Chemistry of Heterocyclic Compounds, Vol. 42, No. 11, 2006

MICROWAVE INDUCED SYNTHESIS OF DIPHENYLTHIOPHENES FROM ELEMENTAL SULFUR AND STYRENE

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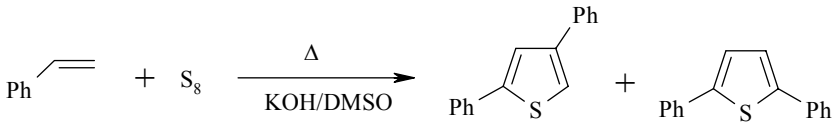
Keywords: 2,4- and 2,5-diphenylthiophenes, styrene, elemental sulphur, microwave irradiation.

Thiophene and its substituted derivatives (particularly diphenylthiophenes) find a wide practical use and they continue to attract the attention of investigators as building blocks for organic synthesis [1-3]. One of the routes to the synthesis of diphenylthiophenes is the reaction of elemental sulfur with styrene. Unfortunately this is unselective and heating elemental sulfur with styrene (140-230°C) forms a complex mixture of acyclic and cyclic (2,4-diphenylthiophene, 2,4-diphenylthiophane, 2,5-diphenyl-1,4-dithiane, 2,5-diphenyl-2,3-dehydrothiane) products among which rubber like polysulfide oligomers and polymers predominate [4-6]. Increasing the selectivity of the synthesis of diphenylthiophenes from styrene and elemental sulfur remains an unresolved problem.

We have found that styrene reacts with elemental sulfur in the strongly basic medium KOH-DMSO [7] in the presence of hydroquinone under microwave irradiation (600 watts, 4 min) to form a 1: 12 mixture of 2,4- and 2,5-diphenylthiophenes **1a,b** in overall 30% yield (not optimized).



1a **1b**

The diphenylthiophenes are not formed when the elemental sulfur and styrene are heated (85-90°C, 6 h) in the system KOH-DMSO-hydroquinone in the absence of the microwave irradiation and the unreacted styrene is recovered.

In the absence of the hydroquinone the reaction is less selective. Along with the thiophenes **1a,b** GC-MS analysis of the reaction mixture shows the presence of bis(2-phenylethyl) sulfide, bis(2-phenylethyl) disulfide, 1,4-diphenylbuta-1,3-diene, and 1,3,5-triphenylbenzene.

* Dedicated to Academician M. G. Voronkov, Russian Academy of Sciences in his 85th year.

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Hence microwave irradiation in the reaction of styrene with elemental sulfur opens up a novel route to the synthesis of 2,5-diphenylthiophene. The preparative possibilities of this reaction are under investigation.

^{1}H NMR spectra were recorded on a Bruker DPX 400 (400 MHz) instrument using $CDCl_3$ and with HMDS as internal standard. Mass spectra were taken on a Hewlett-Packard HP-5971A instrument (EI, 70 eV). A domestic Samsung 181 DNR microwave oven was used for the microwave irradiation.

2,4- and 2,5-Diphenylthiophenes. A mixture of styrene (2.08 g, 20 mmol), elemental sulfur (0.8 g, 25 mmol), hydroquinone (0.02 g, about 1% of the styrene), KOH (2.8 g, 50 mmol), water (0.5 ml), and DMSO (20 ml) was irradiated in the microwave oven (600 watts power, 4 min). The reaction mixture was cooled, diluted with about 20 ml of water, and extracted with benzene (5 × 15 ml). The benzene extracts were washed with water and dried with potassium carbonate. Benzene was removed at reduced pressure and the residue was dried in vacuo to give the diphenylthiophenes **1a,b** in the ratio 1: 12 (GC-MS) as yellow crystals soluble in benzene dioxane, and ether. Found, %: C 80.98; H 5.27; S 13.60. $C_{16}H_{12}S$. Calculated, %: C 81.32; H 5.12; S 13.57.

2,4-Diphenylthiophene (1a). Mass spectrum, *m/z* (I_{rel}, %): 236 $[M]^+$ (100), 191 (14), 165 (5), 134 (5), 121 (9), 105 (2), 89 (6), 77 (7), 63 (10), 51 (7), 39(7).

2,5-Diphenylthiophene (1b). Mass spectrum, *m/z* (I_{rel}, %): 236 $[M]^+$ (100), 202 (10), 189 (5), 134 (7), 121 (19), 115 (8), 101 (6), 89 (6), 77 (11), 63 (6), 51 (8), 39 (5). ^{1}H NMR swpectrum, δ, ppm (*J*, Hz): 7.31 (2H, s, H-3(4)); 7.33-7.38 (4H, m, *m*-C_6H_5); 7.43-7.46 (4H, m, *o*-C_6H_5), 7.65-7.69 (2H, m, p-C_6H_5).

The work was carried out with state support for leading science schools (grant NSh-5444.2006.3) and the Russian Fund for Basic Research (grant 05-03-32859).

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