REACTION OF SULFUR WITH ORGANIC COMPOUNDS

XXII.* NEW ROUTES TO THE SYNTHESIS OF DI- AND TRIPHENYLTHIOPHENES

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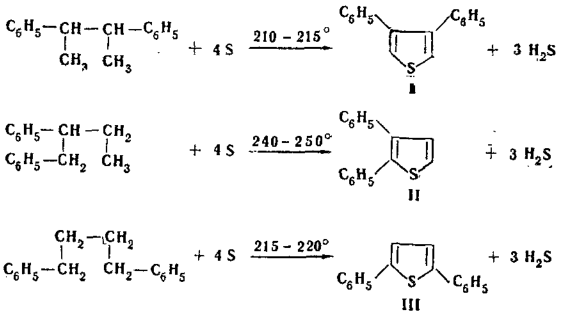
The effect of the number and position of phenyl groups in a four-carbon chain on the yields of di- and triphenylthiophenes in the reaction of sulfur with phenylbutanes was investigated. New, simple methods were developed for the synthesis of 2,3-diphenylthiophene (from 1,2-diphenylbutane), 3,4-diphenylthiophene (from 2,3-diphenylbutane), 2,5-diphenylthiophene (from 1,4-diphenylbutane), and 2,3,5-triphenylthiophene (from 1,3,4-triphenyl-1-butanone). Di-, tri-, and tetrasubstituted butanes, butenes, and butadienes that contain two aromatic substituents attached to the same carbon atom do not react with sulfur under the investigated conditions.

One of us has shown [2-4] that 1- and 2-phenylbutanes react with sulfur with great difficulty to give low yields (5-15%) of 2- or 3-phenylthiophenes, respectively.

We have found that the introduction of a second and third phenyl group into the side chain of phenylbutanes markedly increases the reactivity of the compound with respect to sulfur. Thus 2,3-diphenylbutane reacts smoothly with sulfur at 210-215°C to form 3,4-diphenylthiophene (I) in 50-55% yield. The reaction of sulfur with 1,2-diphenylbutane [the yield of 2,3-diphenylthiophene (II) is 34-36%] and with 1,4-diphenylbutane [the yield of 2,5-diphenylthiophene (III) is 38-42%] proceeds similarly.



These reactions are of considerable preparative interest for obtaining the heretofore difficult-to-obtain 2,3- and 3,4-diphenylthiophenes.

The yields of I-III are not raised when sulfuration catalysts (mercaptobenzothiazole, diphenylguanidine, and mercuriacetamide) are used.

1- and 2-Phenylbutanes react with sulfur with much greater difficulty than the corresponding phenylbutenes. The yields of 2- and 3-phenylthiophenes from $C_6H_5C_4H_9$ are one-fifth to one-eighth the yields from $C_6H_5C_4H_7$ [2,3]. In contrast to this, the yields of diphenylthiophenes in the reaction of sulfur with diphenylbutanes even exceed the yields obtained by the reaction of sulfur with the corresponding diphenylbutenes [5].

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*See [1] for communication XXI.

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TABLE 1. Conditions and Products of the Reaction of Sulfur with Diphenylbutanes, 1,1,4,4-Tetraphenylbutadiene, and 1,3,4-Triphenyl-1-butanone in 1,2-Dichlorobenzene

Starting compound	$m_b : m_S$*	Reaction Temp.	Reaction time, h	Reaction product	mp † °C	Empirical formula	Found %			Calc. %			Yield, %
							C	H	S	C	H	S	
2,3-Diphenyl-butane	1 : 4	210—215	30	I	112,5—113,5	$C_{16}H_{12}S$	81,1	5,2	13,5	81,3	5,1	13,6	50—55
1,2-Diphenyl-butane	1 : 4	240—250	15	II	82—83	$C_{16}H_{12}S$	81,0	5,2	13,3	81,3	5,1	13,6	34—36
1,4-Diphenyl-butane	1 : 4	215—220	30	III	152—153	$C_{16}H_{12}S$	81,1	5,0	13,8	81,3	5,1	13,6	38—42
1,3,4-Triphenyl-1-butanone	1 : 2	250—260	18	IV	142—143	$C_{22}H_{16}S$	84,3	5,1	10,4	84,6	5,1	10,2	42—45
1,1-Diphenyl-butane	1 : 4	240—250	20	—	No reaction								
1,1,4,4-Tetra-phenyl-1,3-butadiene	1 : 2	250—270	20	—	No reaction								

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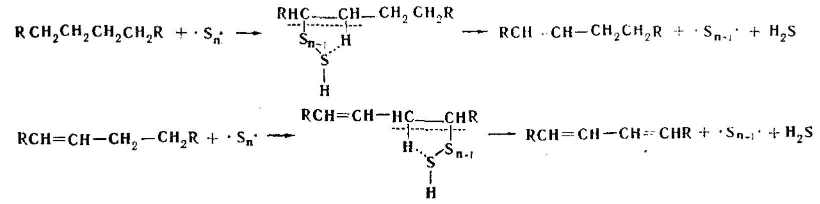
*Compound—sulfur molar ratio.

† The following melting points are reported: I, 112° [14]; II, 83° [5]; III, 152° [14]; and IV, 157° [15].

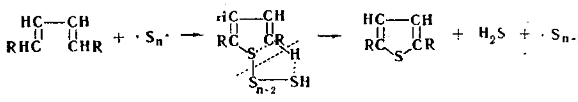
The mechanism of the formation of diphenylthiophenes from the corresponding diphenylbutanes is as follows.

On heating above 169°, cyclic S_8 molecules are opened to form linear $\cdot S_8\cdot$ diradicals capable of both polymerization and depolymerization to $\cdot S_n\cdot$ ($n \geq 2$) [6]. The diradical state of the $\cdot S_n\cdot$ fragments enables them, like carbenes [7], to be incorporated at C—H bonds. This reaction is, in our opinion, responsible for the dehydrogenating action of sulfur — in this case, the conversion of phenylbutane to phenylbutadiene, which is subsequently cyclized to form the thiophene ring. In the case of 1,4-diphenylbutane, these transformations can be represented by two schemes:

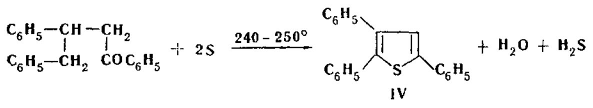
1) formation of diphenylbutene and diphenylbutadiene ($R = C_6H_5$):



2) sulfuration of diphenylbutadiene:



We also obtained 2,3,5-triphenylthiophene (IV) in 45% yield via a new reaction of sulfur with 1,3,4-triphenyl-1-butanone.



In contrast to this, mono- and diphenylbutanones do not form thiophene derivatives by reaction with sulfur.

TABLE 2. Physical Constants and Methods of Synthesis of the Starting Aryl–Aliphatic Hydrocarbons

Hydrocarbon	(pressure, mm)	n_D^{20}	Synthetic scheme	Lit.
1,1-Diphenylbutane	165—167 (25)	1,5570	$C_3H_7CHO + C_6H_6 + AlCl_3$	8
1,2-Diphenyl-1-butane	293—296 (760)	1,5900	$C_2H_5COCH_2C_6H_5 + C_6H_5MgBr - H_2O$	9
1,2-Diphenylbutane	146—148 (10)	1,5531	$C_6H_5CH{=}CH(C_6H_5)CH_2CH_3 + H_2$	10
2,3-Diphenylbutane	mp 124—126	—	$C_6H_5CHBrCH_3 + Na$	11
1,4-Diphenylbutane	mp 51—52	—	$C_6H_5CH_2CH_2Br + Na$	12
Tetraphenyl-1,3-butadiene	mp 193—194	—	—	—

Di-, tri-, and tetrasubstituted butanes, butenes, and butadienes containing two aromatic groups attached to the same carbon atom do not form sulfur-containing heterocycles on heating with sulfur. Thus, for example, prolonged heating of 1,1-diphenylbutane with sulfur at 240° is accompanied only by slight hydrogen sulfide evolution. 1,1,4,4-Tetraphenyl-1,3-butadiene does not react with sulfur on prolonged heating above 250°.

Thus, the reaction of sulfur with di-, tri-, and tetrasubstituted butanes, butenes, and butadienes leads to the formation of a sulfur-containing heterocycle only when the structure of the starting aryl–aliphatic compounds permits.

The conditions for the sulfuration of phenyl-substituted butanes, butenes, butadienes, and 1-butanones and the compounds obtained are presented in Table 1.

EXPERIMENTAL

1,3,4-Triphenyl-1-butanone. Magnesium turnings [7.3 g (0.3 g-atom)] in dry ether were placed in a three-necked flask equipped with a stirrer, reflux condenser, and a dropping funnel, and a solution of 38 g (0.3 mole) of benzyl chloride in 150 ml of ether was added. At the end of the reaction, 62.4 g of benzylideneacetophenone (chalcone) [13] in 100 ml of ether was added. The reaction mixture was heated on a water bath for 4 h, and the resulting viscous mass was decomposed with dilute hydrochloric acid. The precipitate was filtered and recrystallized three times from ethanol to give 70 g (77.4%) of 1,3,4-triphenyl-1-butanone with mp 116-117°. Found %: C 88.1; H 6.5. $C_{22}H_{20}O$. Calculated %: C 88.0; H 6.7.

The physical constants of the remaining synthesized starting hydrocarbons are presented in Table 2.

3,4-Diphenylthiophene (I). A two-necked flask equipped with a reflux condenser and a thermometer was charged with 21.1 g (0.1 mole) of 2,3-diphenylbutane, 12.8 g (0.4 g-atom) of sulfur, and 10 ml of 1,2-dichlorobenzene. The reaction mixture was heated at 210-215° for 30 h, after which it was vacuum distilled to give 14.2 g (61.0%) of I with bp 175-190° (10 mm). Recrystallization from acetic acid and repeated recrystallization from ethanol gave 12.9 g (54.2%) of I with mp 112-113°.

2,3-Diphenylthiophene (II). A mixture of 21.1 g (0.1 mole) of 1,2-diphenylbutane, 12.8 g (0.4 g-atom) of sulfur, and 10 ml of 1,2-dichlorobenzene was heated at 240-250° for 15 h. The reaction mixture was vacuum distilled to give 10.5 g (44.3%) of II with bp 205-210° (30 mm). Recrystallization from alcohol–water gave 8.3 g (35.0%) of II with mp 84-85°.

2,5-Diphenylthiophene (III). A mixture of 21.1 g (0.1 mole) of 1,4-diphenylbutane, 12.8 g (0.4 g-atom) of sulfur, and 5 ml of 1,2-dichlorobenzene was heated at 215-220° for 30 h. Extraction of the reaction mixture with isopropyl alcohol gave 14.4 g of crude III. Subsequent recrystallization from alcohol–benzene (in the presence of 2% activated charcoal) gave 9.5 g (40.2%) of pure III with mp 152-153°.

2,3,5-Triphenylthiophene (IV). A mixture of 15 g (0.05 mole) of 1,2,4-triphenyl-1-butanone, 3.2 g (0.1 g-atom) of sulfur, and 10 ml of 1,2-dichlorobenzene was heated at 240-260° for 18 h. The reaction mixture was vacuum distilled to give 8.2 g (52.3%) of crude IV with bp 250-265° (22 mm). Recrystallization from acetic acid and recrystallization from ethanol gave 6.9 g (44.1%) of IV with mp 142-143°.

Reaction of Sulfur with 1,1,4,4-Tetraphenyl-1,3-butadiene. A mixture of 3.6 g (0.01 mole) of 1,1,4,4-tetraphenyl-1,3-butadiene and 0.64 g (0.02 g-atom) of sulfur was heated at 260-280° for 15 h. The reaction mixture was dissolved in dimethylformamide, the unchanged sulfur was removed by filtration, and the solvent was removed by vacuum distillation. The residue was washed with cold alcohol and recrystallized from ethanol to give 3.2 g of unchanged 1,1,4,4-tetraphenyl-1,3-butadiene with mp 193-194°.

LITERATURE CITED

1. M. G. Voronkov, A. N. Pereferkovich, M. P. Gavar, and G. V. Ozolin', Khim. Geterotsikl. Soedin., 1183 (1970).
2. M. G. Voronkov, A. S. Broun, G. B. Karpenko, and B. L. Gol'shtein, Zh. Obshch. Khim., 19, 1356 (1949).
3. M. G. Voronkov and A. S. Broun, Zh. Obshch. Khim., 18, 70 (1948).
4. M. G. Voronkov and A. N. Pereferkovich, Khim. Geterotsikl. Soedin., 1133 (1967).
5. J. Schmitt, R. Fallard, and M. Suquet, Bull., 1147 (1956); Comptes Rend., 242, 1738 (1956).
6. W. A. Pryor, Mechanisms of Sulfur Reactions, New York (1962).
7. W. Kirmse, Carbene Chemistry, Academic Press (1971).
8. K. Bodendorf, J. Prakt. Chem., 129, 337 (1931).
9. K. T. Serijan and P. H. Wise, J. Am. Chem. Soc., 74, 365 (1952).
10. A. Klages, Ber., 35, 2646 (1902).
11. C. Engler and H. Bethge, Ber., 7, 1127 (1874).
12. J. von Braun and A. Deutsch, Ber., 45, 2171 (1912).
13. S. Kostanecki and G. Rosbach, Ber., 29, 1492 (1869).
14. K. E. Schulte, J. Reich, and L. Horner, Angew. Chem., 72, 920 (1960).
15. S. K. Mitra, J. Indian Chem. Soc., 15, 59 (1938).