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Synthesis of New N-Benzoyl-S-alkyl/aryl-dithiocarbamates

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New N-benzoyl-S-alky/aryldithiocarbamates were synthesized in moderate to good yields by the reactions of benzoyl isothiocyanate with substituted aryl- and akylthiols.

Key Words: Ditihiocarbamates, N-Benzoyl-S-alkyl/aryldithiocarbamates, Thiols, Benzoyl isothiocyanate.

INTRODUCTION

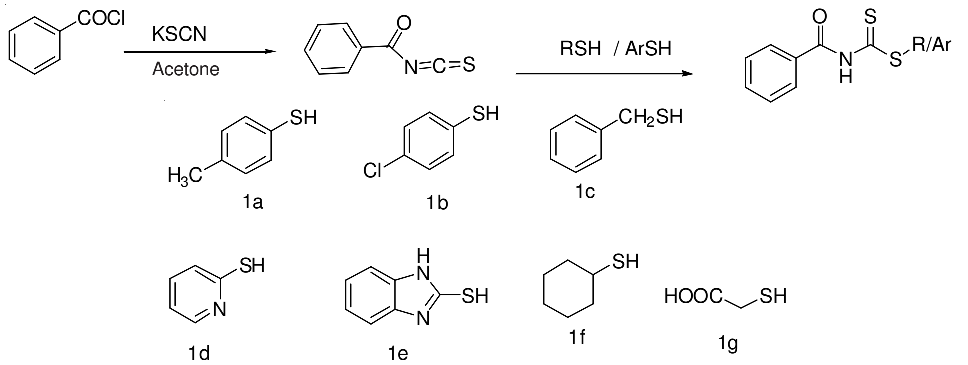
Organic dithiocarbamates (DTCs) have received much attention due to their interesting chemistry and wide utility. They have been used extensively as diverse pharmacological and agrochemicals including potential antimycobacterial, fungicidal, herbicidal, antioxidant[1-5]. They have also been used intermediates in organic synthesis[6], for the protection of amino groups in peptide synthesis[7] and carbamoyl radical precursors as a dithiocarbamate group in place of the classical xanthates[8]. Dithiocarbamate macromolecule heavy-metal flocculants (DMHMFs) has been synthezied as organic macromolecule flocculants. These flocculants have not only the advantages of organic macromolecule flocculants but also a good ability to trap and remove heavy-metal ions in water pollution control[9]. These uses require their preparation by a convenient and safe methodology. The classical synthesis of dithiocarbamates involves the use of costly and toxic reagents such as thiophosgene and its substituted derivatives. However, their formation using carbon disulphide, CS_2, employs harsh reaction conditions such as the use of strong bases, high reaction temperatures and long reaction times[10-12].

Herein, we report the highly efficient synthesis of N-benzoyl-S-alkyl/aryl dithiocarbamates using benzoyl isothiocyanate and alkyl/aryl thiols under mild conditions. Their structural evaluations were performed using FT-IR, ^1H, ^{13}C NMR, MS and UV-vis spectroscopic methods.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE DPX NMR spectrometer operating at 400 and 101.6 MHz. Infrared absorption spectra were obtained from a Perkin Elmer BX II spectrometer in KBr discs and were reported in cm^{-1} units. The UV-visible spectra were measured using a PG instruments T80+ series spectrometer. Melting points were measured on an Electro Thermal IA 9100 apparatus using a capillary tube. LC-mass spectra were obtained on an Agilent 1100 MSD spectrometer with an ion source temperature of 240 °C. TLC was conducted on standard aluminium sheets precoated with a 0.2 mm layer of silica gel. All chemicals were purchased from Merck and Aldrich.

General procedure for the synthesis of dithiocarbamates 1(a-g): Benzoyl isothiocyanate was prepared by adding KSCN (1.938 g, 20 mmol) to 20 mL of anhydrous acetone solution containing benzoyl chloride (2.32 mL 20 mmol) and was kept under reflux with stirring[13] for 1 h. The final mixture was poured into a water-ice bath. To a solution of alkyl/arylthiols (20 mmol) in anhydrous acetone was added benzoyl isothiocyanate suspension a solution in anhydrous acetone. The mixture was stirred magnetically at room temperature and was refluxed until the complete consumption of the substrate. The progress of the reaction was monitored by TLC analysis. After completion of the reaction, yellow solution was filtereted. Organic solvent was concentrated with a rotary evaporator under reduced pressure. Then the product was chromatographed over silica gel using ethyl acetate-hexane (1:4) as the eluent to separate the product. After evaporation of the solvent, the fairly pure solid were crystallized out.



Scheme-I: Synthesis of N-benzoyl-S-alky/aryldithiocarbamates

N-Benzoyl-S-(4-methylphenyl)dithiocarbamates (1a): Pure yellow crystals; yield 88 %; m.p. 127-129 ºC; λ_{max} (nm): 428 (ethyl acetate); IR (KBr, ν_{max}, cm^{-1}): 3214 (N-H), 1669 (C=O), 1595 (C=C$_{arom.}$), 1497 (N-CS), 1468, 1258 (CO-N), 1210 (C=S), 1044, 704 (C-S); ^{1}H NMR (CDCl$_3$), δ: 10.1 (s, 1H, N-H), 2.4 (s, 3H, -CH$_3$), 7.3-8.0 (m, 9H, ArH); ^{13}C NMR (CDCl$_3$), δ: 204 (C=S), 163 (C=O, 142, 135, 133, 130, 129, 127 (C=C$_{arom}$), 21 (CH$_3$); MS: m/z 271.07.

N-Benzoyl-S-(4-chlorophenyl)dithiocarbamates (1b): Brilliant yellow crystals; yield 90 %; m.p. 109-110 ºC; λ_{max} (nm): 427 (ethyl acetate); IR (KBr, ν_{max}, cm^{-1}): 3293 (N-H), 1692 (C=O), 1502 (C=C$_{arom.}$), 1474 (N-CS), 1259 (CO-N), 1210 (s) (C=S), 1042, 697 (C-S); ^{1}H NMR (CDCl$_3$), δ: 10.1 (s, 1H, N-H), 7.90-7.41 (m, 10H, ArH); ^{13}C NMR (CDCl$_3$), δ: 203 (C=S), 164 (C=O), 137, 134, 133, 131, 130, 129, 128, 127 (C=C$_{arom}$); MS: m/z 291.01.

N-Benzoyl-S-benzyldithiocarbamates (1c): Pale yellow crystals; yield 89 %; m.p. 107-109 ºC; λ_{max} (nm): 410 (ethyl acetate); IR (KBr, ν_{max}, cm^{-1}): 3213 (N-H); 1698 (C=O); 1599 ($C=C_{arom.}$), 1469 (N-CS), 1258 (CO-N), 1210 (s) (C=S), 1044, 704 (C-S); ^{1}H NMR ($CDCl_3$), δ: 12.80 (s, 1H, N-H), 4.47 (s, 2H, benzylic-H), 7.96-7.29 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$), δ: 204 (C=S), 166 (C=O), 135, 133, 132, 130, 129, 127, 127 ($C=C_{arom}$), 49 (benzylic-C); MS: m/z 271.07.

N-Benzoyl-S-(2prydinyl)dithiocarbamates (1d): Pale yellow crystals; yield 65 %; m.p. 164-167 ºC; λ_{max} (nm): 405(ethyl acetate); IR (KBr, ν_{max}, cm^{-1}): 3213 (N-H), 1698 (C=O), 1599 ($C=C_{arom.}$), 1469 (N-CS), 1258, 1210 (s)(C=S), 1044, 704 (C-S); ^{1}H NMR ($CDCl_3$), δ: 12.4 (s, 1H, N-H), 7.44, 7.55, 7.82, 7.93 (m, 9H, ArH); ^{13}C NMR ($CDCl_3$), δ: 204 (C=S), 165 (C=O), 160 (C=CAr-S) 134.60, 134.15, 133.78, 113.33 ($C=C_{arom}$); MS: m/z 258.05.

N-Benzoyl-S-(2-benzthioazolyl)dithiocarbamates (1e): Colorless crystals; yield 76 %; m.p. 238-240 ºC; λ_{max} (nm): 296 (ethyl acetate); IR (KBr, ν_{max}, cm^{-1}): 3154 (N-H), 2980, 2878, 1618 (C=O), 1512 ($C=C_{arom.}$), 1466 (N-CS), 1356, 1179 (s) (C=S), 1015, 743(C-S); ^{1}H NMR ($CDCl_3$), δ: 12.3 (s, 1H, NH), 4.2 (br, H, NH-Ar), 6.7-7.9 (m, 9H, ArH); ^{13}C NMR ($CDCl_3$), δ: 162 (C=O), 165 (C=S), 115, 128, 130-138 ($C=C_{arom}$); MS: m/z 297.06.

N-Benzoyl-S-cyclohexyldithiocarbamates (1f): Pale yellow crystals; yield 92 %; m.p. 107-109 ºC; λ_{max} (nm): 410 (ethyl acetate); IR (KBr, ν_{max}, cm^{-1}): 3220 (N-H), 2926 (C-H), 1703 (C=O), 1481 (N-CS), 1258 (CO-N), 1221 (s)(C=S), 1058, 711 (C-S); ^{1}H NMR ($CDCl_3$), δ: 12.54 (s, 1H, N-H), 3.88 (m, 1H, cyclohexyl-$CH_{equatorial}$ -S), 2.80 (q, $2H_{axial}$), 1.73 (q, $2H_{equatorial}$), 1.62(t, $1H_{equatorial}$), 1.52 (m, $4H_{axial}$), 1.35 (q, $1H_{axial}$), 7.94-7.51 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$), δ: 203 (C=S), 165 (C=O), 133, 132, 129, 128 ($C=C_{arom}$), 48, 31, 26, 25; MS (EI, 70 eV): m/z 263.10.

N-Benzoyl-S-(2-carboxymethyl)dithiocarbamates (1g): Pale yellow crystals; yield 75 %; m.p. 149-151 ºC; λ_{max} (nm): 404 (ethyl acetate); IR (KBr, ν_{max}, cm^{-1}): 3213 (N-H), 1698 (C=O), 1599 ($C=C_{arom.}$), 1469 (N-CS), 1258, 1210 (C=S), 1044, 704 (C-S); ^{1}H NMR ($CDCl_3$), δ: 10.68 (s, 1H, N-H), 4,01 (s, 2H, $-CH_2-$), 7.90-7.41 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$), δ: 204 (C=S), 165 (C=O), 170 (-COO) 130.13, 129.76, 129.34, 128.97 ($C=C_{arom}$), 40.44 ($-CH_2-$); MS: m/z 239.03.

RESULTS AND DISCUSSION

N-Benzoyl-S-akyl/aryldithiocarbamates (**1a-g**) were prepared according to the published procedure involving treatment of benzoyl chloride with potassium thiocyanate in acetone followed by reaction with suitably substituted thiols. The structures of all the new compounds were confirmed by FTIR, mass spectrometry, NMR spectrum results. Thus, for example, the characteristic C=O bands of the benzoyl appeared at 1703, 1698, 1618 cm^{-1} *etc.* and absorption bands corresponding to NH groups were observed at 3293-3213 cm^{-1} in IR spectra of the N-benzoyl-S-alkyl/aryldithiocarbamates. They showed absorptions at 1700-1660 cm^{-1} for carbonyl and at 1179, 1210, 1221 cm^{-1} *etc.* for thiocarbonyl groups in IR spectra. In addition, the band appearing at

704 cm^{-1} in the spectrum corresponds to the C-S stretching vibration. They showed absorptions singlets at δ 10.1-12.8 for HN(1) peak at 160- and 220- for carbonyl (C=O) and thiocarbonyl (C=S) were observed in ^{1}H and ^{13}C NMR spectra, respectively.

Conclusion

We have reported a general synthetic procedure providing new N-benzoyl-S-alkyl /aryl dithiocarbamates such as N-benzoyl-S-(4-methylphenyl)dithiocarbamate, N-benzoyl-S-(4-chlorophenyl)dithiocarbamate, N-benzoyl-S-benzyldthiocarbamate, N-benzoyl-S-(2-pyrdinyl)dithiocarbamate, N-benzoyl-S-(2-benzthioazolyl)dithiocarbamate, N-benzoyl-S-cyclohexyldithiocarbamate, N-benzoyl-S-(2-carboxymethyl)-dithiocarbamate under mild conditions in high to excellent yields.

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