Russian Journal of General Chemistry, Vol. 74, No. 3, 2004, pp. 470–471. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 3, 2004, pp. 518–519.

LETTERS TO THE EDITOR

Synthesis of 1,2-Bis(2-phenylethenylsulfanyl)-1-phenylethene from Phenylacetylene and Sodium Disulfide

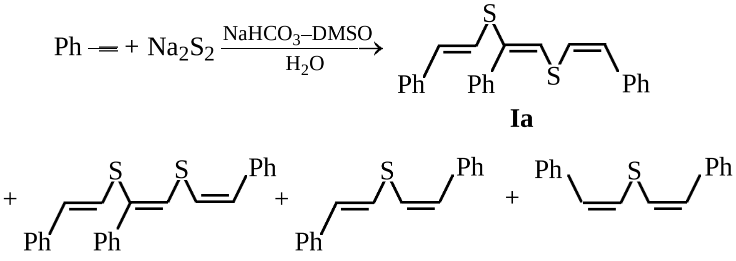
L. A. Oparina, N. K. Gusarova, G. A. Yakimova, L. N. Parshina, O. V. Vysotskaya, A. V. Gusarov, N. A. Korchevin, and B. A. Trofimov

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia

Received April 9, 2003

Polyunsaturated sulfides and disulfides possess a variety of practically useful properties and are widely studied as perspective monomers, comonomers, and building blocks for organic synthesis [1–3].

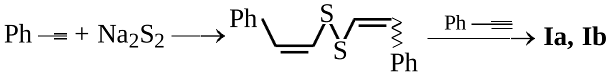
We found that phenylacetylene readily reacts with sodium disulfide in the $NaHCO_3$–DMSO system at room temperature, forming (*E*,*E*,*Z*)- and (*E*,*Z*,*Z*)-1,2-bis(2-phenylethenylsulfanyl)-1-phenylethenes (**Ia**, **Ib**) and (*E*,*Z*)- and (*Z*,*Z*)-bis(2-phenylethenyl) sulfides (**IIa**, **IIb**) with a total yield of 60% and at a 1 : 1 : 10 : 2 ratio (^{1}H NMR data).



Ia

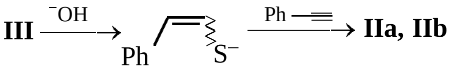
Ib **IIa** **IIb**

Isomers **Ia** and **Ib** were isolated by column chromatography. The expected bis(2-phenylethenyl) disulfide (**III**) was not found in the reaction mixture, even though its formation under these conditions is not excluded. Evidence for this suggestion is provided by the isolation of compound **I** which is probably formed by the known scheme of acetylene insertion into the S–S bond [4, 5].



III

Alkaline cleavage of disulfide **III** and further reaction of intermediate phenylethenylsulfanyl anions with phenylacetylene afford sulfide **II**. Increased basicity of the medium (reaction in the absence of sodium hydrocarbonate) favor this reaction direction, as evidenced by the formation of trace amounts of compound **I** and the higher yield of sulfide **I** (up to 70%).



1070-3632/04/7403-0470 ©2004 MAIK "Nauka/Interperiodica"

Thus, the reaction of sodium disulfide with phenylacetylene is likely to involve initial formation of disulfide **III** and allows preparation of previously unknown polyunsaturated highly reactive reagent **I** containing two sulfide sulfur atoms.

Sodium disulfide was prepared by adding 0.8 g of sulfur to 6.0 g of a hot (60C) sodium sulfide nanohydrate. The reaction mixture was heated at that temperature for an additional 2 h, cooled, diluted with 25 ml of DMSO, stirred for 2 h, and then 2.1 g of $NaHCO_3$, 5.1 g of phenylacetylene, and 0.1 g of hydroquinone (to prevent polymerization of phenylacetylene and reaction products) were added one after another. The mixture was stirred at 20–25°C for 20 h, diluted with 50 ml of water, and treated with ether (6×20 ml). The extracts were combined, washed with water, dried with Na_2SO_4, and the ether was removed in a vacuum to leave an orange brown liquid (3.6 g) containing compounds **I** and **II** (^{1}H NMR data). The isomeric mixture of bis(2-phenylethenylsulfanyl)phenylethenes was isolated by column chromatography on Al_2O_3 (eluent hexane). The second band from bottom was eluted, and the solvent was removed to leave a yellow orange oil that crystallized on standing. ^{1}H NMR spectrum, δ, ppm: 7.56 d.d (4H, 3J 15.6 Hz), 7.48–7.23 m (15H), 6.51 s (1H), 6.44 d.d (2H, ^3J 10.8 Hz), 6.38 s (1H), 6.10 d.d (2H, ^3J 10.8 Hz). Found, %: C 77.54; H 5.58; S 16.90. $C_{24}H_{20}S_2$. Calculated, %: C 77.42; H 5.38; S 17.20.

The ^{1}H NMR spectra were measured on a Bruker DPX-400 spectrometer at 400.13 MHz in $CDCl_3$ solutions, internal reference HMDS.

REFERENCES

1. Trofimov, B.A., Sokolyanskaya, L.V., and Senning, A., *Sulfur Rep.*, 1992, vol. 12, no. 1, p. 1.
2. Trofimov, B.A., *Sulfur Rep.*, 1992, vol. 11, no. 2, p. 207.
3. Chernysheva, N.A., Gusarova, N.K., and Trofimov, B.A., *Zh. Org. Khim.*, 2000, vol. 36, no. 1, p. 11.
4. Trofimov, B.A., *Geteroatomnie proizvodnie atsetilena. Novye monomery, reagenty i poluprodukty* (Heteroatomic Acetylene Derivatives New Monomers, Reagents, and Intrmediate Products), Moscow: Nauka, 1981.
5. Mikhaleva, A.I. and Gusarova, N.K., *Atsetilen: reaktsii i proizvodnie* (Acetylene: Reactions and Derivatives), Novosibirsk: Nauka, 1999.