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Photochemistry and Radiation Chemistry of Sulfur-Containing Amino Acids. A New Reaction of the 1-Propenylthiyl Radicals[1]

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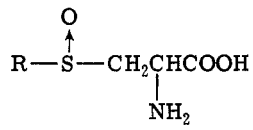
In connection with food-flavor deterioration caused by uv or γ irradiation, a new reaction of the 1-propenylthiyl radicals from *S*-(*cis*-1-propenyl)-L-cysteine irradiated by uv ray or γ-ray in oxygen-free aqueous solutions was investigated. The main products, formed via 1-propenylthiyl radicals, in uv photolysis were 1-propene-1-thiol, 2,4-dimethylthiophene, 3,4-dimethylthiophene, and 3-methylthiophene, while γ radiolysis yielded 1-propene-1-thiol, *n*-propyl 1-propenyl sulfide (cis and trans), and di-1-propenyl sulfide (cis,cis and cis,trans). Furthermore, cis–trans isomerization of 1-propenylthiyl radicals plays an important role in the formation of these products.

Sulfur-containing amino acids, such as *S*-alkyl-L-cysteine (alkyl: methyl, *n*-propyl, allyl, 1-propenyl), are found abundantly in *Allium*,[2] *Brassica*,[3] and *Phaseolus*[4] plants. These sulfoxides are also biologically active, i.e., they exhibit antihypercholesterolemic[5] and allithiamine effects.[6] Furthermore, since sulfur-containing amino acids are known to be highly sensitive to uv and γ irradiation, it is of interest to investigate the photolysis and radiolysis of these compounds.

We have studied the mechanism of formation of the major products when sulfoxide amino acids **1**, which are



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$R = CH_3CH_2CH_2$, $CH_2{=}CHCH_2$, $CH_3CH{=}CH$

precursors of onion and garlic flavors, are irradiated by γ rays in an oxygen-free aqueous solution. This is of importance from the viewpoint of food irradiation.[7]

Recently, during studies on the uv photolysis and γ radiolysis of *S*-alkyl-L-cysteines (alkyl: *n*-propyl, allyl, 1-propenyl), we found that the major products formed from uv photolysis of *S*-*n*-propyl-L-cysteine (**2**) or *S*-allyl-L-cysteine (**3**) were approximately similar to those from γ radiolysis (Figure 1).[8] On the other hand, the uv photolysis of *S*-(*cis*-1-propenyl)-L-cysteine (**7**) proceeded quite differently from its γ radiolysis.

In this paper we report the identification of the products formed by uv photolysis and γ radiolysis of *S*-(*cis*-1-propenyl)-L-cysteine, one of the lachrymatory precursors in onions,[9] and suggest mechanistic schemes to rationalize the major products.

Results and Discussion

Identification of Products. Gas chromatograms of the volatile products from uv photolysis and γ radiolysis of *S*-(*cis*-1-propenyl)-L-cysteine are shown in Figure 2. Comparison of gas chromatographic retention time and mass spectrometric fragmentations with those of reference compounds permitted identification of the volatile compounds shown in Table I.

The major products of uv-irradiated *S*-(*cis*-1-propenyl)-L-cysteine were 1-propene-1-thiol, 2,4-dimethylthiophene, 3,4-dimethylthiophene, and 3-methylthiophene. Minor products were *n*-propyl 1-propenyl sulfides, di-1-propenyl sulfides, 2-methylthiophene, and 2,5- and 2,3-dimethylthiophenes.

The major products of γ radiolysis (10^4–10^6 rad) were 1-propene-1-thiol, *n*-propyl *cis*-1-propenyl sulfide, and *n*-propyl *trans*-di-1-propenyl sulfide. Minor products were *cis,cis*-di-1-propenyl sulfide and *cis,trans*-di-1-propenyl sulfide. No thiophene derivatives could be detected even by using a highly sensitive gas chromatograph and the combined GC–MS method.[10]

The mass spectral fragmentations of the main peaks in Figure 2 are summarized in Table II. Mass spectral fragmentations of 1-propene-1-thiol, *n*-propyl 1-propenyl sul-

Table I: Identification of Volatile Products from *S*-(*cis*-1-Propenyl)-L-cysteine Irradiated by Uv Ray or γ-Ray

Uv photolysis		γ radiolysis	
Peak no.	Compd	Peak no.	Compd
U_1	Propanal	γ_1	1-Propene-1-thiol
U_2	Propane-1-thiol	γ_2	*n*-Propyl *cis*-1-propenyl sulfide
U_3	1-Propene-1-thiol	γ_3	*n*-Propyl *trans*-1-propenyl sulfide
U_4	2-Methylthiophene	γ_4	*cis*,*cis*-di-1-Propenyl sulfide
U_5	3-Methylthiophene	γ_5	*cis*,*trans*-di-1-Propenyl sulfide
U_6	*n*-Propyl 1-propenyl sulfides[a]		
U_7	2,5-Dimethylthiophene		
U_8	2-Methyl-2-pentenal		
U_9	2,4-Dimethylthiophene		
U_{10}	(a) Di-1-propenyl sulfides[b]		
	(b) 2,3-Dimethylthiophene		
U_{11}	3,4-Dimethylthiophene		

[a] Mixture of cis and trans. [b] Mixture of cis,cis and cis,trans.

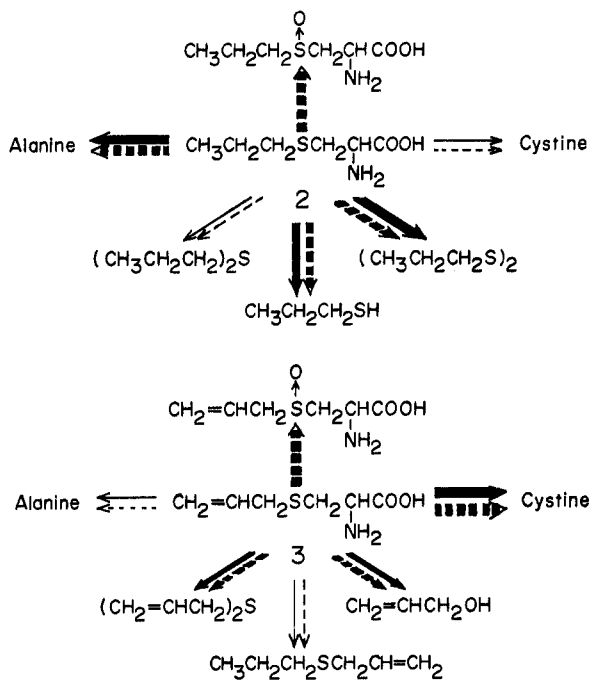


Figure 1. The products from *S*-*n*-propyl-L-cysteine (2) and *S*-allyl-L-cysteine (3) irradiated by uv ray (solid line) or γ-ray (dotted line) in oxygen-free aqueous solutions. Major products are represented with a thick line.

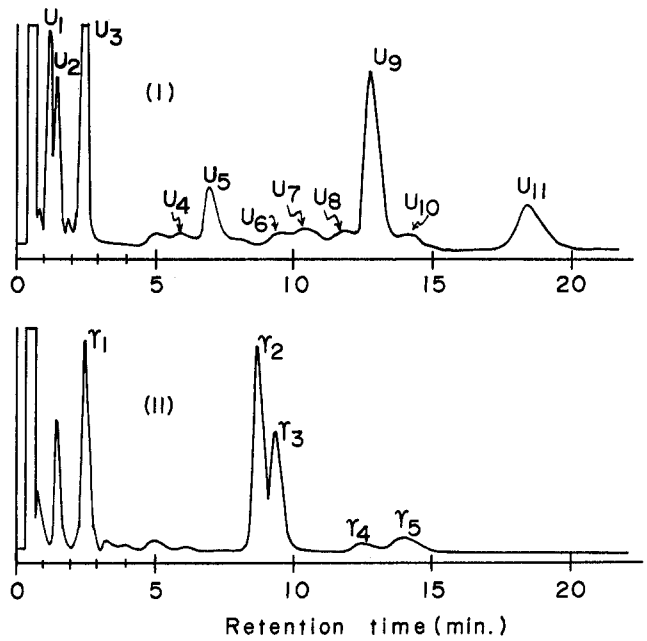


Figure 2. Gas–liquid chromatograms of head space vapor from *S*-(*cis*-1-propenyl)-L-cysteine irradiated in oxygen-free aqueous solutions: (I) uv ray, 20 m*M*, 2537 Å, 20 hr; (II) γ-ray, 20 m*M*, 1×10^6 rad.

fides, and di-1-propenyl sulfides have been rationalized on the basis of metastable ion peaks and distinguished the products from the isomeric allyl compounds.[11] Since the mass spectra of *cis*- and *trans*-1-propenyl sulfides did not differ, the geometrical isomers were characterized by ir and ^{1}H NMR.[12]

In Table II, the relative abundance of a fragment, mass 59 ($CH_3C{\equiv}S^+$), explains a significant difference between 2-methylthiophene and 3-methylthiophene. Although the base peak in the mass spectra of mono- and dimethylthiophenes is usually the (M − 1) ion, the base peak of 2,3-dimethylthiophene only is mass 97 ($M^+ - 15$). A significant difference among the mass spectra of 2,5-, 2,4-, and 3,4-dimethylthiophenes is the relative abundances of mass 59, i.e., 22.1, 8.9, and 4.5%, respectively (Table II).[13]

Among the ninhydrin-positive products of interest concerning the degradation mechanism, alanine (large) and cystine (trace), etc.,[14] were identified by comparing R_f values in two-dimensional thin layer chromatography[15] and gas chromatographic retention times[16] with those of reference compounds.

The formation of hydrogen sulfide was confirmed by lead tetraacetate and it was determined colorimetrically.[17] About 200 times more H_2S was produced by uv photolysis than by γ radiolysis.

Mechanism of Uv Photolysis. The oxygen-free neutral solutions of *S*-(*cis*-1-propenyl)-L-cysteine (2×10^{-2} mol/l.) dissolved in distilled water were irradiated for 0, 1, 2, 5, 10, 20, or 40 hr (2537 Å). The correlation between irradiation time and the yield of products is shown in Figure 3. Since alanine was produced in considerable quantity even at an early stage of uv irradiation, it seems that *S*-(*cis*-1-propenyl)-L-cysteine (7) is cleaved in the initial step to give 1-propenylthiyl radicals and 2-amino-2-carboxyethyl radical **9**. In the electron spin resonance (ESR) spectrum (77 K) of *S*-(*cis*-1-propenyl)-L-cysteine irradiated in aqueous system, an anisotropic signal (g_1 = 2.002, g_2 = 2.025, g_3 = 2.052) was observed in good agreement with reference alkylthiyl radicals (Figure 4).[18] This indicates that thiophene derivatives are produced via 1-propenylthiyl radicals as follows.

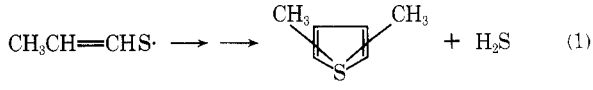


Table II: Mass Spectral Fragmentations of the Volatile Products from Uv Photolysis and γ Radiolysis of *S*-(*cis*-1-Propenyl)-L-cysteine

m/e	A[a]	B[b]	C[c]	D[d]	E[e]	F[f]	G[g]	H[h]	I[i]	J[j]	K[k]
39	54.3	17.0	11.4	13.3	23.6	20.3	22.9	65.1	50.0	77.7	91.9
40	8.6	2.0	1.1	1.9	3.9	3.5	4.0	17.2	5.5	5.0	5.5
41	100.0	1.5	1.1	2.4	5.8	8.2	11.5	94.3	91.8	89.2	97.4
42	8.6			1.1	1.1	1.1	1.2	5.7	4.5	3.3	4.8
43	1.4			1.1	1.1	1.1	2.3	32.5	30.9	4.1	4.1
44	4.3	3.1	2.0	1.0	2.2	1.7	1.9	8.9	1.8	1.7	2.1
45	71.4	21.6	26.8	14.5	31.4	25.5	35.1	82.7	81.8	89.3	98.7
46	18.6	2.5	2.2	1.2	2.1	1.6	2.5	14.9	12.7	8.3	8.2
47	14.6	3.0	2.3	1.8	2.3	1.6	2.5	21.2	20.0	14.9	16.4
48	1.7	1.4	1.0	1.2	1.0	1.1		1.6	1.4	1.6	0.7
49	1.4	3.5	3.0	2.0	1.1	1.7		1.6	1.4	0.8	0.7
50		4.0	7.8	8.1	4.5	10.2	6.3				
51		5.1	6.5	11.2	5.6	13.2	8.0				
52		1.8	3.5	3.5	2.3	4.0	2.2				
53		14.2	8.6	8.5	5.0	10.5	7.5	9.0	9.5	14.9	13.7
54		1.8	1.7	1.1	1.1	1.3	1.1	0.8	0.9	2.5	2.7
55				1.3	2.0	2.0	2.3	0.8	1.8	14.5	13.0
56					1.6	1.1	4.2				
57	5.7			4.4	2.0	5.0	1.8	1.6	1.8	8.3	4.1
58	8.6	5.0	6.6	7.9	3.8	11.2	4.5	3.2	6.4	9.9	9.6
59	18.6	6.2	2.3	22.1	8.9	14.0	4.5	16.3	16.8	23.2	28.8
60	1.4	1.4	1.1	1.7	1.4	1.8	1.3	1.6	1.8	3.3	5.5
61	1.4	2.5	2.0	1.8	2.0	1.9	1.8	1.6	1.8	3.3	10.3
62		2.5	2.0	1.4	3.8	1.9	1.8				
63		2.7	2.8	2.0	5.0	2.7	3.7				
64				1.1	1.1	1.0	1.1				
65		1.5	2.3	1.5	3.0	3.5	4.0				
67										10.7	16.8
68	1.2									1.7	2.7
69	5.7	7.9	8.4	7.1	8.0	8.2	10.5			12.4	13.7
70	1.4	2.5	2.3	2.1	3.3	3.5	4.1			1.6	1.4
71	5.7	3.8	6.0	7.0	9.5	5.0	9.5	11.2	10.0	26.4	30.8
72	1.4	1.2		1.2	2.8	1.1	2.2	10.2	9.1	25.6	31.5
73	22.9	1.2			1.4	1.1	1.1	29.2	29.1	33.1	32.9
74	82.9 (P)							100.0	100.0	12.4	16.5
75	5.7							10.9	10.7		
76	5.7							8.3	6.9		
77				13.8	17.0	13.3	12.5				
78				7.7	7.8	8.0	5.2				
79				4.1	5.5	3.9	5.3			14.9	13.7
80										1.6	2.7
81		1.3	1.4							16.5	21.9
82		1.5	1.4							2.5	7.5
83		1.3		2.0	1.2	1.4	1.1			1.7	2.1
84				2.0	1.8	3.9	1.3				
85				3.1	2.0	7.0	2.0	4.9	3.6	31.4	41.1
86								0.8	0.5	3.3	5.5
87								40.6	35.4	2.5	4.1
88								2.4	1.8		
89								2.5	1.8		
97		100.0	100.0	61.7	53.0	100.0	49.3			13.2	5.5
98		52.0 (P)	50.0 (P)		4.0	7.5	4.3			2.5	2.1
99		5.9	5.8		3.2	4.5	3.5			93.5	83.6
100		3.0	2.9							6.6	6.2
101								3.3	1.8	7.4	5.5
111				100.0	100.0	74.6	100.0				
112				75.7 (P)	76.7 (P)	77.5 (P)	73.7 (P)				
113				10.6	10.7	10.3	10.1			6.6	10.3
114				4.5	4.5	4.6	4.3			100.0 P	100.0 P
115										7.4	9.6
116								55.3 (P)	57.7 (P)	5.8	8.9
117								4.9	5.5		
118								4.1	4.1		

[a] 1-Propene-1-thiol. [b] 2-Methylthiophene. [c] 3-Methylthiophene. [d] 2,5-Dimethylthiophene. [e] 2,4-Dimethylthiophene. [f] 2,3-Dimethylthiophene. [g] 3,4-Dimethylthiophene. [h] *n*-Propyl *cis*-1-propenyl sulfide. [i] *n*-Propyl *trans*-1-propenyl sulfide. [j] *cis,cis*-Di-1-propenyl sulfide. [k] *cis,trans*-Di-1-propenyl sulfide.

As shown in Figure 3, the yield of each thiophene derivative, hydrogen sulfide, 1-propene-1-thiol, alanine, and sulfides increased approximately in parallel with irradiation time to the extent of 0–5 hr, respectively.

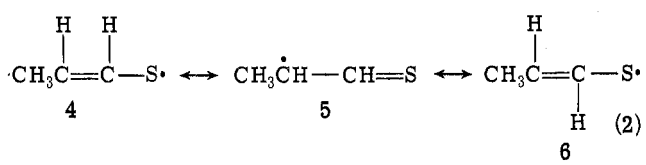
Couture and Lablache-Combier reported the isomerization of 2-methylthiophene to 3-methylthiophene by uv irradiation and suggested an isomerization mechanism.[19] Therefore there is a possibility that each dimethylthiophene is produced by methyl scrambling on the thiophene ring. Only trace amounts of isomerization products were obtained from 2,4-dimethylthiophene and 3,4-dimethylthiophene irradiated for 20–40 hr in aqueous solutions, respectively.

The dimethylthiophenes might also be produced by photocyclization of di-1-propenyl sulfides from uv-irradiated **7**. However, 2,4-dimethylthiophene or 3,4-dimethylthiophene could not be detected even by gas chromatography (FID).[20]

In addition, Block and Corey have reported that β,β′-diphenyldivinyl sulfide undergoes photocyclization to give *trans*-2,3-diphenyl-5-thiabicyclo[2.1.0]pentane and 2,3-dihydro-3,4-diphenylthiophene.[21] However, no cyclization products of this type were obtained from **7** or the di-1-propenyl sulfides.

From the above results, each dimethylthiophene must be produced independently, *via* 1-propenylthiyl radicals (Figure 4).

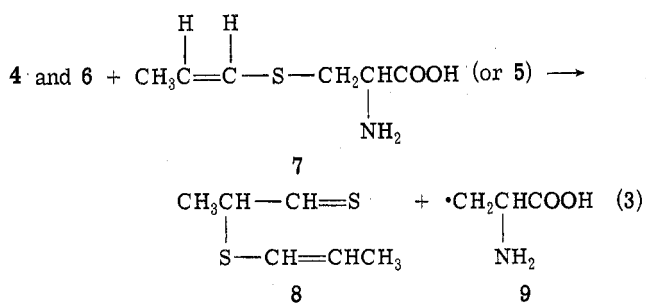
1-Propenylthiyl radicals exist as a resonance hybrid (eq 2), since cis–trans isomerization of the 1-propenylthiyl radicals has been found in the case of γ radiolysis.[1b,22]



(2)

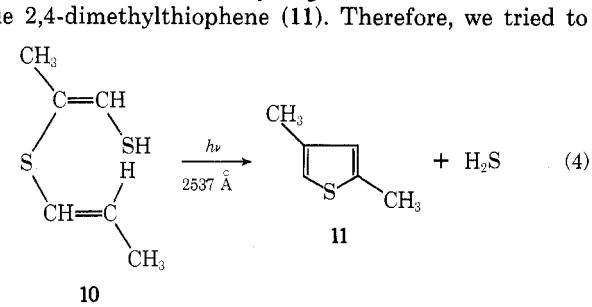
A reasonable tentative mechanism for dimethylthiophene formation is as follows.

1-Propenylthiyl radicals (**4** and **6**) react with **7** or alkyl radical **5** to produce unstable dimeric thioaldehyde **8**. **8** via



(3)

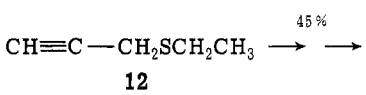
a [1,3]-prototropic shift gives the alkenethiol **10** and the immediate elimination of hydrogen sulfide then leads to stable 2,4-dimethylthiophene (**11**). Therefore, we tried to

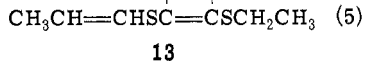


(4)

prepare alkenethiol **10** to determine whether 2,4-dimethylthiophene could indeed be obtained by its irradiation.

First, 5-methyl-3,6-dithia-4,7-nonadiene (**13**) was prepared from ethyl 2-propynyl sulfide (**12**) in about 45% yield. Lithium alkenethiolate, which was prepared by reaction of **13** with lithium in liquid ammonia, gave **10** in low





(5)

yield by treatment with sulfuric acid.[23] A small amount of 2,4-dimethylthiophene was also produced, probably by partial decomposition during the acid hydrolysis and solvent extraction. Thereupon **10** was irradiated by uv ray and the products were characterized by combined GC–MS.[10] The major products were 2,4-dimethylthiophene, hydrogen sulfide, and 1-propene-1-thiol; other thiophene derivatives were produced only in trace amounts. Although the intermediates **8** or **10** could not be isolated at room temperature, the above evidence indicates that **10** might be an intermediate in the formation of 2,4-dimethylthiophene.

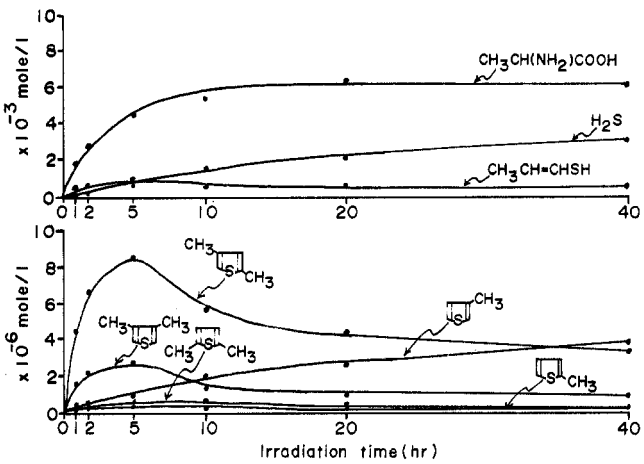


Figure 3. Correlation between irradiation time and products from *S*-(*cis*-1-propenyl)-L-cysteine irradiated in oxygen-free aqueous solutions.

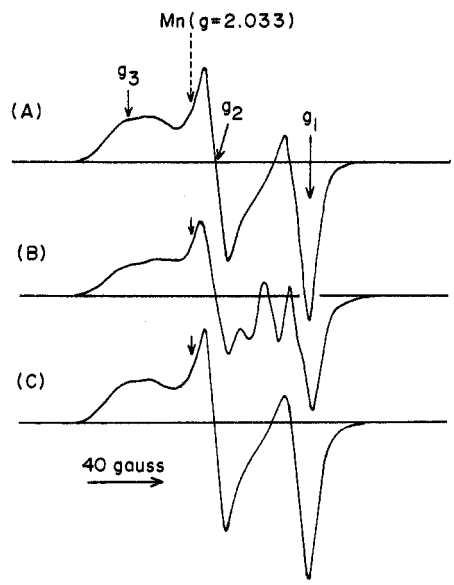


Figure 4. Electron spin resonance spectra of *S*-(*cis*-1-propenyl)-L-cysteine (A, B) and *n*-propyl 1-propenyl sulfide (C) irradiated by uv ray (2537 Å, 10 hr) at 77 K: (A) recorded in 8 hr after irradiation; (B) recorded in 10 min after irradiation; (C) recorded in 2 hr after irradiation. $g_1 = 2.002$, $g_2 = 2.025$, $g_3 = 2.052$.

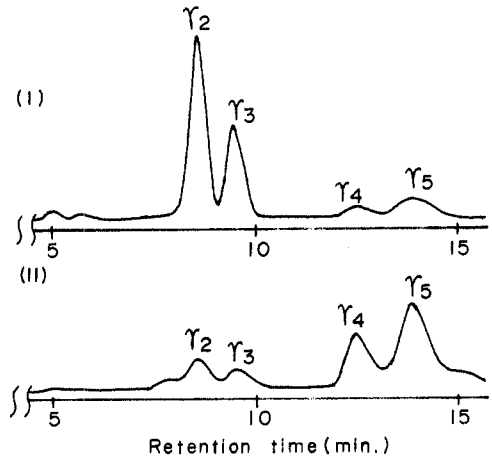
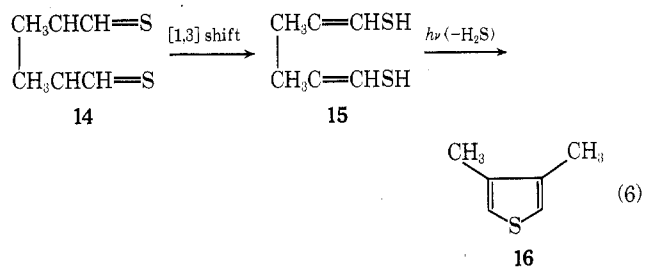


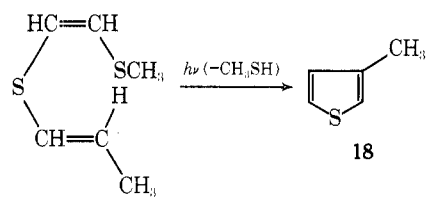
Figure 5. Gas–liquid chromatograms of head space vapor from (I) 2×10^{-2} mol/l. of *S*-(*cis*-1-propenyl)-L-cysteine and (II) mixture of 2×10^{-2} mol/l. of *S*-(*cis*-1-propenyl)-L-cysteine and 1×10^{-2} mol/l. of NaCN irradiated by γ-ray (1×10^6 rad).

Similarly alkyl radical **5** attacks **7** or another radical **5** to produce unstable bisthioaldehyde **14**, which gives dithiol **15** via a [1,3]-prototropic shift. Immediate elimination of hydrogen sulfide from **15** then leads to stable 3,4-dimethylthiophene (**16**).



14 15 16 (6)

The amount of 3-methylthiophene produced after 20-hr irradiation was 20 times the amount of 2-methylthiophene, as shown in Figure 3. 3-Methylthiophene (**18**) is probably produced through intermediate **17** formed by a [1,3]-methyl shift in the thioaldehyde **8** (eq 7).[24]



17 18 (7)

The trace amounts of 2,5-dimethylthiophene and 2,3-dimethylthiophene may have been produced by methyl scrambling on the thiophene ring.

Further confirmation of the intermediates and other evidence for the suggested mechanism will be presented elsewhere.

Mechanism of γ Radiolysis. Some *trans*-1-propenyl sulfides were found from **7** irradiated by γ-ray with 1×10^6 rad (see Table I). These trans products must have been produced via cis–trans isomerization of the 1-propenylthiyl radicals[25] (eq 2).

In recent years, photochemical[26] and radiation-chemical[27] cis–trans isomerizations of olefins have been much investigated in organic solvents and in gaseous systems. However, radiation-induced cis–trans isomerization has not been investigated in aqueous systems in spite of its importance for animal and plant organisms.

The yield of alanine from **7** is considerably greater than

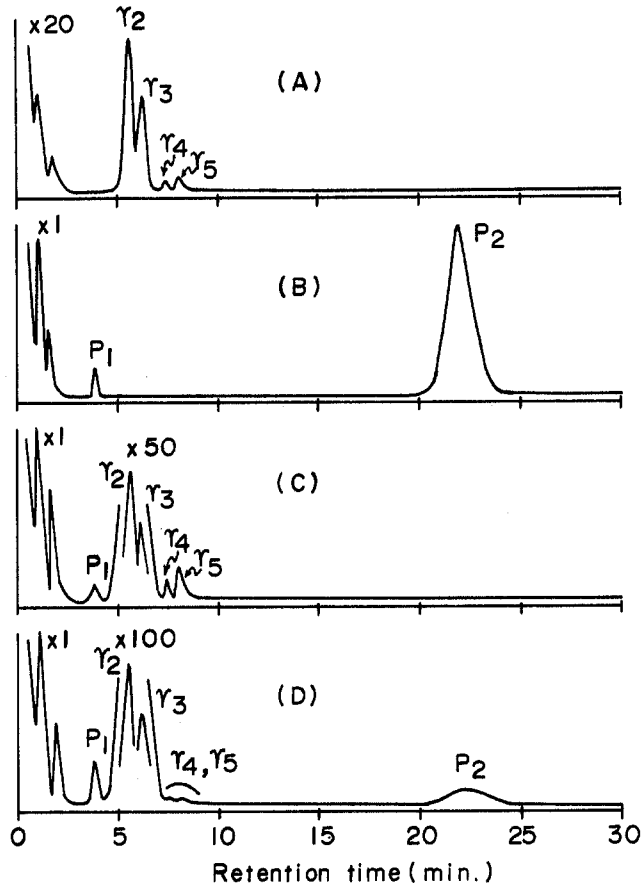


Figure 6. Gas–liquid chromatograms of the mixture of *S*-(*cis*-1-propenyl)-L-cysteine (PeCS) and *S*-*n*-propyl-L-cysteine (PCS) irradiated by γ-ray: (A) 1×10^{-2} mol/l. of PeCS, (B) 1×10^{-3} mol/l. of PCS, (C) mixture of 1×10^{-1} mol/l. of PeCS and 1×10^{-3} mol/l. of PCS, (D) mixture of 1×10^{-2} mol/l. of PeCS and 5×10^{-3} mol/l. of PCS.

that of cystine, in analogy with the case of uv photolysis. This fact indicates that the S–C (alanine moiety) bond in **7** is easily cleaved by γ irradiation.

The radiation-induced decomposition of water in the absence of oxygen proceeds as follows.

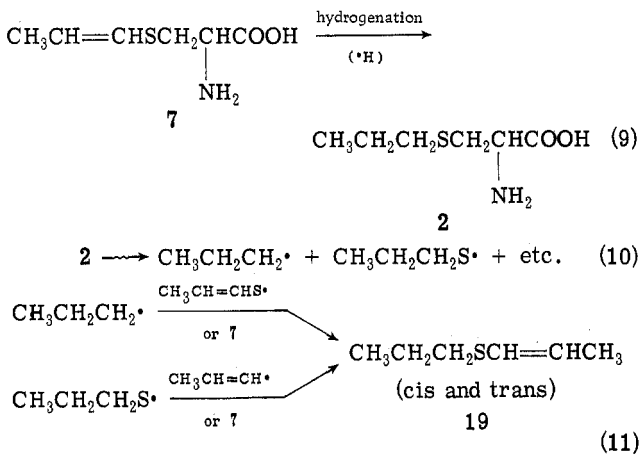
$$H_2O \longrightarrow \cdot H,\ e_{aq},\ \cdot OH,\ H_3O^+,\ H_2,\ H_2O_2{}^{28} \qquad (8)$$

In order to elucidate the mechanism of γ radiolysis of **7**, it was irradiated after several scavengers had been added. The yield of alanine decreased with increasing concentration of N_2O (specific scavenger for e_{aq})[29] and increased with increasing concentration of KBr (specific scavenger for ·OH).[30] Therefore it is considered that **7** reacts with e_{aq} to produce alanine.

With increasing concentration of NaCN (H radical scavenger)[31] in irradiated **7**, both γ_2 and γ_3 decreased. Both γ_4 and γ_5 increased (Figure 5). This evidence indicates that H radicals from γ radiolysis of water contribute to the formation of *n*-propyl 1-propenyl sulfide (cis and trans).

At first we inferred that di-1-propenyl sulfides (**20** and **21**) reacted with two H radicals to produce *n*-propyl 1-propenyl sulfides **19**, but **19** could not be detected in the volatile products formed from **20** or **21** irradiated in an oxygen-free aqueous solution. Therefore we added various concentrations of **2** to aqueous solutions of **7** and irradiated the mixture in an oxygen-free aqueous solution (Figure 6). Di-*n*-propyl sulfide (P_1) and di-*n*-propyl disulfide (P_2) formed by γ radiolysis of 1×10^{-3} mol/l. of *S*-*n*-propyl-L-cysteine[32] could be detected in the same concentration as before (B in Figure 6). Disulfide (P_2) was not produced from the

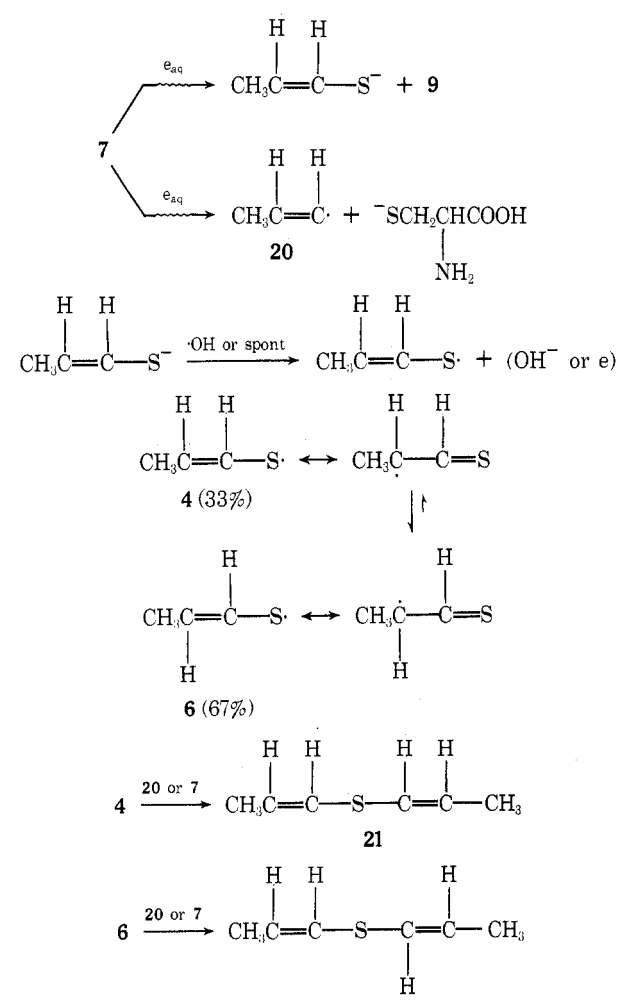
mixture of 2×10^{-2} mol/l. of **7** and 1×10^{-3} mol/l. of **2** (C in Figure 6).[33] On the other hand, the amount of *n*-propyl 1-propenyl sulfides (γ_2 and γ_3) increased steeply. At higher concentration of **2** (5×10^{-3} mol/l.), disulfide (P_2) was barely detected (D in Figure 6). These facts indicate that **7** is hydrogenated by H radicals from the γ radiolysis of water to produce **2**, and *n*-propyl radicals from irradiated **2** attack 1-propenylthiyl radicals or **7** to produce *n*-propyl 1-propenyl sulfides **19** as follows.



When irradiated to the extent of 10^4–10^6 rad, **7** gave di-1-propenyl sulfides (**21** and **22**) in the ratio of cis,cis: cis,trans (γ_4:γ_5) of 33:67. Although radiation-induced cis–trans isomerization of olefins in organic solvents has been observed frequently,[26] authentic cis isomer irradiated in an oxygen-free aqueous solution was not converted to trans isomer. Since the 1-propenyl radical is assumed to react with retention of stereochemistry,[34] the proportion of *cis*- and *trans*-1-propenylthiyl radicals (**4** and **6**) must be 33:67 (%).

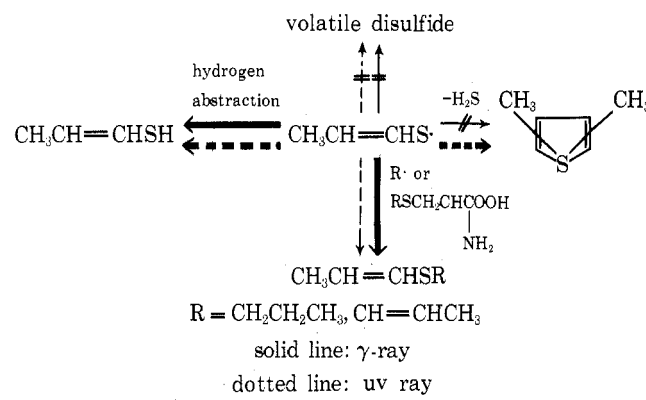
On the basis of the above results and evidence, we suggest that cis–trans isomerization of the 1-propenylthiyl radicals proceeds as shown in Chart I.

Chart I



Conclusions

In the case of γ radiolysis in aqueous systems, such chemical species as hydrated electrons (e_{aq}), hydroxyl radicals (·OH), etc. (eq 8), are produced in the first stage and attack the solute in the second stage. In uv photolysis, the solute is directly excited and decomposed. In spite of this basic difference, the major products from uv photolysis of **2** or **3** were approximately similar to those from γ radiolysis (Figure 1). However, the uv photolysis of *S*-(*cis*-1-propenyl)-L-cysteine was significantly different from its γ radiolysis. In spite of the formation of 1-propenylthiyl radicals from both uv photolysis and γ radiolysis of *S*-(*cis*-1-propenyl)-L-cysteine, thiophene derivatives were mainly produced in uv photolysis, while 1-propenyl-containing sulfides were mainly produced in γ radiolysis (Table I). Also, about 200 times more H_2S was produced by uv photolysis than by γ radiolysis. The main products via 1-propenylthiyl radicals are summarized as follows.



Furthermore, from alkenethiol **10**, 2,4-dimethylthiophene was obtained by uv photolysis but not by γ radiolysis, and instead of thiophenes, small amounts of 1-propene-1-thiol and di-1-propenyl sulfides were obtained by γ radiolysis (5×10^5 rad)[35] of **10** (about 2×10^{-2} mol/l.).

The intermediates, thioaldehyde **8** and **10**, etc., might be the key compounds in explaining the difference between uv photolysis and γ radiolysis of *S*-(*cis*-1-propenyl)-L-cysteine.

Experimental Section

General Instrumentation. The method of GC–MS combination was preferred to obtain the mass spectral data of trace amounts of products. A Watson-Biemann helium separator[10] was used between the gas chromatograph (Hitachi Model K-53 GLC) and the mass spectrometer (Hitachi Model RMS-4). The operating parameters were as follows: gas chromatograph, 1 m × 3 mm i.d. stainless steel column packed with 20% Reoplex 400 on 60–80 mesh acid-washed C-22, flow rate (helium carrier gas) of 25 ml/min, temperature 80°, injection port temperature 150°; mass spectrometer, ion source temperature 200°, ion source pressure 2×10^{-6} mm, target current 60 μA, total emission 80 μA, ionizing voltage 80 eV, accelerating voltage 3 kV. To purify the authentic compounds, a preparative gas chromatograph (Varian Aerograph 90-P) was used. To obtain the small amounts of products, a FID gas chromatograph (Yanagimoto GCG 550PF), in which a splitter was inserted, was also used. Infrared spectra were measured in KBr pellets with a Hitachi EPI-S2 infrared spectrometer. ^{1}H NMR spectral

data were obtained from a Hitachi R-22 apparatus (90 MHz). ESR spectra were taken at 77 K with X-band spectrometers (JeOL P-10).

Uv Irradiation. The oxygen-free neutral solutions of sulfur-containing amino acids (2×10^{-2} mol/l.) dissolved in triply distilled water were placed in stoppered quartz tubes. They were irradiated for 0, 1, 2, 5, 10, 20, or 40 hr at room temperature using a 50-W low-pressure mercury lamp, Ushio UL1-5BQ (2537 Å).

γ Irradiation. Irradiation was carried out by exposure to γ rays from cobalt-60 of 3 kCi at a dose rate of 6.24×10^4 rad/hr at room temperature. The oxygen-free neutral solutions of sulfur-containing amino acids (5×10^{-3} to 2×10^{-2} mol/l.) in triply distilled water were placed in stoppered Pyrex tubes and irradiated to the extent of 10^4–10^6 rad.

Irradiations in the presence of N_2O (specific scavenger for e_{aq}),[28] KBr (specific scavenger for ·OH),[29] or NaCN (H radical scavenger)[30] were also done for studies on the formation mechanism.

Separation and Identification of the Irradiation Products. In both the uv photolysis and γ radiolysis, volatile products from irradiated *S*-(*cis*-1-propenyl)-L-cysteine (5 l. of solution) were distilled off by passing through nitrogen gas as a carrier at approximately 80°, and absorbed into about 5 ml of isopentane trap cooled with Dry Ice–ethanol.

The volatile products were characterized by the combined GC–MS method and the products were further confirmed by comparing with the gas chromatographic retention time and mass spectra of the respective reference compounds.

Two-dimensional thin layer chromatography of ninhydrin-positive products from irradiated *S*-(*cis*-1-propenyl)-L-cysteine was carried out on Avicel SF (microcrystalline cellulose) by using (1) 1-butanol–acetic acid–water (4:1:1 v/v) and phenol–water (4:1 v/v) or (2) 1-butanol–acetic acid–water (63:10:27 v/v) and phenol–acetic acid–water (7:1:2 v/v) as solvent systems and the chromatograms were colored with ninhydrin reagent. Amino acids produced by irradiation were converted into *N*-trifluoroacetylamino acid *n*-butyl esters and were determined by using a FID gas chromatograph (Hitachi K-53).

***S*-*n*-Propyl-L-cysteine (2) and *S*-Allyl-L-cysteine (3).** The synthetic procedure is a modification of the method of du Vigneaud et al.[36] in preparing *S*-methyl-L-cysteine from L-cystine.

S-*n*-propyl-L-cysteine (2): mp 210–212° dec; ir (KBr) 2965–2860, 2580, 2120 (NH_3^+), and 1580 cm^{-1} (COO^-); mass spectrum *m/e* (rel intensity) 163 (M^+, 12.4), 118 (21.7), 90 (40.3), 89 (100), 74 (31.0), 61 (46.5), 47 (65.1), and 43 (89.9); ^1H NMR (D_2O–NaOD) δ 0.90 (3 H, t, J = 7.0 Hz, CH_3), 1.55 (2 H, m, CH_2), 2.50 (2 H, t, J = 7.2 Hz, SCH_2 at *n*-propyl), 2.75–2.85 (2 H, dd, J = 6.2 Hz, SCH_2 at C-β), and 3.45 (1 H, dd, J = 6.2 Hz, CH at C-α).

Anal. Calcd for $C_6H_{13}NO_2S$: C, 44.16; H, 8.03; N, 8.58. Found: C, 44.09; H, 7.99; N, 8.60.

S-Allyl-L-cysteine (3): mp 208–210° dec; ir (KBr) 3020–2870, 2590, 2120 (NH_3^+), 1580 (COO^-), and 990 and 918 cm^{-1} (allyl double bond); mass spectrum *m/e* (rel intensity) 161 (M^+, 14.2), 116 (8.4), 88 (55.8), 87 (100), 74 (90.0), 45 (46.8), 41 (87.6), and 39 (32.4); ^1H NMR (D_2O–NaOD) δ 2.61–2.71 (2 H, dd, J = 6.2 Hz, SCH_2 at C-β), 3.10 (2 H, d, J = 7.0 Hz, SCH_2 at allyl), 3.26 (1 H, dd, J = 6.2 Hz, CH at C-α), 5.01–5.22 (2 H, dd, J = 17.0 and 10.0 Hz, vinylic CH_2), and 5.71 (1 H, m, vinylic CH).

Anal. Calcd for $C_6H_{11}NO_2S$: C, 44.71; H, 6.88; N, 8.69. Found: C, 44.52; H, 6.81; N, 8.60.

***S*-(*cis*-1-Propenyl)-L-cysteine (7).** This compound was prepared by the synthetic procedure of Carson and Wong[37] from *S*-allyl-L-cysteine with potassium *tert*-butoxide in dimethyl sulfoxide: mp 179–180° dec; ir (KBr) 2970, 2840, 2580, 2100 (NH_3^+), and 1580 (COO^-), no absorption at 990 and 918 (allyl double bond) and at 967 cm^{-1} (trans isomer); mass spectrum *m/e* (rel intensity) 161 (M^+, 32.1), 116 (16.0), 88 (72.8), 87 (100), 74 (71.2), 59 (48.8), 45 (71.2), 41 (40.8), and 39 (44.0); ^1H NMR (D_2O–NaOD) δ 1.62 (3 H, d, J = 6.1 Hz, CH_3 at 1-propenyl), 2.85–2.95 (2 H, dd, J = 6.9 Hz, SCH_2 at C-β), 3.36 (1 H, dd, J = 6.9 Hz, CH at C-α), 5.67 (1 H, m, CH at 1-propenyl), and 5.98 (1 H, d, J = 9.0 Hz, SCH at 1-propenyl).

Anal. Calcd for $C_6H_{11}NO_2S$: C, 44.71; H, 6.88; N, 8.69. Found: C, 44.70; H, 6.81; N, 8.66.

The mass spectral fragmentations of such sulfur-containing amino acids as *S*-alkyl-L-cysteines were reported previously.[38]

Di-*n*-propyl Sulfide. Di-*n*-propyl sulfide was prepared from *n*-propyl bromide according to the method of Shriner et al.[39] in preparing dibenzyl sulfide from benzyl chloride with sodium sulfide. The product was distilled at atmospheric pressure: bp 141°; yield 82%; ir (film) 2990, 2890 (methyl C–H stretching vibration), 2960 (CH_2), and 1460 cm^{-1} (C–H); mass spectrum *m/e* (rel intensity) 118 (M^+, 95.2), 89 (100), 76 (81.2), 61 (63.5), 47 (62.3), and 43 (77.6).

Anal. Calcd for $C_6H_{14}S$: C, 60.98; H, 11.94. Found: C, 61.10; H, 11.92.

Diallyl Sulfide. Diallyl sulfide was also prepared by the above-mentioned method: bp 139°; yield 71%; ir (film) 1645 (double bond) and 990 and 913 cm^{-1} (allyl double bond); mass spectrum *m/e* (rel intensity) 114 (M^+, 30.5), 99 (30.8), 73 (78.3), 72 (42.5), 45 (91.2), 41 (100), and 39 (68.2).

Anal. Calcd for $C_6H_{10}S$: C, 63.13; H, 8.83. Found: C, 63.30; H, 8.75.

Di-1-propenyl Sulfides (21 and 22). This compounds were prepared by the method of Tarbell and Lovett,[40] bp 146–150°, yield 42%. cis,*cis*- and *cis*,*trans*-di-1-propenyl sulfides were purified by using the preparative gas chromatograph.

cis,*cis*-Di-1-propenyl sulfide (21): ir (film) 1720, 1610 (double bond), 932 (1-propenyl double bond), and 660 cm^{-1} (cis double bond); mass spectrum *m/e* (rel intensity) 114 (M^+, 100), 99 (93.5), 73 (33.1), 45 (89.3), 41 (89.2), and 39 (77.7); ^1H NMR (CCl_4) δ 1.66 (6 H, dd, J = 6.9 and 1.9 Hz, CH_3), 5.54 (2 H, m, CH at 1-propenyl), and 5.94 (2 H, m, J = 9.5 and 1.9 Hz, SCH at 1-propenyl).

Anal. Calcd for $C_6H_{10}S$: C, 63.13; H, 8.83. Found: C, 63.20; H, 8.80.

cis,*trans*-Di-1-propenyl sulfide (22): ir (film) 1680, 1610 (double bond), 962 (trans double bond), 932 (1-propenyl double bond), and 660 cm^{-1} (cis double bond); mass spectrum *m/e* (rel intensity) 114 (M^+, 100), 99 (83.6), 73 (32.9), 45 (98.7), 41 (97.4), and 39 (91.9); ^1H NMR (CCl_4) δ 1.60–1.75 (6 H, m, CH_3), 5.47–5.76 (2 H, m, CH at 1-propenyl), 5.90 (1 H, m, J = 17.2 and 1.9 Hz, SCH at trans double bond), and 5.96 (1 H, m, J = 9.5 and 1.9 Hz, SCH at cis double bond).

Anal. Calcd for $C_6H_{10}S$: C, 63.13; H, 8.83. Found: C, 63.21; H, 8.79.

***n*-Propyl Allyl Sulfide.** The synthetic procedure is a modification of the method of Kirner and Richter[41] in preparing α-furfuryl ethyl sulfide from furfuryl mercaptide with ethyl bromide. The product was obtained by distillation: bp 140°; yield 78%; ir (film) 2990, 2890 (methyl C–H stretching vibration), 1645 (double bond), and 989 and 912 cm^{-1} (allyl double bond); mass spectrum *m/e* (rel intensity) 116 (M^+, 34.7), 87 (30.2), 74 (63.1), 73 (20.7), 45 (51.8), 43 (20.3), 41 (100), and 39 (49.1).

Anal. Calcd for $C_6H_{12}S$: C, 62.04; H, 10.41. Found: C, 61.90; H, 10.39.

***n*-Propyl 1-Propenyl Sulfides (19).** This compound was prepared by the reaction of *n*-propyl allyl sulfide with sodium methoxide in absolute methanol, bp 139–141°, yield 55%. Cis and trans isomers were purified by the gas chromatograph.

n-Propyl *cis*-1-propenyl sulfide: ir (film) 1612 (double bond) and 936 and 665 cm^{-1} (cis double bond); mass spectrum *m/e* (rel intensity) 116 (M^+, 55.3), 87 (40.6), 74 (100), 73 (29.2), 45 (82.7), 43 (32.5), 41 (94.3), and 39 (65.1); ^1H NMR (CCl_4) δ 0.96 (3 H, t, J = 7.0 Hz, CH_3 at *n*-propyl), 1.56 (2 H, m, CH_2), 2.48 (2 H, t, J = 7.2 Hz, SCH_2 at *n*-propyl), 1.70 (3 H, d, J = 6.1 Hz, CH_3 at 1-propenyl), 5.27–5.72 (1 H, m, CH at 1-propenyl), and 5.78 (1 H, d, J = 9.9 Hz, SCH at 1-propenyl).

Anal. Calcd for $C_6H_{12}S$: C, 62.04; H, 10.41. Found: C, 61.95; H, 10.38.

n-Propyl *trans*-1-propenyl sulfide: ir (film) 1610 (double bond) and 960 cm^{-1} (trans double bond); mass spectrum *m/e* (rel intensity) 116 (M^+, 57.7), 87 (35.4), 74 (100), 73 (29.1), 45 (81.8), 43 (30.9), 41 (91.8), and 39 (50.0); ^1H NMR (CCl_4) δ 0.96 (3 H, t, J = 7.0 Hz, CH_3 at *n*-propyl), 1.56 (2 H, m, CH_2), 1.70 (3 H, d, J = 6.1 Hz, CH_3 at 1-propenyl), 2.48 (2 H, t, J = 7.2 Hz, SCH_2 at *n*-propyl), 5.27–5.72 (1 H, m, CH at 1-propenyl), and 5.82 (1 H, d, J = 15.2 Hz, SCH at 1-propenyl).

Anal. Calcd for $C_6H_{12}S$: C, 62.04; H, 10.41. Found: C, 62.10; H, 10.39.

Di-*n*-propyl Disulfide. This compound was prepared by the application of a synthetic procedure of *p*,*p*′-dinitrophenyl disulfide[42] from *p*-nitrophenyl chloride with Na_2S_2: bp 195°; yield 75%; ir (film) 2990, 2890 (methyl C–H), and 600–800 cm^{-1} (C–S); mass spectrum *m/e* (rel intensity) 150 (M^+, 28.0), 108 (23.6), 66 (10.9), 43 (100), 41 (44.5) and 39 (20.0).

Anal. Calcd for $C_6H_{14}S_2$: C, 47.98; H, 9.40. Found: C, 48.02; H, 9.39.

Diallyl Disulfide. This compound was also derived from allyl bromide by the above-mentioned method: bp 173°; yield 55%; ir (film) 1645 (double bond) and 989 and 915 cm^{-1} (allyl double bond); mass spectrum *m/e* (rel intensity) 146 (M^+, 71.5), 113

(22.0), 105 (40.8), 81 (72.5), 73 (62.9), 45 (81.2), 41 (100), and 39 (89.8).

Anal. Calcd for $C_6H_{10}S_2$: C, 49.31; H, 6.90. Found: C, 49.43; H, 7.04.

1-Propene-1-thiol. This compound was prepared by the synthetic procedure of Brandsma:[23] bp 63–70°; yield 21%; mass spectrum *m/e* (rel intensity) 74 (M^+, 82.9), 59 (18.6), 47 (14.6), 45 (71.4), 41 (100), and 39 (54.3).

Anal. Calcd for C_3H_6S: C, 48.64; H, 8.16. Found: C, 48.55; H, 8.05.

2-Methyl-2-pentenal. This compound was prepared by the synthetic procedure of Paquin:[43] bp 137–138°; yield 32%; mass spectrum *m/e* (rel intensity) 98 (M^+, 68.8), 83 (25.5), 69 (50.8), 55 (52.0), 41 (100), and 39 (38.5).

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.39; H, 10.30.

Ethyl 2-Propynyl Sulfide (12). This compound was prepared by the reaction of propargyl bromide (119 g, 1 mol) with sodium ethanethiolate (84g, 1 mol) in 200 ml of absolute ethanol: bp 29–30° (15 mm); yield 75%; ir (film) 3220 (terminal acetylenic bond) and 2100–2120 cm^{-1} (C≡C); mass spectrum *m/e* (rel intensity) 100 (M^+, 56.7), 85 (35.5), 72 (61.1), 71 (78.9), 45 (100), and 39 (66.4); ^1H NMR (CCl_4) δ 1.23 (3 H, t, J = 7.0 Hz, CH_3), 2.04 (1 H, t, J = 1.2 Hz, CH), 2.60 (2 H, q, J = 7.0 Hz, CH_2 at ethyl), and 3.12 (2 H, d, J = 1.2 Hz, CH_2 at 2-propynyl).

Anal. Calcd for C_5H_8S: C, 59.98; H, 8.05. Found: C, 59.87; H, 8.06.

Isomerization of 2-Propynyl Sulfide to 1-Propynyl Sulfide. Isomerization was carried out by the method of Pourcelot et al.[44] The product was obtained by distillation: bp 35° (18 mm); yield 68%; ir (film) 2200 (C≡C), no absorption at 3220 cm^{-1} (terminal acetylenic bond); mass spectrum *m/e* (rel intensity) 100 (M^+, 84.3), 85 (15.5), 72 (90.2), 71 (100), 45 (66.4), and 39 (23.8); ^1H NMR (CCl_4) δ 1.32 (3 H, t, J = 7.0 Hz, CH_3 at ethyl), 1.90 (3 H, s, CH_3 at 1-propynyl), and 2.58 (2 H, q, J = 7.0 Hz, CH_2).

Anal. Calcd for C_6H_6S: C, 59.98; H, 8.05. Found: C, 59.90; H, 8.14.

5-Methyl-3,6-dithia-4,7-nonadiene (13). The synthetic procedure is a modification of the method of Schuijl and Brandsma.[45] To 200 ml of absolute ethanol was added 5 g of sodium. When the sodium disappeared, the solution was cooled to room temperature and successively 2-propene-1-thiol (14.8 g, 0.2 mol) and ethyl 1-propynyl sulfide (20 g, 0.2 mol) were added with cooling. The mixture was refluxed for 3 hr. 5-Methyl-3,6-dithia-4,8-nonadiene and **13** were detected by GLC. Sodium ethoxide (0.1 mol) was added to the mixture and was heated under reflux for 15 hr. Working up was carried out by pouring the reaction mixture onto 500 g of crushed ice and subsequently extracting three times with ether. The product was obtained by distillation and was purified by the gas chromatograph: yield 65%; ir (film) 1619 and 1580 (double bond), 965 (trans double bond), and 936 cm^{-1} (1-propenyl double bond); mass spectrum *m/e* (rel intensity) 174 (M^+, 74.2), 145 (24.6), 130 (18.9), 113 (100), 73 (36.0), 59 (90.8), 45 (91.5), 41 (33.6), and 39 (54.5); ^1H NMR (CCl_4) δ 1.25 (3 H, t, J = 6.4 Hz, CH_3 at ethyl), 1.68–1.73 (3 H, dd, CH_3 at 1-propenyl), 1.95 (3 H, d, J = 1.7 Hz, $SCCH_3$), 2.59 (2 H, q, J = 6.4 Hz, CH_2), 5.54–5.90 (1 H, m, CH at 1-propenyl), 5.89 (1 H, q, J = 1.7 Hz, SCH at vinyl), and 6.01 (1 H, m, J = 16.3 Hz, SCH at 1-propenyl).

Anal. Calcd for $C_8H_{14}S_2$: C, 55.16; H, 8.10. Found: C, 55.09; H, 8.03.

2-(1-Propenylthio)-1-propene-1-thiol (10). The same procedure as for 1-propene-1-thiol was used. The product was purified by using the preparative gas chromatograph: yield 7%; mass spectrum *m/e* (rel intensity) 146 (M^+, 66.3), 131 (40.7), 113 (52.3), 74 (64.0), 73 (63.2), 59 (76.7), 45 (100), 41 (82.6), and 39 (45.3).

Anal. Calcd for $C_6H_{10}S_2$: C, 49.31; H, 6.90. Found: C, 49.28; H, 6.88.

Synthesis of Authentic Thiophene Derivatives. 2-Methylthiophene. A mixture of levulinic acid (25 g, 0.22 mol) and phosphorus trisulfide (22 g, 0.14 mol) was heated. A vigorous reaction took place. As soon as the reaction had subsided, the product was distilled from the reaction mixture. The crude distillate was purified by using the preparative gas chromatograph: bp 112–113°; yield 14.2% (lit.[46] 15%); ir (film) 845, 815, and 750 cm^{-1} (thiophene ring); mass spectrum *m/e* (rel intensity) 98 (M^+, 52.0), 97 (100), 59 (6.2), 45 (21.6), and 39 (17.0); ^1H NMR (CCl_4) δ 2.47 (3 H, s, CH_3), 6.72 (1 H, m, C-3), 6.85 (1 H, dd, C-4), and 7.02 (1 H, dd, C-5).

Anal. Calcd for C_5H_6S: C, 61.23; H, 6.12; S, 32.65. Found: C, 61.41; H, 6.39; S, 32.14.

3-Methylthiophene was obtained as a by-product in preparation of 2,4- or 3,4-dimethylthiophene. 3-Methylthiophene was purified by using the gas chromatograph: ir (film) 850 and 760 cm^{-1} (thiophene ring); mass spectrum *m/e* (rel intensity) 98 (M^+, 50.0), 97 (100), 59 (2.3), 45 (26.8), and 39 (11.4); ^1H NMR (CCl_4) δ 2.19 (3 H, s, CH_3), 6.68 (1 H, d, J = 4.0 Hz, C-4), 6.73 (1 H, s, C-2), and 7.02 (1 H, d, J = 4.0 Hz, C-5).

2,5-Dimethylthiophene. A mixture of 2,5-hexanedione (25 g, 0.22 mol) and phosphorus trisulfide (22 g, 0.14 mol) was heated for 1 hr. The product was distilled from the reaction mixture: bp 134–135°; yield 50% (lit.[47] 50–60%); ir (film) 790 cm^{-1} (thiophene ring); mass spectrum *m/e* (rel intensity) 112 (M^+, 75.7), 111 (100), 97 (61.7), 59 (22.1), 45 (14.5), and 39 (13.3); ^1H NMR (CCl_4) δ 2.37 (6 H, s, CH_3) and 6.40 (2 H, s, C-3 and C-4).

Anal. Calcd for C_6H_8S: C, 64.27; H, 7.19; S, 28.54. Found: C, 64.73; H, 7.22; S, 28.48.

2,4-Dimethylthiophene. Ethyl 2-methyl-3-ethoxycarbonyl-4-oxopentanoate was prepared by condensation of ethyl acetoacetate and 2-bromopropionate: bp 123° (6 mm); yield 52%; ir (film) 1735 (ester) and 1715 cm^{-1} (carbonyl). Hydrolysis of this ester with concentrated hydrochloric acid gave 2-methyl-4-oxopentanoic acid: ir (film) 1715 (carbonyl) and 1710 cm^{-1} (COOH). A mixture of 2-methyl-4-oxopentanoic acid (24 g, 0.19 mol) and phosphorus trisulfide (22 g, 0.14 mol) was heated in carbon dioxide. The product was distilled from the reaction mixture and was purified by using the gas chromatograph: bp 137–138°; yield 33.8% (lit.[48] 34%); ir (film) 850, 820, and 760 cm^{-1} (thiophene ring); mass spectrum *m/e* (rel intensity) 112 (M^+, 76.6), 111 (100), 97 (53.0), 59 (8.9), 45 (31.4), and 39 (23.6); ^1H NMR (CCl_4) δ 2.07 (3 H, s, 4-CH_3), 2.34 (3 H, s, 2-CH_3), 6.34 (1 H, s, C-3), and 6.40 (1 H, s, C-5).

Anal. Calcd for C_6H_8S: C, 64.27; H, 7.19; S, 28.54. Found: C, 64.15; H, 7.23; S, 28.66.

2,3-Dimethylthiophene. Ethyl 3-methyl-3-ethoxycarbonyl-4-oxopentanoate was prepared by condensation of ethyl 2-methyl-3-oxobutanonate and ethyl bromoacetate, bp 102° (3 mm), yield 50%. Hydrolysis with concentrated hydrochloric acid gave 3-methyl-4-oxopentanoic acid. A mixture of 3-methyl-4-oxopentanoic acid (18 g, 0.14 mol) and phosphorus trisulfide (15 g, 0.1 mol) was heated for 1 hr. The product was obtained by distillation: bp 138–140°; yield 3% (lit.[49] 20%); mass spectrum *m/e* (rel intensity) 112 (M^+, 77.5), 111 (74.6), 97 (100), 59 (14.0), 45 (25.5), and 39 (20.3).

3,4-Dimethylthiophene. Diethyl 2,3-dimethyl-2-cyanosuccinate was prepared by condensation of ethyl 2-bromopropionate and ethyl 2-cyanopropionate: bp 125° (6 mm); yield 66%; ir (film) 2300 (CN) and 1736 cm^{-1} (ester). Hydrolysis of this ester with 6 *N* hydrochloric acid gave 2,3-dimethylsuccinic acid as a crystal, mp 191.2°. A mixture of the sodium salt of 2,3-dimethylsuccinic acid (19 g, 0.1 mol) and phosphorus trisulfide (19 g, 0.12 mol) was subjected to dry distillation in a stream of carbon dioxide. The crude distillate was purified by using the gas chromatograph: bp 144–146°; yield 26.8% (lit.[50] 21–22%); ir (film) 860 and 780 cm^{-1} (thiophene ring); mass spectrum *m/e* (rel intensity) 112 (M^+, 63.7), 111 (100), 97 (49.3), 59 (3.79), 45 (35.1), and 39 (22.9); ^1H NMR (CCl_4) δ 2.07 (6 H, s, CH_3) and 6.72 (2 H, s, C-2 and C-5).

Anal. Calcd for C_6H_8S: C, 64.27; H, 7.19; S, 28.54. Found: C, 64.56; H, 7.54; S, 28.45.

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Registry No.—**2,** 1115-93-1; **3,** 21593-77-1; **7,** 7683-75-2; **10,** 54677-58-6; **11,** 638-00-6; **12,** 7310-92-1; **13,** 54677-59-7; **16,** 632-15-5; **18,** 616-44-4; *cis*-**19,** 37981-34-3; *trans*-**19,** 37981-35-4; **21,** 37981-36-5; **22,** 37981-37-6; di-*n*-propyl sulfide, 111-47-7; diallyl sulfide, 292-88-1; *n*-propyl allyl sulfide, 27817-67-0; di-*n*-propyl disulfide, 629-19-6; diallyl disulfide, 2179-579; 1-propene-1-thiol, 925-89-3; 2-methyl-2-pentenal, 623-36-9; propargyl bromide, 106-96-7; sodium ethanethiolate, 811-51-8; 2-propynyl sulfide, 13702-09-5; 1-propynyl sulfide, 14453-81-7; 2-methylthiophene, 554-14-3; levulinic acid, 123-76-2; 2,5-dimethylthiophene, 638-02-8; 2,5-hex-

anedione, 110-13-4; ethyl 2-methyl-3-ethoxycarbonyl-4-oxopentanoate, 1113-77-5; ethyl acetoacetate, 141-97-9; ethyl 2-bromopropionate, 535-11-5; 2-methyl-4-oxopentanoic acid, 6641-83-4; 2,3-dimethylthiophene, 632-16-6; ethyl 3-methyl-3-ethoxycarbonyl-4-oxopentanoate, 13668-05-8; ethyl 2-methyl-3-oxobutanoate, 609-14-3; ethyl bromoacetate, 105-36-2; 3-methyl-4-oxopentanoic acid, 6628-79-1; diethyl 2,3-dimethyl-2-cyanosuccinate, 54677-60-0; 2,3-dimethylsuccinic acid, 13545-04-5; ethyl 2-cyanopropionate, 1572-99-2.

References and Notes

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(16) Amino acids produced by irradiation were converted into *N*-trifluoroacetylamino acid *n*-butyl esters and examined by gas–liquid chromatography (FID).

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