Phase transfer catalysed synthesis of acyldiazenes from acylhydrazines

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A two-phase catalysed dehydrogenation synthesis of acyldiazenes from acylhydrazines using 2,4,6-tri-*t*-butylphenol/$Fe(CN)_6^{3-}$/NaOH is reported.

Keywords: two-phase transfer catalysed, acyldiazenes

The synthesis of azo compounds is of great interest. They are widely utilised as dyes,[1] analytical reagents,[2] materials in non-linear optics,[3] materials in optical information storage in laser disks, and as oil-soluble dyes in modern photography.[4] In addition, they have also been used as intermediates for the preparation of bioactive heterocycles containing nitrogen atoms and other compounds with special structures that are not easily obtained by conventional methods.[5] More novel azo compounds with good thermal stability and photosensitivity are greatly needed.

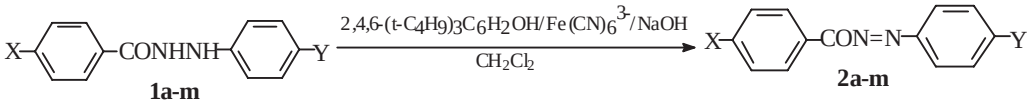
The oxidation of aryl substituted hydrazines into the corresponding azo compounds is an important transformation in organic synthesis. Many reagents and reagent systems, such as, CAN[6], $FeCl_3.6H_2O$[7], $KClO_3/H_2SO_4/FeSO_4$[8] and DMF–NO_X[9] have been used as oxidants. Azo compounds can also be prepared by the standard diazo-coupling method and by reduction of aromatic nitro-compounds.[10-11] These methods, however, have not been used to synthesise acyldiazenes. In our laboratory, NBS/pyridine was used to synthesise acyldiazenes for the first time.[12] Although this method is efficient, its expensive reagents limit its application in organic synthesis. Therefore, it is necessary to find a better reagent or reagent system to replace the existing method and improve the overall synthetic efficiency.

In conjunction with our recent interest in the synthesis of acyldiazenes, we decided to develop a new reagent to overcome the above limitation. In this paper, a two-phase transfer catalysed dehydrogenation of acylhydrazines has been studied (Scheme 1) and 13 acyldiazenes have been synthesised in excellent yield under mild conditions. The structures of acyldiazenes were confirmed by IR, ^{1}H NMR and elemental analysis.

When 2,4,6-tri-*t*-butylphenol was not added to the reaction system, there was no obvious colour change. From consideration of the reaction conditions, a possible free radical oxidation is suggested as in Scheme 2.

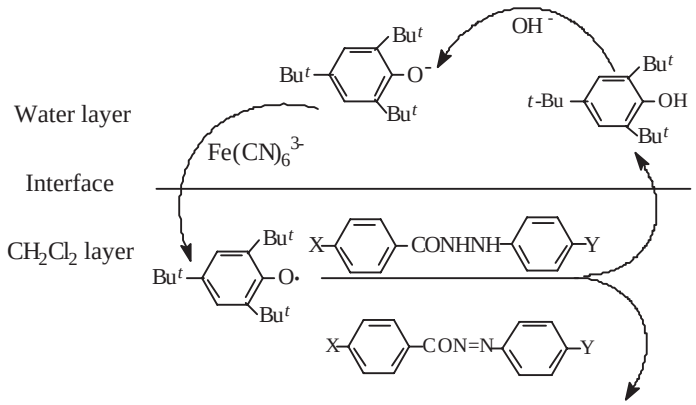
Firstly, 2,4,6-tri-*t*-butylphenol is converted into the 2,4,6-tri-*t*-butylphenoxide anion by sodium hydroxide. Secondly, the 2,4,6-tri-*t*-butylphenoxide anion transfers one electron to potassium ferricyanide and forms the 2,4,6-tri-*t*-butylphenoxide radical. Thirdly, the 2,4,6-tri-*t*-butylphenoxide radical abstracts a hydrogen atom from the acylhydrazine. Acyldiazenes and 2,4,6-tri-*t*-butylphenol were formed.

This method requires only inexpensive reagents, and simple apparatus. All reactions can be carried out smoothly at room temperature and completed within 10 min with excellent yields. In conclusion, this is a rapid and convenient method



a: X=MeO Y=NO_2 **b**: X=MeO Y=Cl **c**: X=MeO Y=Br **d**: X=H Y=NO_2 **e**: X=EtO Y= NO_2
f: X=Br Y=NO_2 **g**: X=EtO Y=Cl **h**: X=Br Y=Cl **i**: X=H Y=Br **j**: X=EtO Y=Br
k: X=Br Y=Br **l**: X=EtO Y=H **m**: X=Br Y=H

Scheme 1 Synthesis of acyldiazenes.



Scheme 2

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for the preparation of acyldiazenes from acylhydrazines with 2,4,6-tri-*t*-butylphenol/$Fe(CN)_6^{3-}$/NaOH as the oxidant.

Experimental

Melting points were determined with a Kofler micro melting point apparatus and were uncorrected. IR spectra were recorded on a SP3-300 spectrophotometer using KBr discs. ^{1}H NMR spectra were measured on a Bruker DPX-400M spectrometer using TMS as internal standard and $CDCl_3$ as solvent. Elemental analyses were performed on PE-2400 CHN elemental analyser.

General procedure for the preparation of acyldiazenes (**2a**–**m):** A mixture of acylhydrazine[13] (1 mmol) and a trace amount of 2,4,6-tri-*t*-butylphenol were dissolved in dichloromethane (50 ml) and shaken with a saturated solution of potassium ferricyanide (12 ml) in 2 mol/l aqueous sodium hydroxide. After 5–10 min, the colour in the organic phase changed to orange-red or deep-red. The dichloromethane layer was separated, and the water layer was extracted with dichloromethane four times. The dichloromethane layers were combined and washed with water until the washing was neutral. The organic solution was dried with anhydrous sodium sulfate overnight. The dichloromethane was distilled off on a water-bath after the sodium sulfate was removed. The crude products were filtered, recrystallised and dried below 30°C *in vacuo* to yield the pure products. All the compounds gave satisfactory analytical and spectra data.

The physical and spectra data of compounds **2a–m:**
The AA'xx' systems in the ^{1}H NMR spectra of the *para* substituted benzene ranges appear as apparent pairs of doublets. *1-(p-Methoxybenzoyl)-2-(p-nitrophenyl)diazene* **(2a):** Red plates; yield: 94 %; m.p. 126–128 °C; IR (KBr) ν 3110,2975,2840, 1699, 1600, 1510, 1453 cm^{-1}; ^{1}H NMR δ: 3.91(s,3H, CH_3),7.00 (d, 2H, *J*=8.8Hz, ArH),8.00(d, 2H, *J*=8.8Hz, ArH), 8.10(d, 2H, *J*=8.8Hz, ArH), 8.44(d, 2H, *J*=8.8Hz, ArH); Anal. calcd. for $C_{14}H_{11}N_3O_4$: C, 58.95; H, 3.9; N, 14.7. Found: C, 58.8; H, 4.0; N, 14.95.

1-(p-Methoxybenzoyl)-2-(p-chlorophenyl)diazene **(2b):** Red plates; yield: 90 %; m.p. 69–71°C; IR (KBr) ν 3075, 2970,2845, 1708, 1602, 1508, 1450 cm^{-1}; ^{1}H NMR δ: 3.89 (s,3H, CH_3), 6.98 (d, 2H, *J*=8.8Hz, ArH),7.53 (d, 2H, *J*=8.4Hz, ArH), 7.93 (d, 2H, *J*=8.4Hz, ArH), 8.03 (d, 2H, *J*=8.8Hz, ArH); Anal. calcd. for $C_{14}H_{11}$ Cl N_2O_2: C, 61.2; H, 4.0; N, 10.0. Found: C, 61.4; H, 4.2; N, 10.2.

1-(p-Methoxybenzoyl)-2-(p-bromophenyl)diazene **(2c):** Red plates; yield: 92 %; m.p. 66–68°C; IR (KBr) ν 3080, 2970, 2842, 1703, 1600, 1505,1445 cm^{-1}; ^{1}H NMR δ: 3.89 (s,3H, CH_3), 6.96 (d, 2H, *J*=8.8Hz, ArH),7.70 (d, 2H, *J*=8.4Hz, ArH), 7.85 (d, 2H, *J*=8.4Hz, ArH), 8.02 (d, 2H, *J*=8.8Hz, ArH); Anal. calcd. for $C_{14}H_{11}$ Br N_2O_2: C, 52.7; H, 3.5; N, 8.8. Found: C, 52.4; H, 3.3; N, 8.6.

1-Benzoyl-2-(p-nitrophenyl)diazene **(2d):** Red plates; yield: 92 %; m.p. 99–100°C; IR (KBr) ν 3108, 1705, 1608, 1596, 1525, 1510, 1450 cm^{-1}; ^{1}H NMR δ: 7.55 (t, 2H, *J*=7.6Hz, ArH), 7.71 (t, 1H, *J*=7.6Hz, ArH), 8.03 (d, 2H, *J*=7.6Hz, ArH), 8.13 (d, 2H, *J*=8.8Hz, ArH), 8.46 (d, 2H, *J*=8.8Hz, ArH); Anal. Calcd. for $C_{13}H_9N_3O_3$: C, 61.2; H, 3.55; N, 16.5. Found: C, 61.05; H, 3.2; N, 16.3

*1-(p-Ethoxybenzoyl)-2(p-nitrophenyl)diazene***(2e):**Brown needles; yield: 91 %; m.p. 140–141°C; IR (KBr) ν 3105, 2985, 2859, 1702, 1606, 1572, 1525, 1505, 1446 cm^{-1}; ^{1}H NMR δ: 1.46 (t, 3H, *J*=7.0Hz, CH_3), 4.14 (q, 2H, *J*=7.0Hz, CH_2), 6.99 (d, 2H, *J*=8.8Hz, ArH), 8.00 (d, 2H, *J*=8.8Hz, ArH), 8.12 (d, 2H, *J*=8.8Hz, ArH), 8.46 (d, 2H, *J*=8.8Hz, ArH); Anal. Calcd. for $C_{15}H_{13}N_3O_4$: C, 60.2; H, 4.4 N, 14.0. Found: C, 60.1; H, 4.2; N, 13.9.

1-(p-Bromobenzoyl)-2(p-nitrophenyl)diazene **(2f):** Brown plates; yield: 92 %; m.p. 134–136°C; IR (KBr) ν 3098, 1697, 1612, 1586, 1505, 1445 cm^{-1}; ^{1}H NMR δ: 7.69 (d, 2H, *J*=8.4Hz, ArH), 7.91 (d, 2H, *J*=8.4Hz, ArH), 8.13 (d, 2H, *J*=8.8Hz, ArH), 8.46 (d, 2H, *J*=8.8Hz, ArH); Anal. Calcd. for $C_{13}H_8BrN_3O_3$: C,46.7; H, 2.4; N, 12.6.Found: C, 46.6; H, 2.3; N, 12.4.

1-(p-Ethoxybenzoyl)-2(p-chlorophenyl)diazene **(2g):** Brown plates; yield: 91 %; m.p. 91.5–92°C; IR (KBr) ν 3070, 2983, 2862, 1700, 1606, 1585, 1510, 1448 cm^{-1}; ^{1}H NMR δ: 1.47 (t, 3H, *J*=7.0Hz, CH_3), 4.13 (q, 2H, *J*=7.0Hz, CH_2), 6.97(d, 2H, *J*=8.8Hz, ArH), 7.52 (d, 2H, *J*=8.4Hz, ArH), 7.92 (d, 2H, *J*=8.4Hz, ArH), 8.04(d, 2H, *J*=8.8Hz, ArH); Anal. Calcd. for $C_{15}H_{13}ClN_2O_2$: C, 62.4; H, 4.5; N, 9.8. Found: C, 62.1; H, 4.7; N, 9.6

1-(p-Bromobenzoyl)-2(p-chlorophenyl)diazene **(2h):** Orange plates; yield: 91 %; m.p. 133–135°C; IR (KBr) ν 3094, 1706, 1609, 1583, 1503, 1426 cm^{-1}; ^{1}H NMR δ: 7.55(d, 2H, *J*=8.4Hz, ArH), 7.70 (d, 2H, *J*=8.8Hz, ArH), 7.87 (d, 2H, *J*=8.8Hz, ArH), 7.96 (d, 2H, *J*=8.4Hz, ArH); Anal. Calcd. for $C_{13}H_8B_rClN_2O$: C, 48.3; H, 2.5; N, 8.7.Found: C, 48.4; H, 2.3; N, 8.45

1-Benzoyl-2-(p-bromophenyl)diazene **(2i):** Yellow powder; yield: 86 %; m.p. 71–72°C; IR (KBr) ν 3077, 1688, 1606, 1583, 1506, 1465 cm^{-1}; ^{1}H NMR δ: 7.52 (d, 2H, *J*=7.2Hz, ArH), 7.68 (t, 1H, *J*=7.2Hz, ArH), 7.77 (d, 2H, *J*=8.4Hz, ArH), 7.89(d, 2H, *J*=8.4Hz, ArH), 8.01 (d, 2H, *J*=7.2Hz, ArH); Anal. Calcd. for $C_{13}H_9BrN_2O$: C, 54.0; H, 3.1; N, 9.7. Found: C, 53.9; H, 2.9; N, 9.55

1-(p-Ethoxybenzoyl)-2(p-bromophenyl)diazene **(2j):** Yellow plates; yield: 91 %; m.p. 121–122°C; IR (KBr) ν 3078, 2986, 2866, 1700, 1605, 1574, 1502, 1445 cm^{-1}; ^{1}H NMR δ: 1.47 (t, 3H, *J*=7.2Hz,CH_3), 4.12 (q, 2H, *J*=7.2Hz,CH_2), 6.92 (d, 2H, *J*=8.8Hz, ArH), 7.76 (d, 2H, *J*=8.4Hz, ArH), 7.87(d, 2H, *J*=8.4Hz, ArH), 8.05 (d, 2H, *J*=8.8Hz, ArH); Anal. Calcd. for $C_{15}H_{13}BrN_2O_2$: C, 54.1; H, 3.9; N, 8.4. Found: C, 53.9; H, 3.7; N, 8.25

1-(p-Bromobenzoyl)-2(p-bromophenyl)diazene **(2k):** Orange plates; yield: 93 %; m.p. 140–142°C; IR (KBr) ν 3078, 1704, 1606, 1586, 1500, 1423 cm^{-1}; ^{1}H NMR δ: 7.66 (d, 2H, *J*=8.4Hz, ArH), 7.75 (d, 2H, *J*=8.8Hz, ArH), 7.84 (d, 2H, *J*=8.8Hz, ArH), 7.93 (d, 2H, *J*=8.4Hz, ArH); Anal. Calcd. for $C_{13}H_8B_{r2}N_2O$: C, 42.4; H, 2.2; N, 7.6. Found: C, 42.2; H, 2.3; N, 7.5

1-(p-Ethoxybenzoyl)-2-phenyldiazene **(2l):** Yellow plates; yield: 87 %; m.p. 54–56°C; IR (KBr) ν 3066, 2986, 2865, 1698, 1605, 1506, 1455 cm^{-1}; ^{1}H NMR δ: 1.45 (t, 3H, *J*=7.0Hz, CH_3), 4.12 (q, 2H, *J*=7.0Hz, CH_2), 6.92 (d, 2H, *J*=8.8Hz, ArH), 7.50 (t, 1H, *J*=7.2Hz, ArH), 7.62 (t, 2H, *J*=7.2Hz, ArH), 7.71 (d, 2H, *J*=7.2Hz, ArH), 8.06 (d, 2H, *J*=8.8Hz, ArH); Anal. Calcd. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.0. Found: C, 70.65; H, 5.3; N, 10.9.

1-(p-Bromobenzoyl)-2-phenyldiazene **(2m):** Yellow plates; yield: 86 %; m.p. 38–39.5°C; IR (KBr) ν 3067, 1702, 1606, 1585, 1501, 1450 cm^{-1}; ^{1}H NMR δ: 7.59 (t, 1H, *J*=7.2Hz, ArH), 7.68 (d, 2H, *J*=8.4Hz, ArH), 7.77 (t, 2H, *J*=7.2Hz, ArH), 7.89 (d, 2H, *J*=8.4Hz, ArH), 8.02 (d, 2H, *J*=7.2Hz, ArH); Anal. Calcd. for $C_{13}H_9BrN_2O$: C, 54.0; H, 3.1; N, 9.7. Found: C, 53.8; H, 2.95; N, 9.5

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