Regioselective Synthesis of Pentathiepinopyrroles

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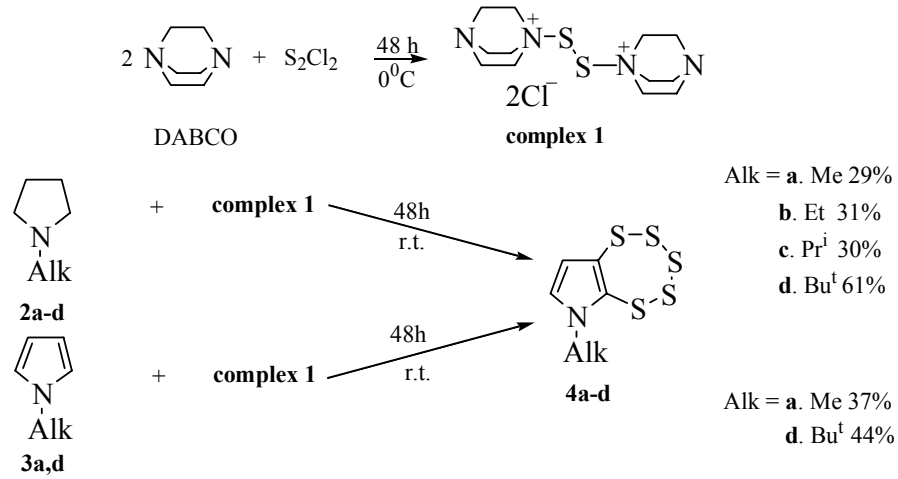
In spite of much recent activity, few different syntheses of pentathiepins are available.[1] Most methods require 1,2- or *ortho*-dithiols and thus pentathiepins fused to other heterocyclic rings are rare. We have shown that treatment of nucleophilic heterocycles like pyrroles and thiophenes, and their tetrahydro derivatives, with S_2Cl_2, and a base provides one-pot synthesis of fused pentathiepins. However these reactions are not regioselective and are sensitive to the the reaction conditions.[2]

We found that a mixture of S_2Cl_2 and DABCO 1:2 in chloroform, stored for 48 h at 0°C before use, gave different products to those formed when the heterocycle, S_2Cl_2 and DABCO were all mixed together at the beginning. We assume that a complex **1** is formed between S_2Cl_2 and DABCO, which was confirmed by IR spectroscopy.

Treatment of *N*-alkylpyrrolidines **2** and pyrroles **3** with complex **1** in chloroform for 48 h at room temperature gave selectively the *N*-alkyl-1,2,3,4,5-pentathiepino[6,7-*b*]pyrroles **4**.



So, preformed complex **1** has a significantly different reaction profile with greater selectivity than a mixture of S_2Cl_2 and DABCO without premixing.

1. L.S. Konstantinova, O.A. Rakitin, C.W. Rees, *Chem. Rev.*, 2004, **104**, 2617.
2. L.S. Konstantinova, O.A. Rakitin, C.W. Rees, *Chem. Commun.*, 2002, 1204.