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Rapid and convenient synthesis of acylhydrazines from acyldiazenes

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The synthesis of acylhydrazines by using phenylhydrazine as the reductant to hydrogenate acyldiazenes is reported.

Keywords: acylhydrazines, acyldiazenes, phenylhydrazine

Acylhydrazines have useful applications. Since they exhibit a broad spectrum of biological activity such as antifungal,[1] antiviral, plant growth regutatory,[2] restraining the insecticidal,[3,4] herbicidal[5] and pesticidal activity.[6,7] Moreover, their metal [Cu(II), Ni(II), Zn(II), Co(II), Ga, In, Iron (III), and Ca] complexes often possess more effective biological activities.[8-12] Acylhydrazines are also extensively used in photographic technology, paint synthesis, textile and as dyes.

In general, acylhydrazines are prepared by the reaction of substituted hydrazines or their derivatives' with esters, acyl chlorides or carboxylic acids. The direct synthesis of acylhydrazines from acyldiazenes has seldom been reported. We have now found that phenylhydrazine is an efficient reductant acyldiazenes to form acylhydrazines. To our knowledge, this is the first time that phenylhydrazine has been used in hydrogenate acyldiazenes.

We now report the use of phenylhydrazine as reductant to form 12 acylhydrazines from the corresponding acyldiazenes in excellent yields under mild conditions. The structures of these products were confirmed by IR, ^{1}H NMR and elemental analysis.

This method only needs simple equipment and is easy to operate. All the reaction periods are only about 5–15 min, the yields of the reaction are more than 75%. In conclusion, it is a rapid and convenient method for the preparation of acylhydrazines from acyldiazenes.

Meanwhile, we have also hydrogenated Ar'NHCON=NAr and Ar'N=NCON=NAr to form Ar'NHCONHNHAr and Ar'NHNHCONHNHAr compounds using phenylhydrazine as reductant under same conditions. However, we found that the reaction rate was very slow and the products were not identifiable.

Experimental

Melting points were determined with a Kofler micro melting point apparatus and were uncorrected. IR spectra were recorded on a FTS-40 spectrophotometer in KBr. ^{1}H NMR spectra were measured on a Bruker DPX-400M spectrometer using TMS as internal standard and DMSO-d_6 as solvent. Elemental analyses were performed on PE-2400 CHN elemental analyzer.

General procedure for the preparation of acylhydrazines **(2a–l):** Acyldiazene (1mmol) and ethyl ether (10ml) were placed in a round bottom flask. Phenylhydrazine (1.05mmol) was added over 5–6min under stirring at room temperature. The mixture was stirred for 5–15min. A pale yellow or white precipitate appeared. It was filtered recrystallised and dried to yield the pure product. All the compounds gave satisfactory analytical and spectra data.

Physical and spectra data of compounds **2a–l:** *1-Benzoyl-2-(p-nitrophenyl)hydrazine* **(2a):** yellow needles; Yield 83%; m.p. 195–196°C (lit.[13] 193°C); IR (KBr) ν: 3321, 3231, 3078, 1631, 1606, 1515 cm^{-1}; ^{1}H NMR δ: 6.82–8.08 (m, 9H, ArH), 9.21 (s, 1H, NH), 10.62 (s, 1H, NH); Anal. calcd. for $C_{13}H_{11}N_3O_3$: C, 60.70; H, 4.31; N, 16.33. Found: C, 60.56; H, 4.10; N, 16.11.

1-(p-Ethoxybenzoyl)-2-(p-nitrophenyl)hydrazine **(2b):** pale-yellow needles; Yield 93%; m.p. 239–240.5°C; IR (KBr) ν: 3310, 3230, 3094, 2981, 1628, 1610, 1512 cm^{-1}; ^{1}H NMR δ: 1.35 (t, 3H, CH_3), 4.11 (q, 2H, CH_2), 6.81–8.09 (m, 8H, ArH), 9.15 (s, 1H, NH), 10.47 (s, 1H, NH); Anal. calcd. for $C_{15}H_{15}N_3O_4$: C, 59.80; H, 5.02; N, 13.95. Found: C, 59.62; H, 5.27; N, 13.72.

1-(p-Methoxybenzoyl)-2-(p-nitrophenyl)hydrazine **(2c):** pale-yellow leaflets; Yield 91%; m.p. 245–246°C (lit.[13] 248°C); IR (KBr) ν: 3323, 3228, 3084, 3011, 2845, 1625, 1604, 1510 cm^{-1}; ^{1}H NMR δ: 3.82 (s, 3H, CH_3), 6.82–8.08 (m, 8H, ArH), 9.15 (s, 1H, NH), 10.48 (s, 1H, NH); Anal. calcd. for $C_{14}H_{13}N_3O_4$: C, 58.53; H, 4.56; N, 14.63. Found: C, 58.76; H, 4.43; N, 14.40.

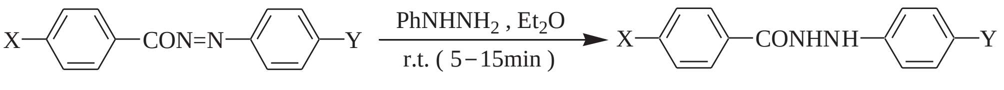
1-(p-Bromobenzoyl)-2-(p-nitrophenyl)hydrazine **(2d)**: pale-yellow needles; Yield 83%; m.p. 243–245°C (lit.[14] 247–249°C); IR (KBr) ν: 3322, 3242, 3084, 1633, 1594, 1506 cm^{-1}; ^{1}H NMR δ: 6.84–8.10 (m, 8H, ArH), 9.22 (s, 1H, NH), 10.71 (s, 1H, NH); Anal. calcd. for $C_{13}H_{10}BrN_3O_3$: C, 46.45; H, 3.00; N, 12.50. Found: C, 46.71; H, 3.32; N, 12.75.

1-(p-Ethoxybenzoyl)-2-(p-chlorophenyl)hydrazine **(2e)**: white leaflets; Yield 82%; m.p. 182–183°C; IR (KBr) ν: 3363, 3262, 3060, 2987, 2944, 1646, 1607, 1491 cm^{-1}; ^{1}H NMR δ: 1.35 (t, 3H, CH_3), 4.10 (q, 2H, CH_2), 6.76–7.89 (m, 8H, ArH), 8.01 (s, 1H, NH), 10.23 (s, 1H, NH); Anal. calcd. for $C_{15}H_{15}ClN_2O_2$: C, 61.97; H, 5.20; N,9.64. Found: C, 61.68; H, 5.04; N, 9.49.

1-(p-Methoxybenzoyl)-2-(p-chlorophenyl)hydrazine **(2f)**: white needles; Yield 81%; m.p. 194–196°C; IR (KBr) ν: 3362, 3245, 3070, 2997, 1646, 1606, 1492 cm^{-1}; ^{1}H NMR δ: 3.82 (s, 3H, CH_3), 6.76–7.90 (m, 8H, ArH), 8.01 (s, 1H, NH), 10.23 (s, 1H, NH); Anal. calcd. for $C_{14}H_{13}ClN_2O_2$: C, 60.77; H, 4.74; N, 10.12. Found: C, 60.60; H, 4.48; N, 10.25.

1-(p-Bromobenzoyl)-2-(p-chlorophenyl)hydrazine **(2g)**: white leaflets; Yield 75%; m.p. 195–197°C; IR (KBr) ν: 3353, 3244, 3062, 1662, 1589, 1492 cm^{-1}; ^{1}H NMR δ: 6.75–7.85 (m, 8H, ArH), 8.07 (s, 1H, NH), 10.44 (s, 1H, NH); Anal. calcd. for $C_{13}H_{10}BrClN_2O$: C, 47.96; H, 3.10; N, 8.60. Found: C, 48.31; H, 3.41; N, 8.38.

1-Benzoyl-2-(p-bromophenyl)hydrazine **(2h)**: white leaflets; Yield 86%; m.p. 172.5–174.5°C; IR (KBr) ν: 3354, 3246, 3040, 1652, 1591, 1488 cm^{-1}; ^{1}H NMR δ: 6.74–7.93 (m, 9H, ArH), 8.09 (s, 1H, NH), 10.38 (s, 1H, NH); Anal. calcd. for $C_{13}H_{11}BrN_2O$: C, 53.63; H, 3.81; N, 9.62. Found: C, 53.40; H, 3.50; N, 9.84.



1 2a-l

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

Scheme 1 Synthesis of acylhydrazines.

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1-(p-Ethoxybenzoyl)-2-(p-bromophenyl)hydrazine **(2i)**: white leaflets; Yield 80%; m.p. 175–177°C; IR (KBr) ν: 3364, 3260, 3063, 2987, 2895, 1646, 1607, 1488 cm^{-1}; ^{1}H NMR δ: 1.35 (t, 3H, CH_3), 4.10 (q, 2H, CH_2), 6.71–7.88 (m, 8H, ArH), 8.02 (s, 1H, NH), 10.22 (s, 1H, NH); Anal. calcd. for $C_{15}H_{15}BrN_2O_2$: C, 53.75; H, 4.51; N, 8.36. Found: C, 53.61; H, 4.63; N, 8.62.

1-(p-Methoxybenzoyl)-2-(p-bromophenyl)hydrazine **(2j)**: white needles; Yield 78%; m.p. 173–175°C; IR (KBr) ν: 3368, 3245, 3068, 2965, 2836, 1652, 1605, 1508 cm^{-1}; ^{1}H NMR δ: 3.82 (s, 3H, CH_3), 6.71–7.91 (m, 8H, ArH), 8.02 (s, 1H, NH), 10.23 (s, 1H, NH); Anal. calcd. for $C_{14}H_{13}BrN_2O_2$: C, 52.36; H, 4.08; N, 8.72. Found: C, 52.50; H, 4.30; N, 8.84.

1-(p-Bromobenzoyl)-2-(p-bromophenyl)hydrazine **(2k)**: white powder; Yield 85%; m.p. 171–173°C; IR (KBr) ν: 3350, 3244, 3062, 1660, 1590, 1488 cm^{-1}; ^{1}H NMR δ: 6.75–7.89 (m, 8H, ArH), 10.47 (s, 1H, NH), 10.64 (s, 1H, NH); Anal. calcd. for $C_{13}H_{10}Br_2N_2O$: C, 42.20; H, 2.72; N, 7.57. Found: C, 42.47; H, 2.99; N, 7.23.

1-(p-Ethoxybenzoyl)-2-phenylhydrazine **(2l)**: white leaflets; Yield 80%; m.p. 161–163°C. IR (KBr) ν: 3333, 3300, 3060, 2985, 2895, 1637, 1604, 1479 cm^{-1}; ^{1}H NMR δ: 1.35 (t, 3H, CH_3), 4.10 (q, 2H, CH_2), 6.77–7.90 (m, 9H, ArH), 7.79 (s, 1H, NH), 10.13 (s, 1H, NH); Anal. calcd. for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.60; H, 6.51; N, 10.76.

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