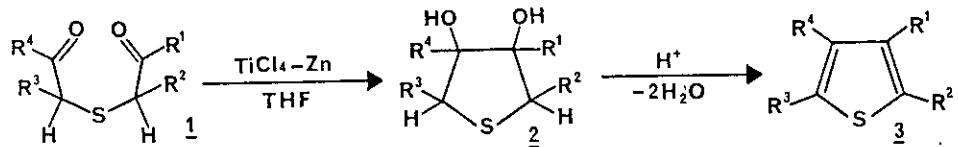


GENERAL SYNTHESIS OF POLYSUBSTITUTED THIOPHENES FROM DIKETO SULFIDES AND APPLICATION TO THE PREPARATION OF POLYTHIOPHENES

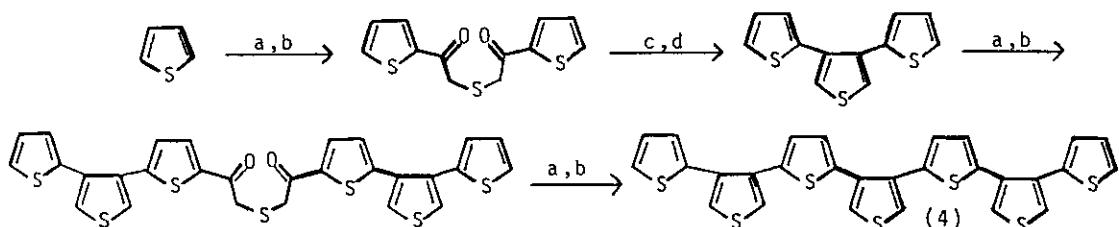
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Diketo sulfides (1) are easily accessible compounds in which three functional groups [carbonyl, active methylene (methine), and sulfide moieties] are suitably arranged for various intramolecular chemical transformations. As a part of our synthetic study with 1, we report a general synthesis of polysubstituted thiophenes (3) from 1. Treatment of 1 with a low-valent titanium reagent, prepared from $TiCl_4$ and zinc powder in THF, at $0^\circ C$ affords a variety of 3,4-dihydroxythiolanes (2) in good yields. The acid-catalyzed (*p*-toluenesulfonic acid) dehydration of 2 leads to the thiophenes 3 in excellent yields.



The above thiophene synthesis was applied to the preparation of polythiophenes. The septithiophene (4) was obtained in a good overall yield starting from thiophene.



a: $CH_2ClCOCl$, $AlCl_3$, CS_2
 b: Na_2S , CH_3COCH_3
 c: $TiCl_4-Zn$, THF , $0^\circ C$
 d: *p*-TsOH, C_6H_6 , refl.