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Chelate synthesis of functionally substituted 2-trichloromethylpyridines

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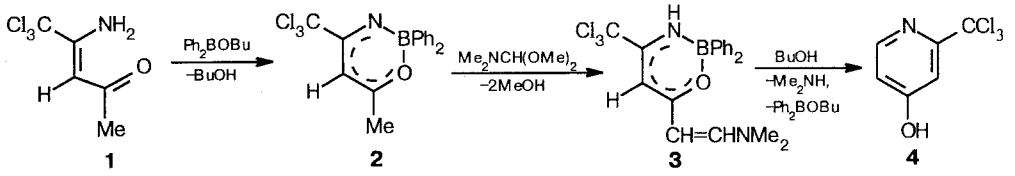
We are proposig new schemes for the synthesis of 2-trichloromethylpyridines *via* chelate-type boron compounds. We found that the diphenylboron chelate (**2**) prepared from 4-amino-5,5,5-trichloro-3-penten-2-one (**1**) reacts with dimethylformamide dimethylacetal to give the condensation product, *viz*, complex (**3**). Boiling the latter in BuOH results in its cyclization to pyridine (**4**) (Scheme 1).

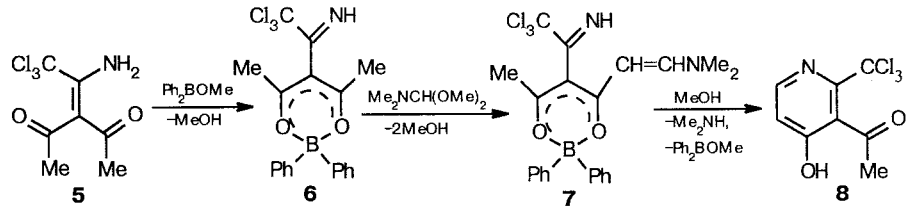
Unexpectedly, it turned out that, when treated with Ph_2BOMe, the *C*-acetyl derivative of enaminone **1**, 4-amino-3-acetyl-5,5,5-trichloro-3-penten-2-one (**5**), behaves as a β-diketone-type chelating ligand, rather than an enaminone-type ligand, and affords complex (**6**), according to the ^1H and ^{13}C NMR spectra. The latter reacts with $Me_2NCH(OMe)_2$ at ~20 °C to yield the condensation product (**7**), which is smoothly converted to pyridine (**8**) when boiled in MeOH (Scheme 2).

The structures of chelates **3**, **6**, and **7** and pyridines **4** and **8** were confirmed by ^1H and ^{13}C NMR and IR spectroscopy and mass spectrometry. The elemental analysis data correspond to the calculated values. The 4-pyridone ⇌ 4-hydroxypyridine equilibria for compounds **4** and **8** are shifted to hydroxypyridines, which is indicated by the signal at ~110 ppm in the ^{17}O NMR spectrum.

Scheme 1



Scheme 2



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Experimental

Chelate **2** [1] and compound **5** [2] were prepared according to the known procedures. All of the operations were carried out under an argon atmosphere.

2-Trichloromethyl-4-hydroxy-pyridine (4). A mixture of compound **2** (0.91 g, 2.5 mmol) and $Me_2NCH(OMe)_2$ (0.73 g, 5 mmol) in ether (10 mL) was boiled for 6—7 h, and the precipitate was filtered off and washed with pentane to give 0.8 g (80 %) of complex **3**, m.p. 163—165 °C (benzene—hexane). IR (CH_2Cl_2), ν/cm^{-1}: 3400 (NH), 1635, 1530. ^1H NMR ($CDCl_3$), δ: 2.90 (s, 3 H, MeN) and 3.19 (s, 3 H, MeN); 5.02 (d, 1 H, CH=CHN); 5.65 (d, 1 H, CH); 6.64 (br.s, 1 H, NH); 7.2—7.5 (m, 10 H, 2 Ph); 7.86 (d, 1 H, CH=CHN). Compound **3** (0.76 g, 1.8 mmol) and BuOH (7 mL) were boiled for 3 h, the excess BuOH was removed *in vacuo*, and the residue was chromatographed on a column with SiO_2 (C_6H_6—$CHCl_3$ and $CHCl_3$ as the eluents) to give 0.29 g (75 %) of pyridine **4**, m.p. 135—136 °C (from $CHCl_3$). MS, *m/z* : 211 $[M]^+$ (for ^{35}Cl). ^1H NMR (DMSO-d_6), δ: 6.90 (d.d, H(5)); 7.43 (d, 1 H, H(3)); 8.38 (d, 1 H, H(6)); 11.34 (br.s, 1 H, OH). ^{13}C NMR (DMSO-d_6), δ: 97.42 (s, Cl_3C); 107.07 (d, C(3)); 112.72 (d, C(5)); 150.22 (d, C(6)); 158.99 (d, C(4)); 165.19 (d, C(2)).

3-Acetyl-2-trichloromethyl-4-hydroxypyridine (8). A solution of Ph_2BOMe (7.1 g, 36.2 mmol) in ether (10 mL) was added dropwise to a solution of compound **5** (6.8 g, 2.78 mmol) in ether (30 mL) over a period of 1—2 min. The mixture was stirred for 2—3 min, the volatile products were immediately evaporated *in vacuo*, the residue (oil) was quickly crystallized from pentane (40 mL), and the crystals were filtered off and washed with pentane (3×20 mL) to give 7.48 g (73.5 %) of chelate **6**, m.p. 121—122 °C. IR (CH_2Cl_2), ν/cm^{-1}: 3255 (br, NH), 1645, 1585. ^1H NMR ($CDCl_3$), δ: 2.39 (s, 6 H, 2 Me); 7.15—7.60 (m, 10 H, 2 Ph); 11.28 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 23.58 (q, MeCO); 97.64 (s, Cl_3C); 112.43 (br.s, C=C=C); 126.92, 127.24, 131.63, 145.67 (Ph); 166.46 (br.s, C=NH); 190.42 (q, C=O). A mixture of compound **6** (7.2 g, 17.6 mmol) and $Me_2NCH(OMe)_2$ (6.3 g, 53.1 mmol) in ether (100 mL) was stirred for 30 min at ~20 °C, and the precipitate was filtered off and washed with ether to give 7.85 g (94 %) of compound **7**, m.p. 136—137 °C. IR (CH_2Cl_2), ν/cm^{-1}: 3275 (br, NH), 1635, 1515. Compound **7** (7.0 g, 15.0 mmol) was boiled in MeOH (100 mL) for 1 h, the solvent was evaporated *in vacuo*, and the residue was chromatographed on a column with SiO_2 (C_6H_6—$CHCl_3$, ~1 : 1, and $CHCl_3$ as the eluents). The solvent was evaporated, 1—2 mL of C_6H_6 was added to the residue (oil), and the crystals were filtered off and washed with hexane to give 2.2 g (60 %) of pyridine **8**, m.p. 139—140 °C (from $CHCl_3$). MS, *m/z* : 253 $[M]^+$ (for ^{35}Cl). ^1H NMR (DMSO-d_6), δ: 2.56 (s, 3 H, MeCO); 7.0 (d, 1 H, H(5)); 8.36 (d, 1 H, H(6)); 10.9 (br.s, 1 H, OH). ^{13}C NMR (DMSO-d_6), δ: 32.28 (q, Me); 96.66 (Cl_3C); 113.29 (d, C(5)); 123.64 (s, C(3)); 148.52 (d, C(6)); 152.57 (s, C(2)); 162.41 (s, C(4)); 200.62 (q, C=O).

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