for $C_{13}H_8Br_2N_2O$: C, 42.43; H, 2.19; N, 7.61. Found: C, 42.20; H, 2.23; N, 7.28.

1-(*p*-Ethoxybenzoyl)-2-phenyldiazene (2i)

Yellow tabular; Yield: 83.7%; mp 54.5-57 °C; IR (KBr) ν 3063, 2984, 2857, 1697, 1605, 1574, 1504, 1455, cm^{-1}; ^{1}H

NMR δ 1.45 (t, 3H, CH_3), 4.12 (q, 2H, CH_2), 6.91-8.05 (m, 8H, ArH); Anal. Calcd. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.60; H, 5.26; N, 10.76.

1-(*p*-Bromobenzoyl)-2-phenyldiazene (2j)

Yellow tabular; Yield: 75.6%; mp 36-38 °C; IR (KBr) ν 3066, 1706, 1610, 1587, 1496, 1451 cm^{-1}; ^1H NMR δ 7.58-8.01 (m, 9H, ArH); Anal. Calcd. for $C_{13}H_9BrN_2O$: C, 54.00; H, 3.14; N, 9.69. Found: C, 53.77; H, 2.90; N, 9.38.

Received June 19, 2002.

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