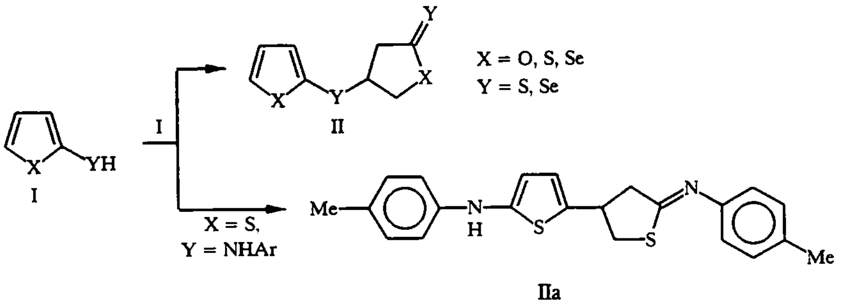
Chemistry of Heterocyclic Compounds, Vol. 33, No. 3, 1997

SPONTANEOUS DIMERIZATION OF 2-(4-METHYLPHENYLAMINO)THIOPHENE

V. Yu. Vvedenskii, E. D. Shtefan, R. N. Malyushenko,
E. V. Shilkin, and É. N. Deryagin

The heteroaromatic chalcogenols (I) (X = O, S, Se; Y = S, Se) are converted to the dimeric forms (II) on storage [1]. Are similar conversions also possible for heteroaromatic amines, e.g., aminothiophenes? It was shown that 2-(4-methylphenylamino)thiophene (Ia) (X = S, Y = p-MeC_6H_4N), synthesized by us for the first time, is also spontaneously converted to the dimer (IIa). However, the reaction has different regiodirectionality.



2-(4-Methylphenylamino)thiophene (Ia). ($C_{11}H_{11}NS$). The mixture of 1.16 g (0.01 mole) of 2-thiophenethiol, 1.07 g (0.01 mole) of p-toluidene, and 10 ml of methanol is boiled under reflux for 6 h until the cessation of the release of hydrogen sulfide is achieved [2]. Vacuum distillation leads to the isolation of 0.63 g (33%) of compound (Ia) with the bp 120-122°C (1 mm of Hg stem). The PMR spectrum (500 MHz, acetone-D_6) is as follows: 2.22 (3H, s, Me), 6.63 (1H, ddd, J = 3.5, 1.5, 0.8 Hz, $H_{(3)}$), 6.85 (1H, ddd, J = 5.5, 3.5, 0.3 Hz, $H_{(4)}$), 6.87 (1H, dd, J = 5.5, 1.4 Hz, $H_{(5)}$), 6.93 (2H, m, o-H), 7.02 (2H, m, p-H), and 7.42 (1H, broad s, NH). The mass spectrum is characterized by the m/z 189 (100%).

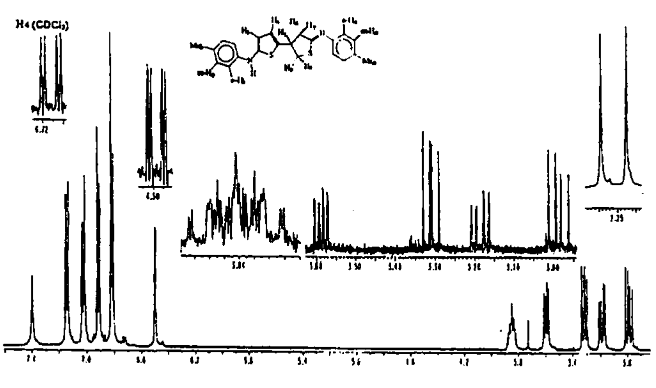


Fig. 1. PMR spectrum of compound (IIa) (500 MHz, acetone-D_6).

Irkutsk Institute of Organic Chemistry, Siberian Section (SO) of the Russian Academy of Sciences (AN), Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 424-425, March, 1997. Original article submitted September 13, 1996.

2-(4-Methylphenylamino)-5-[2-(4-methylphenylamino)tetrahydro-4-thienyl]thiophene (IIa). ($C_{22}H_{22}N_2S_2$). This compound is formed with the yield of 97% from the amine (Ia) in the course of 1 month in a sealed ampul at room temperature. After recrystallization from methanol, the mp is 118°C. The PMR spectrum is shown (see Fig. 1). The ^{13}C NMR spectrum (126 MHz, acetone-D_6) is as follows: 172.6 (C=N), 149.2, 145.4, 143.2, 136.6, 134.1, 129.8 (m-C), 129.7 (m-C), 129.6, 122.7, 120.0 (*o*-C), 117.5, 115.0 (*o*-C), 46.5 (CH), 41.0 (CH_2), 40.2 (CH_2), 20.9 (Me), and 20.5 (Me). The mass spectrum is characterized by the m/z 378 (100%).

The data of the elemental analysis of the compounds (Ia) and (IIa) correspond with the calculated data.

The work was carried out with the financial support of the Russian Fund for Fundamental Investigations (Grant 94-03-08837).

REFERENCES

1. E. D. Shtefan and V. Yu. Vvedenskii, Uspekhi Khimii, **65**, No. 4, 326 (1996).
2. H. Hartmann and S. Sheithauer, J. Prakt. Chem., **311**, No. 5, 827 (1969).