AN ORIGINAL METHOD FOR THE PREPARATION OF SULFIDES AND DISULFIDES INVOLVING COBALT COMPLEXES

UDC 542.97:547.379.1:547.379.3

U. M. Dzhemilev, N. Z. Baibulatova, T. K. Tkachenko, and R. V. Kunakova

Linear and cyclic sulfides and disulfides have been prepared by the combined reaction of elemental sulfur with alkylacetylenes and alkyl halides catalyzed by low-valence cobalt complexes. Heating equimolar amounts of cyclooctasulfane (S_8) , l-hexyne and butyl chloride in DMF solution of 1:2:4 Co(acac)₂-Ph₃P-Et₃Al at 130°C for 6 h gave a mixture of (1-methyl)-1Z-pentenyl butyl sulfide (I), (1-methyl)-1E-pentenyl butyl sulfide (II), 2,5-dibutylthiophene(III), 3,6-dibutyl-1,2-dithiacyclo-3,5-hexadiene (IV), dibutyl disulfide (V), and dibutyl trisulfide (VI) in 23:19:3:35:15:5 ratio with 82% overall yield.

An increase in the concentration of elemental sulfur and BuCl (S:1-hexyne:BuCl = 2:1:2) gave the predominant formation of vinyl sulfides (I) and (II) with 66% combined yield. Product (IV) was obtained in about 20% yield in the absence of butyl chloride.



Compounds (I) + (II)-(IV) were isolated by vacuum distillation. Sulfides (I) and (II) were separated using preparative gas-liquid chromatography. The structures of the sulfides were supported by IR, ¹H, and ¹³C NMR spectroscopy and mass spectrometry. Sulfides (I) and (II), bp 40-42°C (1 mm). (I): ¹³C NMR spectrum (δ , ppm): 13.84 q (C¹), 21.87 t (C²), 30.29 t (C³), 131.21 d (C⁴), 129.18 s (C⁵), 23.57 q (C⁶), 31.46 t (C⁷), 32.18 t (C⁸), 22.59 t (C⁹), 13.71 q (C¹⁰), M⁺ 172. (II): ¹³C NMR spectrum (δ , ppm): 13.71 q (C¹), 22.06 t (C²), 30.88 t (C³), 126.77 d (C⁴), 128.99 s (C⁵), 17.82 q (C⁶), 31.01 t (C⁷), 32.18 t (C⁸), 22.78 t (C⁹), 13.71 q (C¹⁰), M⁺172. The coupling constants of (III)-(VI) corresponded to reported values [1, 2].

LITERATURE CITED

- 1. U. M. Dzhemilev, F. A. Selimov, V. R. Khafizov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1211 (1986).
- 2. B. V. Aibazov, S. M. Petrov, V. R. Khairullina, and V. G. Yapryntseva, Physicochemical Constants of Organosulfur Compounds [in Russian], Khimiya, Moscow (1964), pp. 64, 72.

Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, p. 1918, August, 1987. Original article submitted April 20, 1987.