SHORT PAPER

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An efficient and convenient method for the synthesis of acyldiazenes from acylhydrazines†

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The synthesis of acyl-diazenes by using *N*-bromosuccinimide (NBS) and pyridine as the oxidation system to dehydrogenate acylhydrazines is reported.

Keywords: acyldiazenes, acylhydrazines, diazenes, *N*-bromosuccinimide

It is well known that azo compounds have played many important roles in chemistry and have attracted great interest in organic synthesis. They are widely utilised as analytical reagents and dyes.[1] They can also be used in materials for non-linear optics, information storage on laser disks, and dyes with oil solubility in modern technology in photochromism.[2] Recent studies have shown that some azo compounds possess excellent optical memory and photoelectric properties.[3,4] For example, optical recording media using azo metal chelates show high light resistance and good storage stability and are suited for DVD-R and CD-R. Polymer scaffolds bearing azobenzene units are useful for optical information storage, and azo-dye doped polyimide films are a kind of photosensitive material.[5-7]

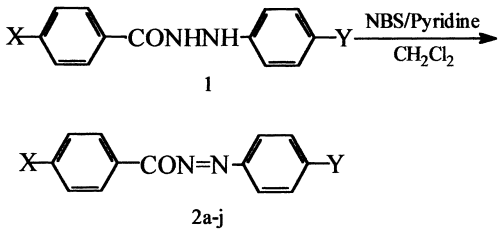
The methods for synthesis of azo compounds are versatile when the –N=N- bonds are connected with aryl groups. However, azocarbonyl compounds cannot be prepared by the standard (diazo-coupling) method. In recent years, the synthesis of diazocarboxamides from substituted semicarbazides has been described, by use of such methods as two-phase catalysed dehydrogenation,[8] $KClO_3/H_2SO_4/FeSO_4$[9], DMF-NO_X[10], NBS (*N*-bromosuccinimide)/pyridine,[11] and solid state methods,[12,13] but these techniques have not been used to synthesise acyldiazenes. On the basis of the above, we have been investigating the synthesis of acyldiazenes.

In this paper, using *N*-bromosuccinimide (NBS) and pyridine as the oxidation system, ten acyldiazenes have been synthesised from acylhydrazines in excellent yields under mild conditions. (Scheme 1) Except for 1-benzoyl-2-(*p*-nitrophenyl) diazene[14] and 1-benzoyl-2-(*p*-bromophenyl)-diazene,[15] the remaining eight compounds are new substances. The structures of the products were confirmed by IR, ^{1}H NMR and elemental analysis. During the course of our experiments we have found that acyldiazenes are unstable under basic conditions.

This method has the merit of needing only simple apparatus, and the experiment is easy to perform. Most of the reaction periods are less than 1 h, the yields of the reaction are more than 75%. In all, the method of using *N*-bromosuccinimide and pyridine as the oxidation system to dehydrogenate acylhydrazines is efficient and convenient.

Experimental

Melting points were determined with a Kofler micro melting point apparatus. 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.



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

Scheme 1 Synthesis of aroylazoarenes (acyldiazenes).

General procedure for the preparation of acyldiazenes (**2a–j**): Acylhydrazine (1 mmol), dichloromethane (20 ml) and dry pyridine (1 mmol) were placed in a round bottom flask. *N*-Bromosuccinimide (1.02 mmol) was added over 5–6 min while stirring at room temperature. The mixture was stirred for 0.5–1 h., in the course of which an orange-red or deep-red solution developed. The solution was washed with water (5 × 20ml) and dried with anhydrous magnesium sulfate. A solid was produced on evaporating the solvent, and the crude product was recrystallised and dried to yield the pure product. The lack of N–H absorption in the infrared spectrum showed the reaction to have taken place and carried to completion.

The physical and spectra data of compounds **2a–j:** *1-Benzoyl-2-(p-nitrophenyl)diazene* (**2a**): red plates; yield 90%; m.p. 98–100 °C; IR (KBr): ν_{max} 3110, 1702, 1612, 1598, 1525, 1510, 1450 cm^{-1}; ^{1}H NMR δ: 7.55–8.46 (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: 79%; m.p. 139.5–141 °C; IR (KBr): ν_{max} 3103, 2984, 2859, 1701, 1606, 1572, 1523, 1505, 1448 cm^{-1}; ^{1}H NMR δ: 1.47 (t, 3H, CH_3), 4.15 (q, 2H, CH_2), 6.99-8.45 (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**): red plates; yield 80%; m.p. 135–137 °C; IR (KBr): ν_{max} 3099, 1703, 1610, 1587, 1530, 1503, 1438 cm^{-1}; ^{1}H NMR δ: 7.70–8.46 (m, 8H, ArH); Anal. calcd. for $C_{13}H_8BrN_3O_3$: C, 46.73; H, 2.41; N, 12.58. Found: C, 46.61; H, 2.30; N, 12.39.

2-(p-Chlorophenyl)1-(p-ethoxybenzoyl)diazene (**2d**): brown plates; yield 76%; m.p. 91.5–93.5 °C; IR (KBr): ν_{max} 3067, 2982, 2862, 1696, 1606, 1581, 1510, 1494, 1450 cm^{-1}; ^{1}H NMR δ: 1.46 (t, 3H, CH_3), 4.13 (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, 62.15; H, 4.31; N, 9.49.

1-(p-Bromobenzoyl)-2-(p-chlorophenyl)diazene (**2e**): red plates; yield 92%; m.p. 134–136 °C; IR (KBr): ν_{max} 3094, 1705, 1611, 1587,

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1503, 1422 cm^{-1}; ^1H 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, 48.36, H, 2.28, N, 8.41.

1-Benzoyl-2-(p-bromophenyl)diazene (**2f**): yellow powder; yield 79%; m.p. 72–73.5 °C (lit.[15] 68 °C); IR (KBr): ν_{max} 3067, 1688, 1605, 1583, 1487, 1466 cm^{-1}; ^1H NMR δ: 7.52–8.02 (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.

2-(p-Bromophenyl)-1-(p-ethoxybenzoyl)diazene (**2g**): yellow plates; yield: 76%; m.p. 120–122.5 °C; IR (KBr): ν_{max} 3078, 2985, 2869, 1702, 1607, 1574, 1502, 1454 cm^{-1}; ^1H NMR δ: 1.46 (t, 3H, CH_3), 4.13 (q, 2H, CH_2), 6.93–8.06 (m, 8H, ArH); Anal. calcd. for $C_{15}H_{13}BrN_2O_2$: C, 54.07; H, 3.93; N, 8.41. Found: C, 53.80; H, 3.62; N, 8.19.

1-(p-Bromobenzoyl)-2-(p-bromophenyl)diazene (**2h**): orange plates; yield 89%; m.p. 141–142.5 °C; IR (KBr): ν_{max} 3078, 1703, 1606, 1587, 1502, 1423 cm^{-1}; ^1H 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, 42.23; H, 2.23; N, 7.28.

1-(p-Ethoxybenzoyl)-2-phenyldiazene (**2i**): yellow plates; yield: 86%; m.p. 55–57.5 °C; IR (KBr): ν_{max} 3062, 2984, 2857, 1697, 1605, 1574, 1504, 1455, cm^{-1}; ^1H NMR δ: 1.45 (t, 3H, CH_3), 4.12 (q, 2H, CH_2), 6.92-8.06 (m, 8H, ArH); Anal. calcd. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.62; H, 5.24; N, 10.76.

1-(p-Bromobenzoyl)-2-phenyldiazene (**2j**): red plates; Yield: 76%; m.p. 37–39 °C; IR (KBr): ν_{max} 3067, 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, 53.79; H, 2.90; N, 9.38.

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