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Free Radical Addition of Thiophenol to 3-Substituted 1-Alkyne with or without Migration of the Substituents

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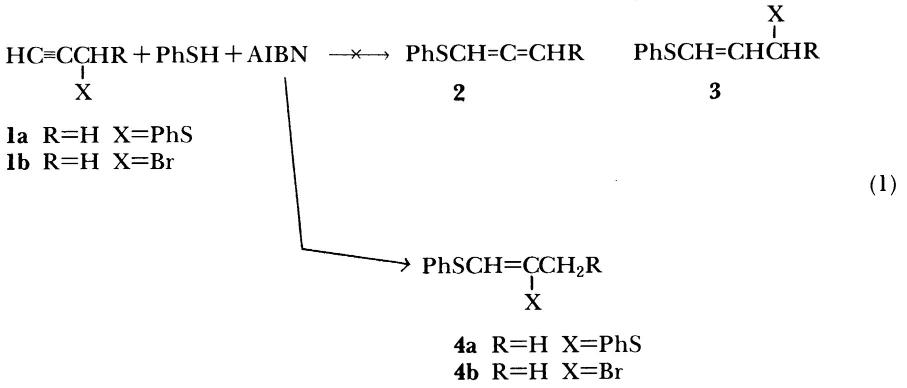
Synopsis. Thiophenol reacts with 3-phenylthio- and 3-bromo-1-alkyne in the presence of radical initiator to give 1,2-bis(phenylthio)-1-alkene and 2-bromo-1-phenylthio-1-alkene.

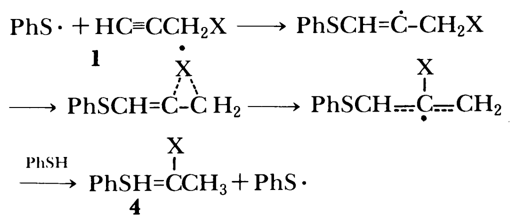
The free radical addition of a thiol to carbon–carbon double or triple bond is a well-established reaction.[1] It is one of the most useful methods to synthesize sulfides, under mild conditions. We studied further application of this reaction. We wish to report that the radical addition of thiophenol to 3-substituted 1-alkyne proceeds with or without migration of the substituents.

By heating thiophenol and 3-substituted 1-propyne such as **1** (X=SPh and Br; R=H), in benzene in the presence of azobis-isobutyronitrile (AIBN), we obtained neither 1-(phenylthio)allene (**2**) nor 3-substituted 1-phenylthio-1-alkene (**3**), but rearranged products **4** (Eq. 1). When the substituent (X) was PhS, 1,2-bis(phenylthio)-1-propene (**4a**) was obtained in an almost quantitative yield. However, when X was Br, 2-bromo-1-phenylthio-1-propene was obtained only in 45% yield with evolving HBr gas.



(1)

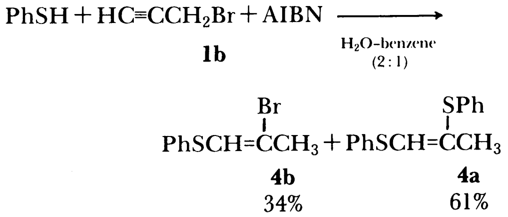
At first glance, this reaction seems to proceed with migration of the substituent (X) with a bridged radical intermediate (Eq. 2).[2] However, a more plausible mechanism is suggested as Scheme 1. It involves an initial attack of PhS· to triple bond followed by elimination of Br· or PhS·, because β-bromo or β-phenylthio radical easily eliminates Br· or PhS· to form double bond,[3] and the formation of 1-(phenylthio)allenes is quite reasonable. 1-(Phenylthio)allenes are more reactive than **1**, and addition of HBr or PhSH occurs smoothly to give the adducts (**4a**, **b**).



(2)

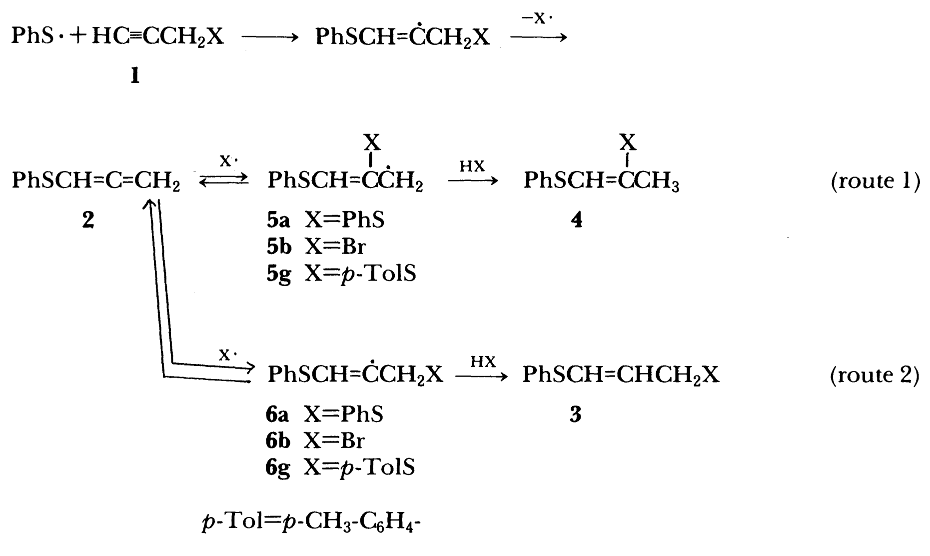
Regioselectivity and the mechanism of the addition of PhSH to allenes have been discussed by Heiba.[4] According to his discussion, the reaction involves (a) an initial attack of PhS· to allene and (b) hydrogen transfer to transient radical. The free radical intermediate formed by route 2 should undergo the reverse reaction.[5] However, the initial radical intermediate formed via route 1, although it may be initially non-allylic, undergoes rapid rotation of 90° around the C–C axis to form the conformation of the stable allylic radical. Such a rotation must have a very low activation energy and the resonance energy of allylic radical will make the reaction via route 1 faster than that via route 2.

This mechanism was supported by the following results. In the case of propargyl bromide, a small amount (<5%) of 1,2-bis(phenylthio)-1-propene (**4a**) was obtained as a by-product, and generation of HBr gas was observed. When two phase system of benzene-H_2O was used as solvent to remove HBr from the organic layer, the yield of **4b** decreased to 34%, and that of **4a** increased to 61% (Eq. 3).



(3)

When 3-(4-methylphenylthio)-1-propyne (**1g**) was



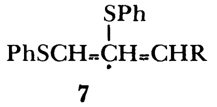
Scheme 1.

treated with 2 equivalent amount of thiophenol and 0.3 equivalent of AIBN, **4a** was obtained in 15% yield (Eq. 4). Although 1-(phenylthio)allene was not isolated, these results indicated the formation of 1-(phenylthio)allene intermediate. However, to our surprise, 2-(4-methylphenylthio)-1-phenylthio-1-propene (**4g**) was not obtained, but 3-(4-methylphenylthio)-1-phenylthio-1-propene (**3g**) was obtained in 66% yield.

$$\underset{\mathbf{1g}}{p\text{-TolSCH}_2\text{C}{\equiv}\text{CH}} + \underset{(2\ \text{equiv})}{\text{PhSH}} \xrightarrow{\text{AIBN}} \underset{15\%}{\mathbf{4a}} + \underset{\substack{\mathbf{3g}\\66\%}}{p\text{-TolSCH}_2\text{CH=CHSPh}} \qquad (4)$$

These results were explained as follows. Allylic radical **5g** was more stable than **5a**, and the activation energy of **5g** for hydrogen abstraction must be higher than that of **5a**. It suggests that the reaction of **1g** via route 1 is slower than that of **1a**. However, the stability of allylic radical **6** was not so influenced by aryl groups of the sulfides as that of **5**. And when **1g** was used, the relative reaction rate via route 2 became faster than that via route 1.

Although R in **1** is H, no simple adduct of thiophenol was obtained, when R is an alkyl group such as CH_3, n-C_3H_7, or n-C_5H_{11}, and X is SPh, a simple adduct like **3** was also obtained. The formation of such by-products as **3c**, **3d**, and **3f**, was similarly explained: Allylic radical **7** was more stable than **5a**, and the relative reaction rate to give **4** became slower. Results were summarized in Table 1.



$$\text{PhSCH}{\cdots}\overset{\text{SPh}}{\underset{\bullet}{\text{C}}}\text{H}{\cdots}\text{CHR}$$

7

R=CH_3, n-C_3H_7, n-C_5H_{11}

When the substituents (X) is OH, OAc, and OCH_2Ph, which are not good leaving groups for the

Table 1. Free Radical Addition of PhSH to **1**

1	R	X	Products (yield/%,[a] E/Z[b])	
1a	H	PhS	$\text{PhSCH=}\underset{\text{SPh}}{\text{C}}\text{CH}_2$ (97, 69/31) **4a**	
1b	H	Br	$\text{PhSCH=}\underset{\text{Br}}{\text{C}}\text{CH}_3$ (45, 70/30) **4b**	
1c	CH_3	PhS	$\text{PhSCH=}\underset{\text{SPh}}{\text{C}}\text{C}_2\text{H}_5$ (53, 64/36) **4c**	$\text{PhSCH=CH}\underset{\text{SPh}}{\text{C}}\text{HCH}_3$ (40, —[c]) **3c**
1b	n-C_3H_7	PhS	$\text{PhSCH=}\underset{\text{SPh}}{\text{C}}\text{C}_4\text{H}_6^{\text{n}}$ (57, 68/32) **4b**	$\text{PhSCH=CH}\underset{\text{SPh}}{\text{C}}\text{HC}_3\text{H}_7^{\text{n}}$ (27, —[c]) **3d**
1e	n-C_3H_7	Br	$\text{PhSCH=}\underset{\text{Br}}{\text{C}}\text{C}_4\text{H}_9^{\text{n}}$ (42, 71/29) **4e**	
1f	n-C_5H_{11}	PhS	$\text{PhSCH=}\underset{\text{SPh}}{\text{C}}\text{C}_6\text{H}_{13}^{\text{n}}$ (61, 66/34) **4f**	$\text{PhSCH=CH}\underset{\text{SPh}}{\text{C}}\text{HC}_5\text{H}_{11}^{\text{n}}$ (22, —[c]) **3f**

a) Isolated yield. b) Determined with isolation of each isomers. c) Not determined.

radical reaction, the migration of the substituents did not occur, and simple adducts of thiophenol were obtained. Results were shown below.

$$HC{\equiv}CCH_2X + PhSH \xrightarrow{AIBN} PhSCH{=}CHCH_2X$$

		isolated yield (%),	(E/Z)
X=OH	**3h**	83	(7/3)
X=OAc	**3i**	84	(7/3)
X=OCH$_2$Ph	**3j**	82	(7/3)

The E/Z ratio was determined by ^{1}H NMR.

This method is useful for synthesizing vinylic sulfides. Further application of this type of reaction is now under investigation.

Experimental

Reaction Procedure. As a typical experiment, the reaction of 3-phenylthio-1-propyne (**1a**) with thiophenol is as follows: 3-Phenylthio-1-propyne (**1a**) (1.48 g, 10 mmol), thiophenol (1.20 g, 10 mmol), and AIBN (0.49 g, 3 mmol) in benzene (10 ml) were stirred at 80 °C for 1 h. After removing the solvent under a reduced pressure, the product was purified by column chromatography on silica gel to give (*E*)-1,2-bis(phenylthio)-1-propene (1.74 g, 6.7 mmol) and (*Z*)-1,2-bis(phenylthio)-1-propene (0.80 g, 3.1 mmol) (**4a**).

(*E*)-1,2-Bis(phenylthio)-1-propene ((*E*)-4a): IR(neat): 800, 1435, 1472, and 1580 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=2.05 (s, 3H), 6.30 (s, 1H), 7.0—7.4 (m, 10H); Anal. ($C_{15}H_{14}S_2$) C, H.

(*Z*)-1,2-Bis(phenylthio)-1-propene ((*Z*)-4a): IR(neat): 830, 1440, 1475, and 1582 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=1.95 (s, 3H), 6.35 (s, 1H), 7.0—7.4 (m, 10H); Anal. ($C_{15}H_{14}S_2$) C, H.

(*E*)-2-Bromo-1-phenylthio-1-propene ((*E*)-4b): IR(neat): 823, 1438, 1478, and 1582 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=2.30 (s, 3H), 6.30 (s, 1H), 7.0—7.4 (m, 5H); Anal. (C_9H_9SBr) C, H.

(*Z*)-2-Bromo-1-phenylthio-1-propene ((*Z*)-4b): IR(neat): 810, 1438, 1478, and 1582 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=2.40 (s, 3H), 6.43 (s, 1H), 7.0—7.4 (m, 5H); Anal. (C_9H_9SBr) C, H.

(*E*)-1,2-Bis(phenylthio)-1-butene ((*E*)-4c): IR(neat): 1040, 1440, 1477, and 1582 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=1.05 (t, 3H), 2.35 (q, 2H), 6.20 (s, 1H), 7.0—7.4 (m, 10H); Anal. ($C_{16}H_{16}S_2$) C, H.

(*Z*)-1,2-Bis(phenylthio)-1-butene ((*Z*)-4c): IR(neat): 1440, 1478, and 1580 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=1.05 (t, 3H), 2.35 (q, 2H), 6.45 (s, 1H), 7.0—7.4 (m, 10H); Anal. ($C_{16}H_{16}S_2$) C, H.

1,3-Bis(phenylthio)-1-butene (3c): IR(neat): 942, 1022, 1438, 1478, and 1583 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=1.35 (t, 3H), 3.5—4.0 (m, 1H), 5.7—5.9 (m, 2H), 6.8—7.4 (m, 10H); Anal. ($C_{16}H_{16}S_2$) C, H.

(*E*)-1,2-Bis(phenylthio)-1-hexene ((*E*)-4d): IR(neat): 1040, 1437, 1478, and 1580 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=0.90 (t, 3H), 1.0—1.8 (m, 4H), 2.40 (t, 2H), 6.25 (s, 1H), 7.1—7.4 (m, 10H): Anal. ($C_{18}H_{20}S_2$) C, H.

(*Z*)-1,2-Bis(phenylthio)-1-hexene ((*Z*)-4d): IR(neat): 1040, 1437, 1476, and 1580 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=0.90 (t, 3H), 1.0—1.8 (m, 4H), 2.25 (t, 2H), 6.50 (s, 1H), 7.1—7.4 (m, 10H); Anal. ($C_{18}H_{20}S_2$) C, H.

1,3-Bis(phenylthio)-1-hexene (3d): IR(neat): 1020, 1437, 1480, and 1580 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=0.90 (t, 3H), 1.1—1.8 (m, 4H), 3.5—3.8 (m, 1H), 5.7—5.9 (m, 2H), 7.0—7.5 (m, 10H); Anal. ($C_{18}H_{20}S_2$) C, H.

(*E*)-2-Bromo-1-phenylthio-1-hexene ((*E*)-4e): IR(neat): 820, 1438, 1478, and 1580 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=0.90 (t, 3H), 1.1—1.7 (m, 4H), 2.45 (t, 2H), 6.43 (s, 1H), 7.1—7.4 (m, 5H); Anal. ($C_{12}H_{15}BrS$) C, H.

(*Z*)-2-Bromo-1-phenylthio-1-hexene ((*Z*)-4e): IR(neat): 810, 1438, 1478, and 1580 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=0.90 (t, 3H), 1.1—1.7 (m, 4H), 2.4—2.7 (m, 2H), 6.45 (s, 1H), 7.0—7.4 (m, 5H); Found: C, 53.49; H, 5.78%. Calcd for $C_{12}H_{15}BrS$: C, 53.14; H, 5.58%.

(*E*)-1,2-Bis(phenylthio)-1-octene ((*E*)-4f): IR(neat): 815, 1438, 1478, and 1580 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=0.90 (t, 3H), 1.1—1.8 (m, 6H), 2.40 (t, 2H), 6.30 (s, 1H), 7.1—7.4 (m, 10H); Found: C, 72.78; H, 7.40%. Calcd for $C_{20}H_{24}S_2$: C, 73.11; H, 7.36%.

(*Z*)-1,2-Bis(phenylthio)-1-octene ((*Z*)-4f): IR(neat): 820, 1438, 1478, and 1580 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=0.90 (t, 3H), 1.1—1.8 (m, 6H), 2.25 (t, 2H), 6.50 (s, 1H), 7.0—7.4 (m, 10H); Anal. ($C_{20}H_{24}S_2$) C, H.

1,3-Bis(phenylthio)-1-octene (3f): IR(neat): 1020, 1437, 1478, and 1578 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=0.90 (t, 3H), 1.1—1.8 (m, 8H), 3.5—3.6 (m, 1H), 5.7—5.9 (m, 2H), 7.0—7.5 (m, 10H); Anal. ($C_{20}H_{24}S_2$) C, H.

3-(4-Methylphenylthio)-1-phenylthio-1-propene (3g): IR (neat): 1015, 1025, 1440, 1480, 1492, and 1583 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=2.30 (s, 3H), 3.50 (d, 2H), 5.8—6.1 (m, 2H), 6.9—7.4 (m, 9H), Anal. ($C_{16}H_{16}S_2$) C, H.

3-Phenylthio-2-propen-1-ol (3h): IR(neat): 850, 1305, 1437, 1475, 1580, and 3400 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=2.3—2.8 (m, 1H), 4.10 (d, 1.4H, *E*-isomer), 4.30 (d, 0.6H, *Z*-isomer), 5.8—6.4 (m, 2H), 7.0—7.4 (m, 5H); Found: C, 64.69; H, 6.20%. Calcd for $C_9H_{10}OS$: C, 65.02; H, 6.06%.

3-Phenylthio-2-propenyl Acetate (3i): IR(neat): 1437, 1477, 1580, and 1740 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=2.00, 2.10 (two singlets, total 3H), 4.50 (d, 1.4H, *E*-isomer), 4.70 (d, 0.6H, *Z*-isomer), 5.5—6.0 (m, 1H), 6.3—6.6 (m, 1H), 7.0—7.4 (m, 5H): Anal. ($C_{11}H_{12}SO_2$) C, H.

3-Benzyloxy-1-phenylthio-1-propene (3j): IR(neat): 1308, 1440, 1480, and 1582 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=3.95 (d, 1.4H, *E*-isomer), 4.15 (d, 0.6H, *Z*-isomer), 4.3—4.45 (m, 2H), 5.5—6.0 (m, 1H), 6.2—6.6 (m, 2H), 7.0—7.4 (m, 10H); Anal. ($C_{16}H_{16}OS$) C, H.

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