

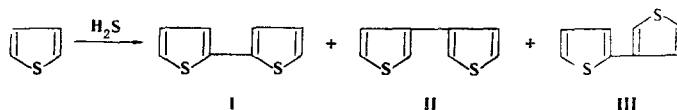
M. G. Voronkov, É. N. Deryagina,
É. N. Sukhomazova, O. I. Randin,
V. V. Keiko, and I. D. Kalikhman

UDC 547.734:542.915:543.422.4

The pyrolysis of thiophene in a hydrogen sulfide atmosphere in a system of the flow-recirculation type leads to almost quantitative formation of a mixture of isomeric dithienyls enriched with the 2,3' and 3,3' isomers.

It is known [1, 2] that the pyrolysis of thiophene at 850°C leads to a mixture of isomeric dithienyls and a number of other compounds (benzothiophene, phenylthiophene, etc.) in an overall yield of 7-8%.

We have shown that thiophene is dehydrodimerized to a mixture of three isomeric dithienyls (in 95% yield) with high conversion at 780-800° in a hydrogen sulfide atmosphere in a system of the flow-recirculation type:



The pyrolysis of thiophene proceeds considerably more slowly and profoundly in a nitrogen atmosphere under similar conditions to give a mixture of isomeric diethienyls (30%), benzothiophene (20%), and phenylthiophene (10%]; the ratio between the isomeric dithienyls is retained (I:II:III = 1:3:6).

Since for the first time it has been established that the difficult-to-obtain 2, 3'- and 3,3'-dithienyls are intermediates in the pyrolysis of thiophene, we made a comparison of the physicochemical characteristics of I-III, which were separated by preparative gas-liquid chromatography (GLC) with the literature data for dithienyls synthesized by different methods.

The protons of the thiophene ring in the PMR spectra of isomer I are represented by a multiplet of the ABC type. The chemical shifts of the 3-H and 5-H protons are close (7.03 and 7.02 ppm), and the 4-H quartet is centered at 6.85 ppm. The distances between the components of the quartet (3.6 and 5.1 Hz) are characteristic for $J_{4,5}$ and $J_{3,4}$ in 2-substituted thiophenes [3].

The resonance of the protons of III is observed in the form of a broad singlet (7.24 ppm). Superimposition of the spectra of 2- and 3-substituted thiophenes is characteristic for isomer II. The signal at 7.22 ppm is related to the protons of a 3-substituted thiophene, and the signals at 7.05 and 6.91 ppm are related to the protons of a 2-substituted thiophene.

The spectral features of dithienyls I-III coincide completely with those previously described for 2,2', 3,3', and 3,4'-dithienyls [4]. Moreover, in [4], deuteration and variation of the solvents made it possible to make a more detailed analysis of the ABCA'B'C' system.

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 9, pp. 1186-1187, September, 1976. Original article submitted June 9, 1975; revision submitted December 23, 1975.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.

Thus, the data from the PMR spectra confirm the structure of I-III.

The IR spectrum of I contains a band at 700 cm^{-1} (out-of-plane deformation vibrations of adjacent hydrogen atoms of the thiophene ring), and the spectra of II and III contain bands at 773 and 778 cm^{-1} , respectively (out-of-plane deformation vibrations of an isolated hydrogen atom). The band at $777\text{--}778\text{ cm}^{-1}$ is absent in the IR spectrum of isomer I.

The UV spectra of dithienyls I and III coincide with the literature data for 2,2'- and 2,3'-dithienyls, respectively [5].

The dipole moments of I-III [0.78, 0.87, and 1.06 D, respectively (octane)] correspond to the literature data [6] for isomeric dithienyls.

EXPERIMENTAL

Compounds I-III were separated with a Khrom-4 chromatograph; the liquid phase was 30.5% SE, the support was Chezasorb, the carrier gas was helium, and the column temperature was 150° .

The PMR spectra of CCl_4 solutions of I-III were obtained with a Tesla BS-487 spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of heptane solutions of the compounds were obtained with a Specord UVvis spectrophotometer.

Pyrolysis of Thiophene. Thiophene vapors [20 g, (0.24 mole)] were fed with a stream of hydrogen sulfide (2-3 liters/h) from the still of the recirculation apparatus into an empty quartz tube heated to the necessary temperature, in which they condensed and were returned to the still. The reaction was complete after 6 h, during which the temperature in the still increased from 80 to 200° . Vacuum fractionation of the still residue yielded 16.5 g of a crystalline mixture of the isomeric dithienyls (82.5% based on the starting thiophene or 95% based on the converted thiophene); the melting points of I-III were 32 , 128 , and 64° , respectively (mp $31\text{--}33^{\circ}$ [7-9], $128\text{--}132$, and $63\text{--}67^{\circ}$, respectively).

The elementary compositions (C, H, and S) of I-III were in agreement with the calculated values.

The mass spectra of I-III contained a peak with m/e 166 corresponding to the molecular mass.

UV spectra, λ , nm: I 250 (ϵ 6500), 300 (ϵ 10,800); II 2.2 (ϵ 21,550), 262 (ϵ 11,400); III 236 (ϵ 9160), 285 (ϵ 12,600).

LITERATURE CITED

1. R. Nahnsen, Ber., 17, 789, 2197 (1884).
2. H. Wynberg and A. Wantjes, J. Org. Chem., 24, 1421 (1959).
3. S. Gronowitz and B. A. Hoffman, Ark. Kemi, 16, 515 (1960).
4. R. M. Kellog, A. P. Schaap, and H. Wynberg, J. Org. Chem., 34, 343 (1969).
5. J. H. Uhlenbroek and J. D. Byloo, Rec. Trav. Chim., 79, 1181 (1960).
6. H. Wynberg, Angew. Chem., 75, 453 (1963).
7. A. Töhl, Ber., 27, 666 (1894).
8. W. Steinkopf and J. Roch, Ann., 482, 251 (1930).
9. H. Wynberg, A. Logathetis, and D. V. Ploeg, J. Am. Chem. Soc., 79, 1972 (1957).