FORMATION OF THIOPHENE-3-THIOL IN THE HIGH-TEMPERATURE REACTION OF DI(2-THIENYL) SULFIDE WITH HYDROGEN SULFIDE

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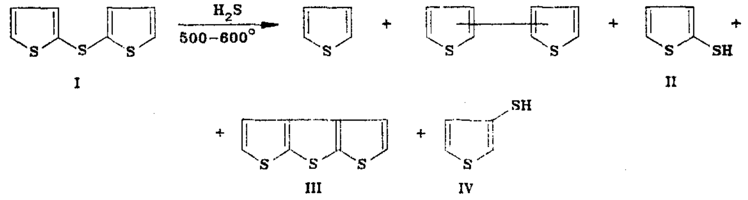
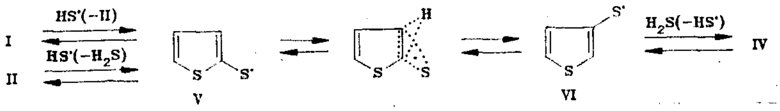
Aromatic and heteroaromatic sulfides are distinguished by their high thermal stabilities [1, 2]. We have shown that the thermolysis of 2,2'-dithienyl sulfide (I) in an inert gas atmosphere commences at temperatures >500°C; thiophene, isomeric dithienyls, thiophene-2-thiol (II), and dithienothiophene (III) are formed. At 600°C the degree of conversion of dithienyl sulfide is 40%. In the presence of hydrogen sulfide the thermolysis of sulfide I commences at 400°C. Above 500°C thiophene-3-thiol (IV) is formed along with the indicated products. When the temperature is increased from 500°C to 600°C, the percentage of thiol II in the hydrothiolysis products decreases, whereas the percentage of thiol IV increases. The degree of conversion of dithienyl sulfide in the presence of hydrogen sulfide at 500°C is 80%, whereas it is 100% at 600°C.



The formation of thiol IV is probably due to thermal isomerization of intermediate thiyl radical V:



The shift of the V $\rightleftarrows$ VI equilibrium to favor VI when the temperature is raised is in agreement with the increased thermal stability of 3-substituted thiophenes (as compared with 2-substituted thiophenes) (see [3]).

The reactions were carried out in a flow system (a 650 by 30 mm quartz tube) in an atmosphere of nitrogen and hydrogen sulfide. Sulfide I was fed into the reaction zone at a rate of 15 ml/h, and nitrogen and hydrogen sulfide were fed in at a rate of 2-3 liters/h. The yields of thiols II and IV were 11% at 500°C and 8% at 600°C. Thiophene, the isomeric dithienyls, and II and III were identified by means of gas-liquid chromatography (GLC) by comparison with genuine samples. Thiol VI was isolated in a mixture with II (in a ratio of 3:1 according to GLC data) [the fraction with bp 70-75°C (20 mm)]. A band at 2560 cm^{-1}, which corresponds to thiol IV, and a shoulder at 2525 cm^{-1}, which corresponds to the band observed for pure thiol II, are observed in the IR spectrum of the mixture (liquid film) in the region of SH absorption.

The experimental values of the molecular mass (obtained by mass spectrometry), the results of elementary analysis, and the PMR data correspond to structure IV.

LITERATURE CITED

1. M. G. Rudenko and V. N. Gromova, Dokl. Akad. Nauk SSSR, 81, 207 (1951).

Irkutsk Institute of Organic Chemistry, Siberian Branch. Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, p. 1134, August, 1985. Original article submitted December 6, 1984.

0009-3122/85/2108-0952$09.50

2. I. N. Tits-Skvortsova, A. I. Leonova, and S. Ya. Levina, Zh. Obshch. Khim., 23, 303 (1953).
3. C. D. Hurd and H. J. Anderson, J. Am. Chem. Soc., 75, 3517 (1953).

PHOTOCHEMICAL OXIDATIVE DEHYDROGENATION OF CYCLIC ENAMINO DIKETONES OF THE 8-AZASTEROID SERIES

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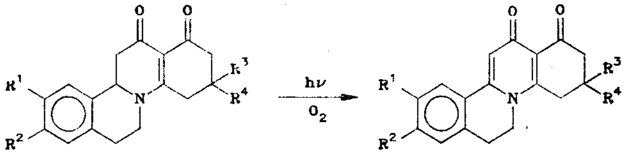
We have previously found [1, 2] that tetracyclic enamino diketones of the 8-azasteroid series (Ia-c) are dehydrogenated under the influence of chloranil or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, as well as catalytically over palladium, to give γ-pyridones IIa-c. These products were also obtained by condensation of dihydroisoquinoline N-oxides with 2-acetylcycloalkane-1,3-diones [1].



I a–c

II a–c

I, II a $R^1=R^2=R^3=R^4=H$; b $R^1=R^2=H$, $R^3=R^4=CH_3$; c $R^1=R^2=CH_3O$, $R^3=R^4=CH_3$

We have shown for the first time that the dehydrogenation of enamino dicarbonyl compounds Ia-c can be realized photochemically by irradiation of alcohol solutions of Ia-c in a quartz reactor with the light of a DRSh-1000 UV lamp at room temperature and while passing oxygen and air through the reaction mixture. The reaction in an oxygen atmosphere takes place in 2.5-4 h, as compared with 15-20 h in an air atmosphere. The yields of tetracyclic γ-pyridones IIa-c, obtained as a result of normal workup, range from 60% to 80%. The structures of the isolated IIa-c were confirmed by the IR, UV, and PMR spectra and were in agreement with the data in [1, 2].

It should be noted that virtually no dehydrogenation occurs in the case of irradiation in an argon atmosphere and in an oxygen atmosphere without irradiation.

The observed photochemical oxidative dehydrogenation is of considerable interest in connection with the problem of the preparation of new biologically active substances of the 8-azasteroid series that are characterized by valuable pharmacological properties [3] and may find application in the synthesis of some alkaloids and other nitrogen-containing rings.

LITERATURE CITED

1. A. A. Akhrem, A. M. Moiseenkov, V. A. Krivoruchko, and A. I. Poselenov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1853 (1973).
2. A. A. Akhrem, F. A. Lakhvich, L. G. Lis, S. U. Sagaidak, N. I. Garbus, and V. Z. Kurbako, Zh. Org. Khim., 17, 1527 (1981).
3. A. A. Akhrem, F. A. Lakhvich, L. G. Lis, and B. B. Kuz'mitskii, Izv. Akad. Nauk Belorussk. SSR, Ser. Khim., No. 6, 81 (1982).

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