UNEXPECTED FORMATION OF 2-ETHYLTHIOPHENE BY THERMOLYSIS OF 1,1-DIPROPENYLSULFIDE

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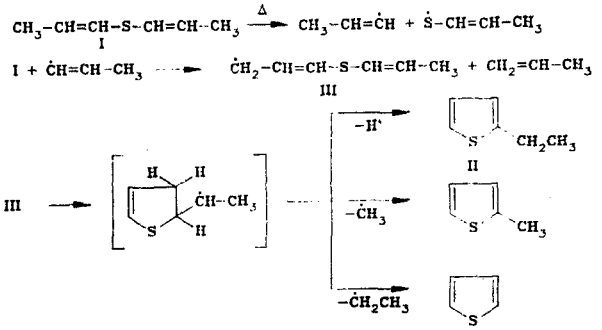
Thermal dehydrocyclization of divinylsulfide at 450-460°C leads to thiophene in a yield up to 40% [1]. With a view to exploring the possible thermal synthesis of alkyl thiophenes we have studied the gas phase thermolysis of 1,1-dipropenylsulfide (I). Instead of the expected 3,4-dimethylthiophene or its isomers, formed by thermocatalytic cyclization of dipropenyldifulfide [2], one of the basic thermolysis products at 500-520°C is 2-ethylthiophene (II, yield 20-25%). Also formed were: thiophene (22-32%), a mixture of 2- and 3-methylthiophene (3-6%), unidentified compounds (10%), and gaseous substances (H_2S, hydrocarbons). 3,4-Dimethylthiophene was not found in the reaction products.

This unexpected mode of thermolysis of sulfide I is apparently due to the increased stability of the intermediate allyl radical III. Subsequent cyclization of III can occur to give the ethylthiophene II as well as the other main reaction products. The reaction is initiated even by partial decomposition of sulfide I with breaking of the C–S bond:



The reaction was carried out in a flow system (hollow quartz tube with a heating zone of 650 × 30 mm) at atmospheric pressure in a nitrogen stream (5 liter/h). The sulfide I was added with the aid of an automatic dispenser (21 ml/h) and the thiophene products identified by GLC and chromatography-mass spectrometry. Distillation of the condensate gave the ethylthiophene (II) with bp 130-136°C and n_D^{25} 1.5138 (lit. data [3]: bp 134-136°C, n_D^{20} 1.5122). PMR Spectrum (Tesla BS-567A, 100 Mhz, $CDCl_3$, HMDS): 1.26 (3H, t, CH_3CH_2); 2.79 (2H, q, CH_3CH_2); 6.73 (1H, m, 3-H), 6.85 (1H, m, 4-H); 7.02 ppm (1H, m, 5-H).

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