# REACTION OF THIOPHENOL WITH UNSATURATED SULFIDES IN THE PRESENCE OF IRON CARBONYL*

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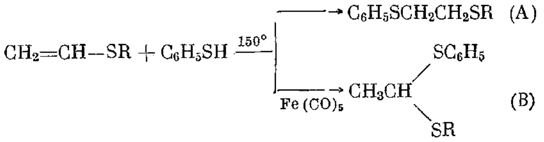
The radical addition of thiols to vinyl sulfides goes easily even in the absence of specially added initiators. In particular, when thiols are vinylated with acetylene it is necessary to take special precautions in order to suppress the secondary reaction of the formed vinyl sulfides with thiols, leading to the formation of 1,2-dialkyl(aryl)thioethanes [1, 2]. The electrophilic addition of thiols to vinyl sulfides is usually accomplished in the presence of acid catalysts like HCl and $SO_2$, using hydroquinone as the radical addition inhibitor; here a mixture of products, formed by Markovnikov as well as anti-Markovnikov addition, is frequently obtained [1]. The radical addition of thiols to allyl sulfides goes with greater difficulty than to vinyl sulfides, and the reaction requires initiation with either peroxides or UV-irradiation [3]. Electrophilic addition to allyl sulfides proceeds only in the presence of ionic catalysts and radical reaction inhibitors [4]. We found that iron pentacarbonyl is an effective inhibitor of radical chain reactions, in which thiyl radicals serve as chain carriers. Thus, $Fe(CO)_5$ inhibits the radical addition of thiols to α-olefins [5] and acetylenes [6, 7], and also the cis – trans isomerization of β-substituted vinyl sulfides [7]. The inhibiting effect of $Fe(CO)_5$ is apparently associated with its ability to trap thiyl radicals according to Scheme (1):

$$Fe(CO)_5 \xrightarrow{RS^{\cdot}} [Fe(CO)_3SR]_2 \xrightarrow{RS^{\cdot}} Fe(SR)_2 \qquad (1)$$

In the present paper we studied the reaction of thiophenol with the following unsaturated sulfides: vinyl aryl and vinyl alkyl sulfides, α- and β-aryl-substituted vinyl sulfides, and α,β-diaryl-substituted vinyl sulfides, and also with allyl phenyl sulfide, in the presence of either iron pentacarbonyl or hexacarbonyldiethylthiodiiron (HTI) $[Fe(CO)_3SC_2H_5]_2$. For comparison the indicated reactions were studied under the same conditions in all cases, but in the absence of iron compounds. The reactions were run in sealed ampuls in an argon atmosphere, and analysis of the reaction mixtures and proof of the structure of the reaction products was accomplished employing NMR spectroscopy. The obtained results are given in Tables 1-3.

As can be seen from Table 1, vinyl phenyl sulfide (I) at 35° quantitatively carries out anti-Markovnikov addition to thiophenol (Expt. 1); the addition of $Fe(CO)_5$ inhibits this reaction completely (Expt. 2). At 150° the reaction of thiophenol with vinyl phenyl sulfide (I) (Expt. 3) and butyl vinyl sulfide (IV) (Expt. 5), in the absence of iron compounds, also proceeds with the exclusive formation of the corresponding 1,2-bissulfides (II) and (V), i.e., products that are formed by anti-Markovnikov addition according to Scheme 2A, but, under the same conditions, in the presence of $Fe(CO)_5$, the manner in which thiophenol adds is reversed completely (Expts. 4, 6), and mercaptals – the products of Markovnikov addition (Scheme 2B) are formed in high yield:



$$CH_2{=}CH{-}SR + C_6H_5SH \xrightarrow{150^\circ} \begin{cases} \longrightarrow C_6H_5SCH_2CH_2SR & (A) \\ \xrightarrow[Fe(CO)_5]{} CH_3CH(SC_6H_5)(SR) & (B) \end{cases} \qquad (2)$$

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TABLE 1. Reaction of Thiophenol with Unsaturated Sulfides*

| Experiment No. | Starting sulfide | T., °C | Additive | Reaction products |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | formed as a result of anti-Markovnikov addition | yield, % | formed as a result of Markovnikov addition | yield, % | other products | yield, % |
| 1 | $C_6H_5SCH{=}CH_2$ (I) | 35 | — | $C_6H_5SCH_2CH_2SC_6H_5$ (II) | 100 | — | 0 | — | 0 |
| 2 | $C_6H_5SCH{=}CH_2$ | 35 | Fe (CO)$_5$ | — | 0 | — | 0 | — | 0 |
| 3 | $C_6H_5SCH{=}CH_2$ | 150 | — | $C_6H_5SCH_2CH_2SC_6H_5$ | 100 | — | 0 | — | 0 |
| 4 | $C_6H_5SCH{=}CH_2$ | 150 | Fe (CO)$_5$ | — | 0 | $C_6H_5SCH(SC_6H_5)CH_3$ (III) | 100 | — | 0 |
| 5 | $C_4H_9SCH{=}CH_2$ (IV) | 150 | — | $C_4H_9SCH_2CH_2SC_6H_5$ (V) | 100 | — | 0 | — | 0 |
| 6 | $C_4H_9SCH{=}CH_2$ | 150 | Fe (CO)$_5$ | — | 0 | $C_4H_9SCH(SC_6H_5)CH_3$ (VI)<br>$C_4H_9SCH(SC_4H_9)CH_3$ (VII)<br>$C_6H_5SCH(SC_6H_5)CH_3$ (III) | 100 | — | 0 |
| 7 | $C_6H_5SC(C_6H_5){=}CH_2$ (VIII) | 150 | — | $C_6H_5CH(SC_6H_5)CH_2SC_6H_5$ (IX) | 56 | $C_6H_5C(SC_6H_5)_2CH_3$ (X) | 27 | $C_6H_5CH(SC_6H_5)CH_3$ (XI) | 17 |
| 8 | $C_6H_5SC(C_6H_5){=}CH_2$ | 150 | Fe (CO)$_5$ | — | 0 | — | 0 | $C_6H_5CH(SC_6H_5)CH_3$ | 100 |
| 9 | $C_6H_5SC(C_6H_5){=}CH_2$ | 150 | [Fe(CO)$_3$SC$_2$H$_5$]$_2$ | $C_6H_5CH(SC_6H_5)CH_2SC_6H_5$ | 10 | — | 0 | $C_6H_5CH(SC_6H_5)CH_3$ | 90 |
| 10 | $C_6H_5SC(C_6H_5){=}CH_2$ | 80 | — | $C_6H_5CH(SC_6H_5)CH_2SC_6H_5$ | 32 | $C_6H_5C(SC_6H_5)_2CH_3$ | 32 | — | 0 |
| 11 | $C_6H_5SC(C_6H_5){=}CH_2$ | 80 | Fe (CO)$_5$ | $C_6H_5CH(SC_6H_5)CH_2SC_6H_5$ | 6 | $C_6H_5C(SC_6H_5)_2CH_3$ | 55 | $C_6H_5CH(SC_6H_5)CH_3$ | 3 |
| 12 | $C_6H_5SC(C_6H_5){=}CH_2$ | 80 | [Fe(CO)$_3$SC$_2$H$_5$]$_2$ | — | 0 | $C_6H_5C(SC_6H_5)_2CH_3$ | 65 | — | 0 |
| 13 | $C_6H_5CH{=}CHSC_4H_9$ (XII) | 150 | — | $C_6H_5CH(SC_6H_5)CH_2SC_4H_9$ (XIII) | 0 | $C_6H_5CH_2CH(SC_6H_5)SC_4H_9$ (XIV) | 50 | — | 0 |
| 14 | $C_6H_5CH{=}CHSC_4H_9$ | 150 | Fe (CO)$_5$ | — | 0 | $C_6H_5CH_2CH(SC_6H_5)SC_4H_9$ | 50 | — | 0 |
| 15 | $C_6H_5CH{=}C(SC_4H_9)C_6H_5$ (XV) | 150 | — | — | 0 | — | 0 | — | 0 |
| 16 | $C_6H_5CH{=}C(SC_4H_9)C_6H_5$ | 150 | Fe (CO)$_5$ | — | 0 | — | 0 | $C_6H_5CH_2CH(SC_4H_9)C_6H_5$ (XVI) | 50 |

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* Compounds (I)-(IV), (VIII)-(XII), (XV), and (XVI) were identified in the reaction mixtures by comparison with authentic specimens. In Expt. Nos. 10-16, besides the indicated compounds, only the starting compounds were present in the reaction mixture.

TABLE 2. Reaction of Thiophenol with Phenyl Allyl Sulfide (XVII)

| Expt. No. | T., °C | Additive | Addition products* | | | |
|---|---|---|---|---|---|---|
| | | | as a result of anti-Markovnikov addition | yield, % | as a result of Markovnikov addition | yield, % |
| 1 | 35 | — | — | 0 | — | 0 |
| 2 | 35 | $Fe(CO)_5$ | — | 0 | — | 0 |
| 3 | 80 | — | $C_6H_5S(CH_2)_3SC_6H_5$<br>(XVIII) | 24 | $C_6H_5SCH_2CH(SC_6H_5)CH_3$<br>(XIX) | 2 |
| 4 | 80 | $Fe(CO)_5$ | — | 0 | — | 0 |
| 5 | 150 | — | (XVIII) | 32 | (XIX) | 7 |
| 6 | 150 | $Fe(CO)_5$ | (XVIII) | 2 | (XIX) | 3 |

* In Expt. Nos. 3, 5, and 6, besides the indicated compounds, only the starting phenyl allyl sulfide was present in the reaction mixture.

Thus, acetaldehyde diphenyl mercaptal (III) is formed in the case of vinyl phenyl sulfide, while a mixture of mercaptals, containing acetaldehyde butyl phenyl mercaptal (VI) and the two symmetrical mercaptals (III) and (VII), is formed in the case of butyl vinyl sulfide. The course of the reaction of thiophenol with 1-phenyl-1-phenylthioethylene (VIII) (Expts. 7-12) is more complex. Apparently, the high nucleophilicity of this unsaturated sulfide facilitates the electrophilic addition of thiophenol; consequently, even in the absence of iron compounds both at 80° and at 150°, together with the product of anti-Markovnikov addition, namely 1-phenyl-1,2-diphenylthioethane (IX), the product of Markovnikov addition, namely 1-phenyl-1,1-diphenylthioethane (X), is also formed (Expts. 7, 10). At 80° this reaction in the presence of either $Fe(CO)_5$ or HTI leads, as was to be expected, to the formation of the product of Markovnikov addition (X), with only a small amount of the isomeric product (IX) as impurity (Expts. 11, 12). In addition, it was found that running the discussed reaction at 150° leads to the formation of a certain amount of 1-phenyl-1-phenylthioethane (XI) (Expt. 7); in the presence of iron carbonyls this sulfide becomes the main reaction product (Expts. 8, 9). This is explained by the fact that, as was shown earlier [8], 1-phenyl-1,1-diphenylthioethane is thermally unstable and at 150°, in the presence of thiophenol, it undergoes decomposition with the formation of the saturated monosulfide and diphenyl disulfide according to the scheme:

$$\underset{(X)}{C_6H_5—C(SC_6H_5)_2—CH_3} \xrightarrow[150°]{C_6H_5SH} \underset{(XI)}{C_6H_5—CH(SC_6H_5)—CH_3} + (C_6H_5S)_2 \qquad (3)$$

As a result, in the case of 1-phenyl-1-phenylthioethylene it can be stated that also at 150° the addition of thiophenol in the presence of either $Fe(CO)_5$ or HTI proceeds in harmony with the formation of mercaptol (X). The reaction of thiophenol with 1-phenyl-2-butylthioethylene (XII) (Expts. 13, 14) proceeds with more difficulty than in the case of the vinyl sulfides, which contain a terminal methylene group; here the conversion of the starting sulfide reaches only 50%. In this case the manner in which thiophenol adds by both the radical and the electrophilic type is apparently the same; actually, the same product, namely 1-phenyl-2-butylthio-2-phenylthioethane (XIV),* is formed both in the absence and the presence of $Fe(CO)_5$. Although in the given case it is difficult to estimate the effect of the $Fe(CO)_5$ additive on the reaction course, still, by analogy with the other studied examples, it is possible to assume that also here the addition of thiophenol in the absence of $Fe(CO)_5$ goes by a radical mechanism, while in the presence of $Fe(CO)_5$ it has a heterolytic character. In the absence of iron carbonyls the addition of thiophenol to $\alpha,\beta$-diaryl-substituted vinyl sulfides practically does not go (Expt. 15); in the presence of $Fe(CO)_5$ the sole reaction product was 1,2-diphenyl-1-butylthioethane (XVI) (Expt. 16), the formation of which is apparently also explained by the initial Markovnikov addition of thiophenol and subsequent decomposition of the obtained adduct by a scheme analogous to Scheme (3).

As was to be expected, the radical addition of thiophenol to phenyl allyl sulfide proceeds with more difficulty than to phenyl vinyl sulfide (see Table 2, Expts. 1, 3, 5). Iron pentacarbonyl inhibits this reaction

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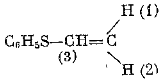
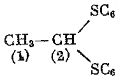
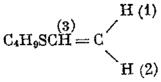
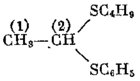
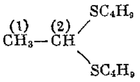
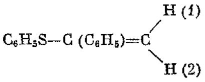
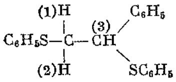
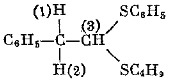
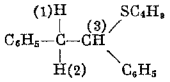
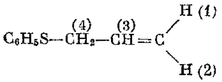
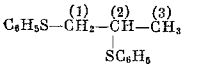
* The identity of the adducts, obtained in Expts. 13 and 14 (see Table 1), was proved by comparing their NMR spectra. In this reaction the formation of both the compound $C_6H_5CH_2CH(SC_6H_5)SC_4H_9$ (XIV) and the compound $C_6H_5CH(SC_6H_5)CH_2SC_4H_9$ (XIII) is formally possible. Assignment of the obtained NMR spectrum to structure (XIV) was made on the basis of the characteristic chemical shift of the $CH_2$ group in the fragment $C_6H_5-CH_2-C-S$ [compare with structure (XVI)]. For compound (XIII) the signal of the protons of the $CH_2$ group in the fragment $C_6H_5-CH-CH_2-S$ is apparently, as was to be expected, shifted downfield by 0.3-0.4 ppm [compare with structure (IX)].

TABLE 3. Parameters of NMR Spectra of Studied Compounds

| Compound | Chemical shifts, ppm, and spin – spin coupling constants, Hz |
|---|---|
|  (I) | $\delta_1 = 5,18$(d); $\delta_2 = 5,15$(d); $\delta_3 = 6,38$(dd);<br>$J_{12} = 0$; $J_{13} = 9,3$; $J_{23} = 17,3$ |
| $C_6H_5S\overset{(1)}{C}H_2\overset{(1)}{C}H_2SC_6H_3$ (II) | $\delta_1 = 2,94$(s) |
|  (III) | $\delta_1 = 1,46$(d); $\delta_2 = 4,44$(q) $J_{12} = 6,7$ |
|  (IV) | $\delta_1 = 5,03$(d); $\delta_2 = 4,97$(d); $\delta_3 = 6,27$(dd);<br>$J_{12} = 0$; $J_{13} = 10,5$; $J_{23} = 17,2$ |
| $C_4H_9S\overset{(1)}{C}H_2\overset{(2)}{C}H_2SC_6H_5$ (V) | Multiplet, characteristic for the $A_2B_2$ system, in the range $\delta = 2.20-3.01$ |
|  (VI) | $\delta_1 = 1,45$(d); $\delta_2 = 4,12$(q) $J_{12} = 6,7$ |
|  (VII) | $\delta_1 = 1,45$(d); $\delta_2 = 3,81$(q); $J_{12} = 6,7$ |
|  (VIII) | $\delta_1 = 5,51$(s); $\delta_2 = 5,25$(s); $J_{12} = 0$ |
|  (IX) | $\delta_1 = 3,27$(dd); $\delta_2 = 3,45$(dd); $\delta_3 = 4,31$(dd);<br>$J_{12} = 13,0$; $J_{13} = 5,3$; $J_{23} = 9,3$ |
| $C_6H_5C(SC_6H_5)_2\overset{(1)}{C}H_3$ (X) | $\delta_1 = 1,76$(s) |
| $\overset{(1)}{C}H_3-\overset{(2)}{C}H(C_6H_5)SC_6H_5$ (XI) | $\delta_1 = 1,47$(d); $\delta_2 = 4,25$(q); $J_{12} = 7,3$ |
| cis-$C_6H_5\overset{(1)}{C}H=\overset{(2)}{C}HSC_4H_9$ (XII) | $\delta_1 = 6,05$(d); $\delta_2 = 6,28$(d); $J_{12} = 10,5$ |
|  (XIV) | $\delta_1 = 2,92$(dd); $\delta_2 = 3,09$(dd); $\delta_3 = 4,19$(dd);<br>$J_{12} = 12,6$; $J_{13} = 6,0$; $J_{23} = 8,0$ |
| cis- and trans- $C_6H_5\underset{(1)}{C}H=C(SC_4H_9)C_6H_5$ (XV) | $\delta_1 = 6,68$(s) (cis –); $\delta_1 = 6,88$(s) (trans –) |
|  (XVI) | $\delta_1 = 2,99$(dd); $\delta_2 = 3,14$(dd); $\delta_3 = 3,98$(dd);<br>$J_{12} = 12,0$; $J_{13} = 7,3$; $J_{23} = 8,0$ |
|  (XVII) | $\delta_1 = 4,98$(m); $\delta_2 = 4,89$(m); $\delta_3 = 5,76$(m);<br>$\delta_4 = 3,36$(m); $J_{12} = 1,2$; $J_{13} = 16,8$; $J_{23} = 9,3$;<br>$J_{14} = 1,3$; $J_{24} = 0,9$; $J_{34} = 6,4$ |
| $C_6H_5S\overset{(1)}{C}H_2\overset{(2)}{C}H_2\overset{(1)}{C}H_2SC_6H_5$ (XVIII) | $\delta_1 = 2,80$(t); $\delta_2 = 1,72$(m); $J_{12} = 7,1$ |
|  $C_6H_5S-\overset{(1)}{C}H_2-\underset{SC_6H_5}{\overset{(2)}{C}H}-\overset{(3)}{C}H_3$ (XIX) | $\delta_1 = 2,85$(m); $\delta_2 = 3,0$(m); $\delta_3 = 1,33$(d); $J_{23} = 6,$ |

Note: s = singlet; d = doublet; dd = doublet of doublets; t = triplet; q = quarter; m = multiplet.

but in this case, in contrast to phenyl vinyl sulfide, even at 150°, only a small amount of the Markovnikov addition product is formed, which is associated with the much smaller nucleophilicity of the double bond in phenyl allyl sulfide.

As a result, it was shown in a number of examples that the addition of thiophenol to vinyl sulfides and phenyl allyl sulfide, in the absence of either added initiators or catalysts, in most cases does not obey the Markovnikov rule and has a radical mechanism. Only in the case of strongly nucleophilic sulfides (for example, 1-phenyl-1-phenylthioethylene) does this direction compete with Markovinikov addition, which has a heterolytic mechanism.

In the presence of iron pentacarbonyl or HTI, at elevated temperature, thiophenol adds to vinyl sulfides in harmony with the Markovnikov rule. Apparently, also in this case, iron carbonyls effectively inhibit radical addition, in this way creating conditions for the heterolytic Markovnikov addition of thiophenol.

## EXPERIMENTAL

The Preparation of 1-Phenyl-1-phenylthioethylene (VIII) and Vinyl Phenyl Sulfide (I). This was carried out using the modified procedure reported in [9]. Into a 0.5 liter steel autoclave were charged 64 g of 1-phenyl-1,2-diphenylthioethane and a solution of $(CH_3)_3COK$ (0.8 g of K in 100 ml of $t\text{-}C_4H_9OH$); the autoclave was purged with $N_2$ and then $C_2H_2$, after which $C_2H_2$ was admitted up to a pressure of 12 atm, and the autoclave was heated at 110° for 5 h. The excess $t\text{-}C_4H_9OH$ was distilled from the obtained reaction mixture, and 40 ml of water was added to the residue; the organic layer was separated, while the aqueous layer was extracted with ether, and the ether extracts were combined with the main portion and the whole was dried over $CaCl_2$. After distilling off the solvent the residue was vacuum-distilled. We obtained 28 g (65%) of (VIII); bp 141-143° (2 mm); $n_D^{30}$ 1.6282; $d_4^{30}$ 1.0988 and 19 g (70%) of (I); bp 54° (2 mm). The structure of both sulfides was confirmed by the NMR spectra (see Table 3).

Reaction of Thiophenol with Unsaturated Sulfides. All of the experiments listed in Tables 1 and 2 were run using the following procedure. In a 4 ml glass ampul were placed 5-10 mmoles of the unsaturated sulfide, 1-3 mole % of the iron compound, and 10-20 mmoles of thiophenol. The ampul was cooled to −70°, evacuated, filled with argon, sealed, and placed in a thermostat for 8 h at either 80 or 150°, or for 72 h at 35°. The experiments without the iron additive were run in the same manner. The reaction mixtures, which contained iron compounds, were washed with 15% HCl solution, then with water, dried over $CaCl_2$, and analyzed by the NMR method (in a separate experiment it was shown that this treatment does not affect the ratio of the reaction products). The yield of the reaction products was determined by comparing the integral intensities of the characteristic signals of the protons of each product. The NMR spectra were taken on a "Perkin – Elmer" R-12 spectrometer, using hexamethyldisiloxane ($\delta = 0.05$ ppm) as the internal standard.

The addition of thiophenol to vinyl phenyl sulfide was also carried out on a preparative scale using the conditions of Expt. 4 (see Table 1). The 1,1-diphenylthioethane was obtained in quantitative yield; bp 169-170° (2 mm); $n_D^{20}$ 1.6312. According to [10]; bp 166-171° (1.2 mm); $n_D^{20}$ 1.6317.

## CONCLUSIONS

We accomplished the Markovnikov addition of thiophenol to various $\alpha,\beta$-unsaturated sulfides in the presence of $Fe(CO)_5$ or $[Fe(CO)_3SC_2H_5]_2$, which inhibit the radical direction of the reaction.

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