A Rapid and Convenient Method for Preparing Acylhydrazines from Acyldiazenes

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The synthesis of acylhydrazines by using hydrazine hydrate as the reductant to hydrogenate acyldiazenes is reported. Twelve acylhydrazines have been synthesized from acyldiazenes in excellent yields under mild conditions. This method is rapid, convenient, and efficient.

Keywords: Acylhydrazines; Acyldiazenes; Hydrazine hydrate.

INTRODUCTION

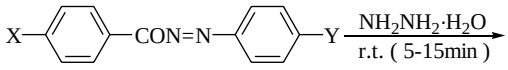
Acylhydrazine compounds have caused great interest in organic synthesis because of their extensive applied values. Some acylhydrazines and their derivatives exhibit a broad spectrum of biological activities such as antifungal,[1] antiviral, regulating plant growth,[2] restraining the reproduction of multi-cell parasites and are used as insecticides,[3,4] herbicides[5] and pesticides.[6,7] Moreover, as a kind of widely-used intermediate, their metal [Cu(II), Ni(II), Zn(II), Co(II), Ga, In, Iron(III), and Ca] complexes possess more effective biological activities.[8-12] Besides, acylhydrazine compounds are also extensively used in heterocyclic chemistry,[13] photographic technology, paint synthesis, textile fabrics dyes, chemical luminescence reactions, etc.

In general, acylhydrazines are prepared by substituted hydrazines or their derivatives' interactions with ester, acyl chloride and carboxylic acid. The synthesis of acylhydrazines from acyldiazenes directly has seldom been reported. In the process of our further research on acyldiazenes, we found that hydrazine hydrate is an efficient reductant to hydrogenate acyldiazenes to form acylhydrazines. To our knowledge, it is the first time for hydrazine hydrate to be used in hydrogenating this type of acyldiazenes. This reaction has its peculiarities and has potential applied value to some extent.

RESULTS AND DISCUSSION

Hydrazine hydrate is a traditional reductant which is used in a variety of reactions. But its reactions often need expensive catalysts and operations are tedious. In this paper, using hydrazine hydrate without a catalyst as reductant, twelve acylhydrazines have been synthesized from acyldiazenes in excellent yields under mild conditions. The structures of these products were confirmed by IR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis.

Scheme



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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

In the course of the experiments, it is found that the reaction speed of acyldiazenes with a substitution group of nitryl(-NO_2) on the aromatic rings is much quicker than others. The possible reason is that nitryl is a strong electron-attracting group which is relevant to reaction speed.

This method only needs simple instruments and is easy to operate. All the reaction periods are only about 5-15 min.

In conclusion, it is a rapid and convenient method for the preparation of acylhydrazines from acyldiazenes with hydrazine hydrate as reductant.

EXPERIMENTAL SECTION

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 and ^{13}C NMR spectra were measured on a Bruker DPX-400M (^{13}C NMR spectra on DPX-100M) spectrometer using TMS as internal standard and DMSO-d_6 as solvent. MS were implemented on an HP-5989B mass spectrograph with acetone as solvent. Elemental analyses were performed on a PE-2400 CHN elemental analyzer.

General procedure for the preparation of acylhydrazines (2a-l)

Acyldiazene (1 mmol) and ethyl ether (10 mL) were placed in a round bottomed flask. Hydrazine hydrate (1.05 mmol) was added over 5-6 min under stirring at room temperature. The mixture was stirred for 5-15 min. Pale-yellow or white precipitate came into being. It was filtrated, recrystallized and dried to yield the pure product.

The yields of the reactions are more than 80%. According to the emergence of the N-H absorption in the ^{1}H NMR, IR and MS spectrum, the reaction was proved to take place and be carried out completely. All the compounds gave satisfactory analytical and spectral data.

1-Benzoyl-2-(p-nitrophenyl)hydrazine (2a)

Yellow needles; Yield: 81%; mp 195-196 °C (lit.[14] 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)hydrazi-ne (2b)

Pale-yellow needles; Yield: 82%; mp 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); ^{13}C NMR δ: 166.73 (C=O), 162.53, 156.20, 139.17, 130.39, 126.93, 125.26, 115.26, 111.76 (Ar-C), 64.46 (CH_3), 15.53 (CH_2). 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: 96%; mp 245-246 °C (lit.[14] 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%; mp 243-245 °C (lit.[15] 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: 89%; mp 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); ^{13}C NMR δ: 166.91 (C=O), 162.29, 149.70, 130.22, 129.50, 125.84, 122.96, 115.14, 114.83 (Ar-C), 64.39 (CH_3), 15.53 (CH_2). 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: 93%; mp 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); ^{13}C NMR δ: 166.88 (C=O), 163.00, 149.64, 130.21, 129.51, 125.95, 122.94, 114.87, 114.75 (Ar-C), 56.42 (CH_3). MS (EI) *m/z*: 276 (M^+), 135 (B), 107, 92, 77, 51. 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: 87%; mp 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); ^{13}C NMR δ: 166.54 (C=O), 149.27, 132.93, 132.57, 130.45, 129.56, 126.53, 123.16, 114.93 (Ar-C). 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: 85%; mp 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); ^{13}C NMR δ: 167.34 (C=O), 149.92, 133.87, 132.73, 132.38, 129.51, 128.34, 115.37, 110.46 (Ar-C). 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-(p-Ethoxybenzoyl)-2-(p-bromophenyl)hydrazine (2i)

White leaflets; Yield: 88%; mp 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); ^{13}C NMR δ: 166.83 (C=O), 162.28, 150.10, 132.34, 130.21, 125.83, 115.34, 115.15, 110.33 (Ar-C), 64.39 (CH_3), 15.54 (CH_2). MS (EI) *m/z*: 336, 334 (M^+), 171, 149 (B), 121, 93, 65, 39. 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: 95%; mp 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); ^{13}C NMR δ: 166.86 (C=O), 163.00, 150.04, 132.35, 130.21, 125.98, 115.38, 114.75, 110.41 (Ar-C), 56.43 (CH_3). MS (EI) *m/z*: 322, 320 (M^+), 171, 135 (B), 107, 93, 77, 65, 51. 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: 83%; mp 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); ^{13}C NMR δ: 166.44 (C=O), 149.68, 134.95, 132.57, 132.40, 130.45, 126.54, 115.42, 110.64 (Ar-C). 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%; mp 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); ^{13}C NMR δ: 166.88 (C=O), 162.20, 150.67, 130.16, 129.71, 126.03, 119.64, 115.13, 113.41 (Ar-C), 64.38 (CH_3), 15.55 (CH_2). MS (EI) *m/z*: 256 (M^+), 149 (B), 121, 93, 65, 39. 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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REFERENCES

1. Patel, C. L.; Parekh, H. *J. Inst. Chem*. **1989**, *61*, 1456.
2. Giardello, M. A.; Sabat, M.; Rbeingold, A. L. *J. Am. Chem. Soc*. **1994**, *116*, 10212.
3. Hsu. Adam Chi-Tung. (Rohm and Haas Company) EP 0 232 075, **1987**.
4. Shimizu, B.; Nakagawa, Y.; Hattori, K. et al. *Steroids* **1997**, *62*, 638.
5. Li, Z.-M.; Chen, H.-S.; Zhao, W.-G. et al. *Chemical Journal of Chinese Universities* **1997**, *18*, 1794.
6. Nakagawa, Y.; Smagghe, G.; Kugimiya, S. *Pestic. Sci.* **1999**, *55*, 909.
7. Zou, X.-J.; Jin, G.-Y. *Chinese Journal of Pesticide Science* **2001**, *3*, 17.
8. Adeniyi, A. A.; Patel, K. S. *Synth. React. Inorg. Met. Org. Chem*. **1993**, *23*, 199.
9. Molina, P.; Tarraga, A.; Lopez, J. L. et al. *J. Organomet. Chem*. **1999**, *584*, 147.
10. Chohan, Z. H.; Faroog, M. A.; Iqbal, M. S. *Metal Based Drugs* **2000**, *7*, 133.
11. Chohan, Z. H. *Synth. React. Inorg. Met. Org. Chem.* **2001**, *31*, 1.
12. Chohan, Z. H.; Perrez, H.; Kausar, S. et al. *Synth. React. Inorg. Met. Org. Chem*. **2002**, *32*, 529.
13. Jadhav, V. K.; Wadagaonkar, P. P.; Salunkhe, M. M. *J. Chin. Chem. Soc.* **1998**, *45*, 831.
14. Elkaschef, M. A. F.; Nosseir, M. H.; Atwa, A. I. *J. Chem. U. A. R.* **1966**, *9*, 175.
15. Scott, F. L.; Aylward, J. B. *Tetrahedron Lett*. **1965**, *13*, 841.