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Reaction of Sulfenyl Chlorides with Sulfides. IV.[1] The Reaction with 1-Phenylvinyl Sulfides

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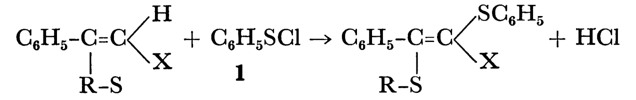
The reaction of benzenesulfenyl chloride (**1**) with α-methylthiostyrene (**2**) gives no adducts but causes the formation of α-methylthio-β-phenylthiostyrene (**3**) in an almost quantitative yield.[2] Since styrene is known to react with sulfenyl chlorides to give the addition products,[3] the presence of a sulfur atom at the alpha-position of styrene appears to be essential for the displacement reaction on β-hydrogen by a phenylthio group to occur. This paper describes the results of an extended investigation on the reaction of 1-phenylvinyl sulfides with **1**.

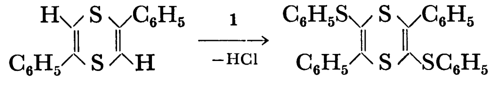
The reaction of α-phenylthiostyrene (**4**) with one equivalent of **1** was examined at room temperature in carbon tetrachloride. Evolution of hydrogen chloride was observed and an isomeric mixture of *cis*- and *trans*-α,β-bis(phenylthio)styrene (**5**) was obtained in 70% yield.



$$C_6H_5\text{-}\underset{\text{R-S}}{C}{=}C\begin{matrix}H\\X\end{matrix} + \underset{\mathbf{1}}{C_6H_5SCl} \rightarrow C_6H_5\text{-}\underset{\text{R-S}}{C}{=}C\begin{matrix}SC_6H_5\\X\end{matrix} + HCl$$

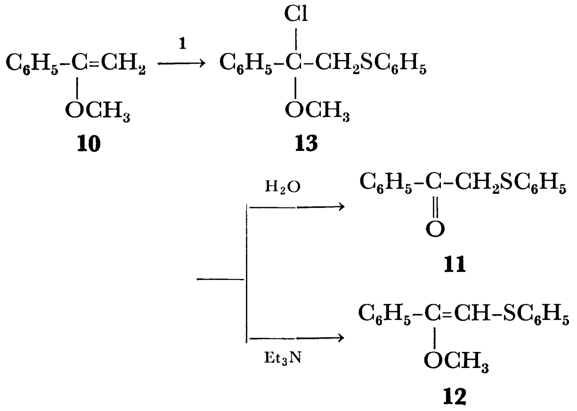
2; R=CH_3, X=H	**3**; R=CH_3, X=H
4; R=C_6H_5, X=H	**5**; R=C_6H_5, X=H
6; R=C_6H_5, X=Cl	**7**; R=C_6H_5, X=Cl

In a similar manner the reaction of α-phenylthio-β-chlorostyrene (**6**) with **1** led to the formation of α,β-bis(phenylthio)-β-chlorostyrene (**7**) in 48% yield. When 2,5-diphenyl-1,4-dithiin (**8**) was treated with two equivalents of **1** in chloroform, 2,5-diphenyl-3,6-bis(phenylthio)-1,4-dithiin (**9**) was obtained in 54% yield.



8 **9**

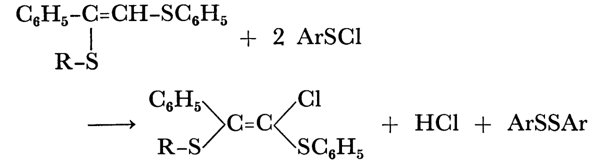
In contrast to the 1-phenylvinyl sulfides, the oxygen analog, α-methoxystyrene (**10**), afforded the Markownikoff-type adduct: the isolated product from the reaction of **10** with **1** was only α-phenylthioacetophenone (**11**), which would be formed by hydrolysis of the adduct **13** during the course of work-up. When the reaction mixture obtained from **10** and **1** was treated with triethylamine, α-methoxy-β-phenylthiostyrene



$$\underset{\mathbf{10}}{C_6H_5\text{-}\underset{OCH_3}{C}{=}CH_2} \xrightarrow{1} \underset{\mathbf{13}}{C_6H_5\text{-}\overset{Cl}{\underset{OCH_3}{C}}\text{-}CH_2SC_6H_5} \xrightarrow{H_2O} \underset{\mathbf{11}}{C_6H_5\text{-}\underset{O}{\overset{}{C}}\text{-}CH_2SC_6H_5}, \quad \xrightarrow{Et_3N} \underset{\mathbf{12}}{C_6H_5\text{-}\underset{OCH_3}{C}{=}CH\text{-}SC_6H_5}$$

(**12**) was obtained in 63% yield. The marked difference in behavior between the sulfur analog and the oxygen analog is of interest for more detailed study.

In extending the β-phenylthio displacement reaction to **3**, a new chlorination reaction was found; the treatment of an isomeric mixture of **3** with one equivalent of **1** in carbon tetrachloride at room temperature led to the formation of an unexpected α-methylthio-β-phenylthio-β-chlorostyrene (**14**) in 34% yield. Although hydrogen chloride was evolved, the anticipated α-methylthio-β,β-bis(phenylthio)styrene was missing and *ca.* 40% of **3** was recovered. Diphenyl disulfide was also isolated in 81% yield. When **3** was treated with one equivalent of *p*-toluenesulfenyl chloride, the results were similar to those obtained from **1** except that di-*p*-tolyl disulfide was obtained in 67% yield instead of diphenyl disulfide. The results indicate that **14** arises according to the stoichiometry indicated below.



$$C_6H_5\text{-}\underset{\text{R-S}}{C}{=}CH\text{-}SC_6H_5 + 2\,ArSCl \longrightarrow \begin{matrix}C_6H_5\\ \text{R-S}\end{matrix}{>}C{=}C\begin{matrix}Cl\\SC_6H_5\end{matrix} + HCl + ArSSAr$$

14; R=CH_3
7; R=C_6H_5

The reaction of **5** with **1** also afforded β-chlorinated product, α,β-bis(phenylthio)-β-chlorostyrene (**7**), in 22% yield. In this case, α,β,β-tris(phenylthio)styrene (**15**) was also isolated in 16% yield.

Treatment of **5** with two equivalents of methanesulfenyl chloride in carbon tetrachloride afforded **14** in 24% yield together with 61% methyl phenyl disulfide as detected by vpc analysis. Thus the chlorination reactions to give **14** may be supposed to involve the anti-Markownikoff addition of benzenesulfenyl

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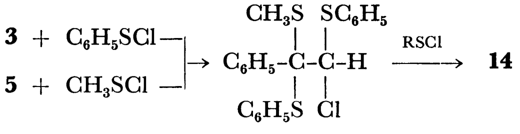
chloride to **3** and methanesulfenyl chloride to **5**, giving rise to the formation of **16** as an intermediate.



$$\left.\begin{array}{l}\mathbf{3} + C_6H_5SCl \\ \mathbf{5} + CH_3SCl\end{array}\right] \rightarrow \begin{array}{c} CH_3S\ \ SC_6H_5 \\ |\quad\ | \\ C_6H_5\text{-}C\text{-}C\text{-}H \\ |\quad\ | \\ C_6H_5S\ \ Cl\end{array} \xrightarrow{RSCl} \mathbf{14}$$

16

Experimental

*α,β-Bis(phenylthio)styrene (**5**).* To a mixture of **4**[4] (5.0 g, 0.023 mol) and carbon tetrachloride (100 ml), **1**[5] (3.5 g, 0.024 mol) was added at room temperature and the solution was stirred until it turned pale yellow and no further color change took place. The mixture was washed with saturated sodium bicarbonate, dried over anhydrous sodium sulfate and concentrated. The resulting yellow oil was chromatographed on alumina. Elution with petroleum ether-benzene (2 : 1) gave 5.3 g (70%) of **5** as viscous oil. M^+: 320; IR (cm^{-1}): 1580, 1540, 1025, 820, 760, 740, 690, 680; NMR (τ): 2.3—3.1 (m).

Found: C, 74.67; H, 4.91%. Calcd for $C_{20}H_{16}S_2$: C, 74.96; H, 5.03%.

An analytically pure sample of **5** showed the presence of two components attributed to the geometrical isomer on vpc.

*α,β-Bis(phenylthio)-β-chlorostyrene (**7**).* The reaction of **6**[6] with **1** was carried out as for **5**. The crude product mixture was chromatographed on alumina. Elution with benzene followed by recrystallization from petroleum ether-benzene (2 : 1) gave 48% of pure **7**, mp 89°C. M^+: 354; IR (cm^{-1}): 1580, 1540, 855, 750, 735, 690; NMR (τ): 2.90 (5H, s), 2.6—3.0 (10H, m).

Found: C, 67.93; H, 4.44; S, 17.87%. Calcd for $C_{20}H_{15}ClS_2$: C, 67.68; H, 4.26; S, 18.07%.

*2,5-Diphenyl-3,6-bis(phenylthio)-1,4-dithiin (**9**).* A solution of **8**[7] (1.5 g, 0.0056 mol) in chloroform (15 ml) was allowed to react with **1** (1.7 g, 0.012 mol) at room temperature for 30 min. The reaction mixture was washed, dried and concentrated. The residual oil was chromatographed on alumina. The yellow solid eluted with benzene was recrystallized from ethanol to give 1.4 g (54%) of **9**, mp 150—152°C. M^+: 484; IR (cm^{-1}): 1570, 1525, 1068, 1020 837, 775, 738, 692; NMR (τ): 2.72 (10H, s), 2.60—2.45 (6H, m), 2.32—2.28 (4H, m).

Found: C, 69.34; H, 3.98; S, 26.02%. Calcd for $C_{28}H_{20}S_4$: C, 69.38; H, 4.16; S, 26.46%.

*α-Methoxy-β-phenylthiostyrene (**12**).* To a solution of **10**[8] (13.4 g, 0.1 mol) in carbon tetrachloride (100 ml) was slowly added **1** (14.5 g, 0.1 mol) at 0°C and then triethylamine (18 g, 0.18 mol). Usual work-up and distillation under reduced pressure gave 15.2 g (63%) of **12**, bp 149—152°C/2 mmHg. M^+: 242; IR (cm^{-1}): 2820, 765, 740; 700; NMR (τ): 6.39 (3H, s), 3.99 (1H, s), 2.7 (10H, m) and 6.34 (3H, s), 4.61 (1H, s), 2.7 (10H, m).

Found: C, 74.08; H, 5.80; S, 13.35%. Calcd for $C_{15}H_{14}OS$: C, 74.35: H, 5.82; S, 13.23%.

*α-Methylthio-β-phenylthio-β-chlorostyrene (**14**).* To a solution of **3** (8.0 g, 0.031 mol) in carbon tetrachloride (50 ml) was added **1** (5.0 g, 0.035 mol). After decolorization of **1**, the mixture was washed with saturated sodium bicarbonate, dried and concentrated. The oily residue was chromatographed on alumina. Elution with petroleum ether gave 3.1 g (81%) of diphenyl disulfide and that with benzene afforded 3.1 g (34%) of **14**, mp 98—99°C. M^+: 292; IR (cm^{-1}): 1580, 1540, 858, 750, 735, 700, 692, 622; NMR (τ): 8.15 (3H, s), 2.80 (5H, s), 2.75 (5H, m).

Found: C, 61.57; H, 4.50; S, 22.01%. Calcd for $C_{15}H_{13}ClS_2$: C, 61.54; H, 4.44; S, 21.90%.

A similar treatment of **3** with *p*-toluenesulfenyl chloride gave 43% of **14** and 67% of di-*p*-tolyl disulfide.

*Reaction of **5** with **1**.* The reaction of **5** (5.7 g, 0.018 mol) with **1** (4.1 g, 0.028 mol) in carbon tetrachloride (15 ml) was carried out as described for the reaction of **3** with **1** to give 1.1 g of diphenyl disulfide, 1.4 g (22%) of **7**, and 1.3 g (16%) of *α,β,β*-tris(phenylthio)styrene, mp 79—80°C (lit,[9] 77—78°C).

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