SYNTHESIS OF 3-METHYL-2-PHENYLTHIOFURAN AND 1-FORMYL-3-METHYL-2,2-DI(PHENYLTHIO)CYCLOPROPANE

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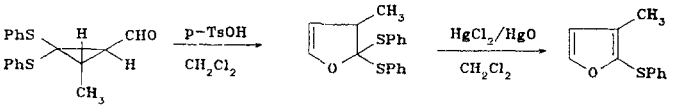
UDC 547.512'722.2:541.621.2

The development of convenient methods for obtaining arylthiofurans is of interest in view of the wide possibilities of the use of these substances in synthesis of compounds of the furan series [1, 2].

We have found that, in the presence of catalytic amounts of p-toluenesulfonic acid in methylene chloride, 1-formyl-3-methyl-2,2-di(phenylthio)cyclopropane (I), unlike the corresponding ketone [3], isomerizes [4] into 3-methyl-2,2-di(phenylthio)-2,3-dihydrofuran (II) [isolated in the form of an oil; PMR spectrum (CCl_4), δ, ppm: 1.20 (3 H, d, J = 6 Hz); 3.1-3.5 (1 H, m); 4.82 (1 H, t, J = 2 Hz); 5.98 (1 H, d.d, J = 2 and 3 Hz); 7.1-7.6 (10 H, m)].



I II III

The splitting out from the dihydrofuran (II) of a molecule of thiophenol under the action of an equimolar mixture of mercury(II) chloride and oxide led to 3-methyl-2-(phenylthio)furan (III) [bp 100-103°C (2 mm); n_D^{25} 1.5906. PMR spectrum (CCl_4), δ, ppm: 2.08 (3 H, s), 6.26 (1 H, d, J = 2 Hz); 6.9-7.2 (5 H, m); 7.42 (1 H, d, J = 2 Hz)] with a yield of 80% calculated on the initial aldehyde (I). The conversion of the aldehyde (I) into the furan (III) can be performed without the intermediate isolation of the dihydrofuran (II). In this case, a solution of the aldehyde is stirred with an equivalent amount of a mixture of mercury(II) chloride and oxide in the presence of p-toluenesulfonic acid at room temperature for 30 min.

The purity of the compounds obtained was checked by the TLC method; the elementary analyses of the compounds corresponded to the calculated figures.

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V. I. Lenin Belorussian State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, p. 132, January, 1984. Original article submitted February 17, 1983.

 0009-3122/84/2001-0112$08.50