

**A. V. BOGDANOVA,  
Corresponding Member of  
the Academy of Sciences  
of the USSR M. F.  
SHOSTAKOVSKII**

and G. I. PLOTNIKOVA

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this reaction proceeds analogously to substituted monoacetylenes, i.e., follows the rule of trans-addition<sup>(9)</sup>. The authors characterized the isomers of 1,4-bis(butylthio)-1,3-butadiene in the form of sulfones obtained by separation of the oxidized mixture of the former. In the work of one of us with Chekulaeva and Kondrat'eva<sup>(13)</sup>, the validity of this rule was also shown for synthesis under ionic conditions of N-containing diacetylene derivatives.

The aim of our investigation was to study the conditions of stereodirection in the syntheses of 1,4-bis-(arylothio)-1,3-butadienes based on diacetylene and aryl mercaptans, to isolate their stereoisomers, and also to examine some of their properties and transformations. For this purpose we chose thiophenol, which forms crystalline 1,4-bis-(phenylthio)-1,3-butadienes with diacetylene. We carried out the synthesis of these compounds under conditions of ionic and radical addition, and also under the simultaneous action of both factors (Table 1). Two crystalline products were isolated, which were subjected—

undergoing oxidation, isomerization, and optical investigation. One of the isolated products proved to be an individual cis-cis isomer of 1,4-bis(phenylthio)butadiene-1,3 (IIa), and the other was a mixture containing 80% IIb and 20% IIc. This mixture was separated after oxidation under conditions

**Table 1**

No.	Catalyst, solvent	Expt. temp., °C	Duration, h	Yield, %	M.p. II, °C
1*	KOH, hydroquinone, dioxane, alcohol	30-35	12	40.0	81-82 IIa
2**	Oxygen of air, heptane	70	12	43.7	40-41 IIb and c
2a	» » »	35	12	8; 19.7	40-41 IIb and c; 81-82 IIa
3***	KOH, oxygen of air, dioxane, alcohol	35-70	9	26.2 ± 23.1	81-82 IIa; 40-41 IIb and c

No.	Catalyst, solvent	Expt. temp., °C	Duration, h	Yield, %	M.p. II, °C
4**	Oxygen of air, heptane (from ethynyl vinyl phenyl thioether)	70	12	80.0 based on I	40-41 IIb, c

\* Crystals of IIa, which separated on cooling the flask to room temperature, were filtered off, washed with water, and recrystallized from alcohol, as in all cases, to a constant melting point.

\*\* The mixture of IIb, c was isolated by crystallization from alcohol of the residue after removal of heptane and thiophenol in vacuo.

\*\*\* The reaction was conducted at 35° for 6 h; the mixture was left overnight at room temperature and then heated at 70° for 3 h. Isolation of IIa as in experiment 1. From the dioxane solution, a noncrystallizing oil was precipitated with water; from this, by distillation in vacuo, a mixture of IIb and c was obtained.

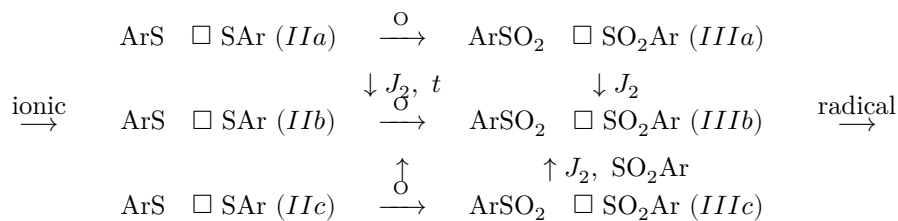
**Table 2**

Isolated stereoisomer	Assigned configuration	Found, % C	Found, % H	Found, % S	Calculated, % C	Calculated, % H	Calculated, % S
ArS	cis	71.14	7.23	23.64	71.06	5.21	23.71
ArS	mixture	71.11	7.85	23.70	71.06	5.21	23.61
ArS	trans						
ArS	and cis-trans						
ArS	cis	71.14	7.23	23.64	71.06	5.21	23.71
ArS	trans	71.11	7.85	23.70	71.06	5.21	23.61

Isolated stereoisomerAr = C <sub>6</sub> H <sub>5</sub>	Assigned con-figuration	Found, % C	Found, % H	Found, % S	Calculated, % C	Calculated, % H	Calculated, % S
M.p., °C	ra-tion	57.31	57.41	19.18	57.16	4.21	19.17
ArSO <sub>2</sub> -SO <sub>2</sub> -Ar	cis-trans						
IIIc							

excluding isomerization. As a result, all three possible isomers of 1,4-bis(phenylsulfonyl)butadiene-1,3 (IIIa, b, c) were isolated and their stereochemical transformations were investigated. To the isolated stereoisomers (Table 2) we assign configurations on the basis of their physical properties and isomeric transformations according to the following scheme, where Ar = C<sub>6</sub>H<sub>5</sub>. The cis-cis structure (IIa) is proved by the quantitative isomerization of it on heating or under the influence of I<sub>2</sub> and illumination

a mixture of IIb and IIc, which is characteristic of 1,4-disubstituted butadienes-1,3<sup>(7,11)</sup>, and also by obtaining from (IIa) sulfone (IIIa) in quantitative yield. The product with m.p. 40-41° is a mixture of IIb and IIc, which is proved by the formation, upon its oxidation, of sulfones readily separable into IIIb and IIIc, similarly to other butadiene sulfones<sup>(11)</sup>. The relation between the melting points of the isolated isomers IIa, b, c and IIIa, b, c is characteristic of the previously studied<sup>(7-13)</sup> substituted butadienes-1,3, i.e., the lowest-melting proved to be the cis-trans isomer, and the highest-melting the trans-trans isomer.



Mixed samples do not give a depression of the melting point, but melt over broad temperature intervals. The smooth isomerization with J<sub>2</sub><sup>(7,11)</sup> of IIIa and IIIc into IIIb also confirms the correctness of the assigned structures.

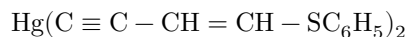
In the UV spectra all the isolated isomers have an absorption band in the region of 240 mμ, which confirms their butadiene structure. In the IR spectra absorption bands were found for IIIa at 702 and 760 cm<sup>-1</sup>, absent from the spectrum of IIIb; for IIIb, a very intense band at 992 cm<sup>-1</sup>, absent from the spectrum of IIIa. The IR spectra of IIIc contain absorption bands at 697, 765, and 992 cm<sup>-1</sup>, which are common to IIIa and IIIb. All the absorption bands

found are characteristic of geometric isomers of butadiene derivatives studied previously (<sup>11-13</sup>).

Thus, the study of syntheses based on diacetylene and thiophenol, carried out under various conditions, showed the possibility of conducting them stereodirectionally. Thus, under ionic conditions (experiment 1) we effected a stereospecific synthesis of *cis-cis*-1,4-bis(phenylthio)butadiene-1,3 (IIa), while under conditions of free-radical addition of thiophenol to diacetylene and under mixed conditions a mixture of all three isomers was obtained, the composition of which depends on the temperature of the experiment (experiments 2 and 2a). Free-radical addition of thiophenol to ethynylvinyl phenyl sulfide (I), which smoothly forms the individual bis-mercuriacetylene derivative (Ia), leads to the formation of a mixture of IIb and IIc (experiment 4).

The results obtained indicate that the interaction of diacetylene with thiols under ionic conditions consists in the addition of 2 molecules of thiol to both acetylenic bonds, similarly to the addition of thiols to mono- (<sup>9,10</sup>) and disubstituted (<sup>10</sup>) acetylenes, i.e., according to the rule of "transnucleophilic addition," and agrees with the conclusions drawn for the addition reaction of butyl mercaptan to ethynylvinyl butyl sulfide (<sup>12</sup>). Under conditions of free-radical interaction of diacetylene with thiophenol, the reaction described proceeds non-stereospecifically, with formation of a mixture of isomers.

**Diacetylene and ethynylvinyl phenyl sulfide (I)** were synthesized by the method we described (<sup>1</sup>). Bismercuriethynylide



(Ia) was prepared as described (<sup>2,12</sup>), in 75% yield, m.p. of Ia 167.5-168° (from toluene).

Found, %: C 46.78; H 2.90; S 12.24

C<sub>20</sub>H<sub>14</sub>S<sub>2</sub>Hg. Calculated, %: C 46.28; H 2.72; S 12.33

**Synthesis of stereoisomeric 1,4-bis(phenylthio)butadienes-1,3.** Syntheses of IIa, b, and c were carried out from diacetylene (4 g) and thiophenol (18 g) (molar ratio 1:2) in a flask equipped with a stirrer and thermometer. Data for the most typical experiments are collected in Table 1; the characteristics of the isolated isomers, in Table 2. In experiment 4 the starting products were ethynylvinyl phenyl sulfide (3 g) and thiophenol (4.1 g). The product with m.p.

81-82° (IIa)—white needle-like crystals, stable on storage at room temperature and unchanged on melting. The product with m.p. 40-41° (IIb and c)—colorless lustrous plates, distills at 200-201° (2.5 mm); on storage it rapidly darkens, turning into an oil from which crystals of diphenyl disulfide with m.p. 58.5-59° separate.

**Preparation of *cis-cis*-1,4-bis(phenylsulfonyl)butadiene-1,3 (IIIa).** To 0.5 g (0.0018 mole) of IIa in 7 ml of abs. ether, with stirring and cooling to

(-5)-(+3°), 0.36 g (0.006 mole) of peracetic acid was added. The mixture was stirred for a further 12 hr; the precipitate of IIIa was filtered off, washed with ether, and recrystallized from alcohol. Yield of IIIa 0.55 g (91.6% of theory). M.p. 157.3-157.8° (Table 2).

**Separation of a mixture of cis-trans and trans-trans isomers (IIb and c).** Under the conditions described above, from 0.5 g of the product with m.p. 40-41° there was obtained in all 0.5 g (84% of theory) of disulfones. The precipitate that first separated from the reaction mixture was isolated, washed with water, and recrystallized from alcohol. M.p. IIIb 188-189°, weight 0.4 g, which amounts to 80% of the mixture of isolated sulfones. From the ether solution, 0.09 g (18%) of IIIc with m.p. 112.5-113° (from alcohol) was obtained.

**Isomerization of cis-cis-1,4-bis(phenylthio)butadiene-1,3 (IIa).** 1.5 g of IIa was heated in a flask with a reflux condenser for 30 min at 200°. After cooling, the product was recrystallized from alcohol, m.p. 40-41° (IIb and IIc), yield 1.4 g (93%).

Found, %: C 70.61; 70.55; H 5.27; 5.19; S 23.49; 23.57  
C<sub>16</sub>H<sub>14</sub>S<sub>2</sub>. Calculated, %: C 71.06; H 5.21; S 23.71

0.10 g of IIa in 2 ml of dioxane with a crystal of J<sub>2</sub> was irradiated with a daylight lamp at 25-30° for 1.5 hr. After removal of the dioxane, washing with water, and crystallization from alcohol, 0.095 g (95%) of product with m.p. 40-41° was obtained. On more prolonged irradiation, the yield of product decreased, and diphenyl disulfide with m.p. 58-59° was isolated from the residue. Isomerization of IIa also occurred during its distillation in vacuum.

**Isomerization of cis-cis-1,4-bis(arylsulfonyl)butadiene-1,3 (IIIa).** 0.1 g of IIIa in dioxane with J<sub>2</sub> was left in sunlight for 2 days. 0.99 g of IIIb with m.p. 188-189° (from alcohol) was isolated, giving no depression with an analytically pure sample of IIIb.

**Isomerization of cis-trans-1,4-bis(phenylarylsulfonyl)butadiene-1,3.** From 0.05 g of IIIc with m.p. 112.5-113° in dioxane with J<sub>2</sub>, after irradiation with a quartz lamp for 3 hr, 0.05 g of IIIb with m.p. 188-189° was isolated, giving no depression with analytically pure IIIb.

Institute of Organic Chemistry named after N. D. Zelinskii  
Academy of Sciences of the USSR

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