BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 3167—3170 (1971)

Photolytic and Thermal Decompositions of 5-Substituted 1,2,3,4-Thiatriazoles in the Presence of Olefins. Reactions of Sulfur Atoms

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(Received June 15, 1971)

Photochemical decompositions of 5-phenyl- and 5-amino-1,2,3,4-thiatriazoles in the presence of cyclohexene or tetramethylethylene led to the formation of the corresponding episulfide, the production of which has been explained in terms of sulfur atom reactions with the olefins. Kinetic measurements revealed the limitation of the reactions as a synthetic method of an episulfide from an olefin. Mechanism of the episulfide formation was briefly discussed. Thermal decompositions of these thiatriazoles in the presence of olefins gave rise to no episulfides.

Reactions of sulfur atoms have been extensively studied by Strausz and Gunning[1–3] using the photolysis of carbonyl sulfide. Almost all the reactions, however, have been carried out in gas phase and the precursor of sulfur atoms has been restricted only to carbonyl sulfide. Although carbonyl sulfide is probably the most useful source of sulfur atoms for mechanistic studies, the gaseous sulfide is an inconvenient precursor for synthetic studies. There are a few data on reactivities of sulfur atoms in solution,[4,5] and very recently Leppin and Gollnick reported direct photolysis of carbonyl sulfide in diverse organic solvents and reactions of sulfur atoms, thus formed, in solution.[6–8]

This paper describes the reactions of sulfur atoms generated from 5-substituted 1,2,3,4-thiatriazoles in organic solvents and their applicability as a synthetic method of episulfides from olefins.

Results and Discussion

5-Phenyl-1,2,3,4-thiatriazole (I) has been reported to decompose thermally into nitrogen, benzonitrile, and sulfur, and photochemically into the above three compounds and phenyl isothiocyanate.[9]

We found that photolysis of I in the presence of cyclohexene yielded cyclohexene episulfide (II). Results are summarized in Table 1. Identification and yield determination of the reaction products were carried out by means of gas chromatography (g.l.c.). Episulfide (II) was a sole product derived from reactions of sulfur atoms with cyclohexene, no cyclohexene thiols, insertion products, being formed.

Irradiation with high pressure or low pressure mercury lamp (HP or LP lamp) gave rise to II in a similar yield. Irradiation time was chosen so that the amount of II monitored by glc became approximately maximum, since II was found to decompose partially under these reaction conditions. Decomposition rates of I (rate constant k_1) were determined spectrophotometrically by following the decrease in the absorption ($\lambda_{max}^{CH_2Cl_2}$ 283 nm, ε 12000) and the decomposition was found to obey good first-order kinetics (see Table 1 for k_1 values).

Episulfide (II) was found to decompose also according to the first-order kinetics with rate constants (k_2) of 0.218 hr^{-1} (LP lamp) and 0.0848 hr^{-1} (HP lamp). Using these rate constants (k_1 and k_2) and assuming that k_3 and k_3' (rate constants of formation of II and

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[1] H. E. Gunning and O. P. Strausz, "Advances in Photochemistry," Vol. 4, ed. by N. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Interscience Publishers, New York, N. Y. (1966), p. 143.

[2] O. P. Strausz, "Organosulfur Chemistry," ed. by M. J. Hanssen, Interscience Publishers, New York, N. Y. (1967), Chapter 2.

[3] O. P. Strausz and H. E. Gunning, "The Chemistry of Sulfides," ed. by A. V. Tobolsky, Interscience Publishers, New York, N. Y. (1968), Part I, p. 23.

[4] U. Schmidt, K. Kabitzke, I. Boie, and C. Osterroth, *Chem. Ber.*, **98**, 3819 (1965).

[5] M. Luria and A. Tereinin, *J. Phys. Chem.*, **72**, 305 (1968).

[6] K. Gollnick and E. Leppin, *J. Amer. Chem. Soc.*, **92**, 2217 (1970).

[7] E. Leppin and K. Gollnick, *ibid.*, **92**, 2221 (1970).

[8] E. Leppin and K. Gollnick, *Chem. Ber.*, **103**, 2894 (1970).

[9] W. Kirmse, *ibid.*, **93**, 2353 (1960).

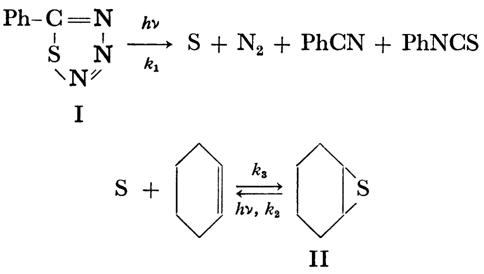
Table 1. Products, rate constants (k_1), and α values[a] of photodecomposition of the thiatriazole (I) in the presence of cyclohexene

Solvent (dichloromethane): 150 m*l*; cyclohexene: 50 m*l*; I: 5.00 g (30.7 mmol); reaction temperature: 20°C; reaction time: 18 and 10 hr for irradiation with HP[b] and LP,[b] respectively.

Ligth source[b]	Run	Products (%)				Recovered I (%)	k_1 (hr^{-1})	α
		$C_6H_{10}S$	PhCN	PhNCS	S_8			
LP	1	11	70	7	23	0	0.147	0.35
	2	11	87	11	—[c]	0	0.148	0.35
HP	1	8	44	4	30	—[c]	0.0395	0.26
	2	8(12)[d]	39(55)	5(7)	33(46)	29	0.0428	0.25

a) For definition, see Text.
b) HP and LP denote high pressure and low pressure mercury lamps, respectively.
c) Not determined.
d) Yield in parenthese based on I decomposed.

molecular sulfur, respectively) are much larger than k_1 and k_2, we can derive equation (1) on the basis of the following scheme and accordingly can estimate a hypothetical mole ratio (α) of II formed to I decomposed[10)] when II is assumed not to photodecompose.



$$S \xrightarrow{k_3'} \frac{1}{8}S_8$$

$$[II]_t = \alpha\frac{k_1}{(1-\alpha)k_2-k_1}[I]_0(e^{-k_1t}-e^{-(1-\alpha)k_2t}) \qquad (1)$$

where $[I]_0$ and $[II]_t$ stand for the concentration of I before irradiation and that of II at time *t*, respectively. The α values thus obtained (Table 1) indicate that, even if II were stable under these photochemical conditions, the yields might not exceed 35% and 26% under irradiation conditions with LP lamp and HP lamp, respectively. The low values of α seem to reveal the limitation in using sulfur atoms in solution as a reagent for episulfide syntheses.

Comparison of the present data with those of triplet sulfur atom reactions in gas phase deserves some mention. A triplet sulfur atom in gas phase has been reported to react with cyclopentene, structurally similar to cyclohexene, forming cyclopentene episulfide in 54% yield. In the case of other olefins such as ethylene, propylene and butene, the corresponding episulfides have been obtained in more than 80% yield.[11)] The great difference in the yield of episulfides is probably attributable to the fact that sulfur atoms generated in solution become less reactive due to deactivation by collision with solvent molecules and readily polymerize into molecular sulfur instead of reacting with cyclohexene.

In this connection, the following two observations are noteworthy. First, the thermal decomposition of I in the presence of an olefin gave no episulfide. This is probably explicable in terms of low excess kinetic (translational) energy of sulfur atoms generated in the thermal reaction. Second, no thiols were formed in the photochemical reactions with cyclohexene. This suggests that the reactive species formed in the photodecomposition of I is a triplet sulfur atom.[1,8)] According to Leppin and Gollnick, a singlet sulfur atom generated from carbonyl sulfide is effectively deactivated into a triplet species in alcohol, alkyl cyanide and aromatic hydrocarbon solvents.[6)] It is reasonable that dichloromethane, used as solvent in the present study, might be also a solvent favorable for the intersystem-crossing because of heavy atom effect of the chlorine atoms.

Table 2. Quenching of photodecomposition of thiatriazole (I) with naphthalene or piperylene in dichloromethane-cyclohexene (3:1)

Quencher	Products (%)			Recovered I (%)
	$C_6H_{10}S$	PhCN	PhNCS	
Naphthalene[a]	12	80	6	0
Piperylene[b]	5[c]	74[c]	6[c]	20[c]

a) With LP lamp. See Experimental.
b) With HP lamp. See Experimental.
c) Yield based on I decomposed.

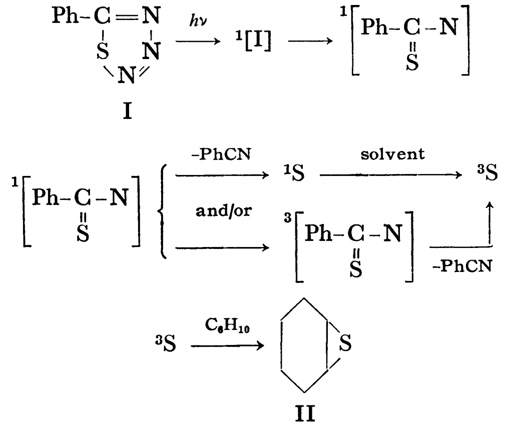
Quenching experiments were carried out with naphthalene and piperylene which are known as efficient quenchers for a triplet species. Comparison of the results listed in Table 2[12)] with those in Table 1 leads to the conclusion that the reactions were not affected by the quenchers and accordingly the triplet state of I would not be involved in the photoreactions, though the possibility that a short-lived triplet state might be involved cannot be excluded completely.

On the basis of the observations described so far, the

[10)] Since a small amount of phenyl isothiocyanate was actually formed, the exact value is equal to $\alpha/(1-P/100)$, where *P* is a percentage yield of phenyl isothiocyanate based on I decomposed. However, here we use the approximate value of α for simplicity.

[11)] E. M. Lown, E. L. Dedio, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 1056 (1967).

[12)] Although the yield of II in the reaction with piperylene as quencher is lower than that in one without the quencher, this can be readily explained from the fact that a diene also reacts with sulfur atoms.[1)] following scheme is plausible for formation of II.[13]



Difference in α values (0.35 and 0.26) caused by change of irradiation conditions can be accounted for probably by the difference in energy content of sulfur atoms; the triplet sulfur atom generated under irradiation with LP lamp might have much more energy than that generated under irradiation with HP lamp.

Table 3. Effect of cyclohexene concentration upon the yield of cyclohexene episulfide[a)]

C_6H_{10}/CH_2Cl_2 (m*l*/m*l*)	Products (%)[b)]			
	$C_6H_{10}S$	PhCN	PhNCS	S_8
10/190	7	78	11	—[c)]
50/150	11	70	7	23
150/50	20	63	9	51

a) I used, 5.00 g (30.7 mmol); light source, LP lamp; reaction time, 10 hr; reaction temperature, 20°C.
b) Yield based on I decomposed.
c) Not determined.

Attempts were made to increase the α value and consequently the yield of II by increasing the concentration of cyclohexene in the reaction solution. Results are given in Table 3. In 75% (v/v) cyclohexene solution the yield of II amounted to 20%. This value, though not satisfactory for synthetic purpose, is larger than other ones reported for episulfide formation with sulfur atoms in liquid phase; in the presence of cyclohexene, photodecomposition of ethyl isothiocyanate,[4] thermal decomposition of diethyl tetrasulfide,[14] and photodecomposition of carbonyl sulfide[8] have been reported to give the episulfide (II) in 7, 8, and 2% yields, respectively.

Table 4. Yields of episulfide in photodecompositions of thiatriazoles (I and III) in the presence of olefin

Thiatriazole	Light source	Olefin[c)] (m*l*)	Solvent (m*l*)	Reac. time (hr)	Episulfide (%)
I[a)]	HP	C(50)	150	18	6
I[a)]	LP	C(80)	110	5	7
I[a)]	HP	T(10)	190	16	1
I[a)]	LP	T(10)	190	12	6
III[b)]	HP	C(50)	150	10	0.4
III[b)]	LP	C(50)	150	6	7
III[b)]	HP	T(20)	140	19	0.5
III[b)]	LP	T(20)	140	9	6

a) 5.00 g (30.7 mmol) in benzene.
b) 2.70 g (26.5 mmol) in methanol.
c) C and T stand for cyclohexene and tetramethylethylene, respectively.

When the photodecomposition of I was carried out in the presence of cyclohexene or tetramethylethylene with benzene as solvent, similar results were obtained though the yields of the episulfide were somewhat low (Table 4). The reason for the low value in the reaction with tetramethylethylene is not clear.

5-Amino-1,2,3,4-thiatriazole (III) ($\lambda_{\max}^{\text{MeOH}}$ 267 nm, ε 4600), which is quite easily accessible from semicarbazide, could be employed as sulfur atom precursor (Table 4). In this case again, however, the yields of the episulfide were low, especially when irradiated with HP lamp.

Experimental

5-Phenyl-[15] and 5-amino-1,2,3,4-thiatriazoles,[16] cyclohexene episulfide,[17] and tetramethylethylene episulfide[18] were prepared by the methods described in literature. Gas chromatographic analyses were carried out using diethylene glycol polysuccinate column at 100°C.

Photodecomposition of 5-Phenyl-1,2,3,4-thiatriazole (I) in Dichloromethane. A General Procedure: Dichloromethane solution of the thiatriazole (5.00 g, 30.7 mmol) and cyclohexene was irradiated with high pressure (HP lamp) (Rikosha, 100 W) or low pressure mercury lamp(LP lamp) (Rikosha, 160 W). All the reactions were carried out under nitrogen atmosphere at 20°C. Rate measurements were performed spectrophotometrically by following the decrease of absorption at 283 nm (ε 12000). Product analyses were made as follows. The residue obtained after evaporation of the excess olefin and the solvent was dissolved again in dichloromethane. The insoluble part was sulfur. The soluble part was decanted into a volumetric flask and subjected to gas chromatographic analyses.

Photodecompositions of 5-Phenyl- (I) or 5-Amino-1,2,3,4-thiatriazole (III) in Benzene or Methanol. The reactions were carried out in a similar manner to that in the reactions in dichloromethane. Product analyses were not made except for episulfide (II).

Photodecomposition of Cyclohexene Episulfide (II). The episulfide (1.04 g) dissolved in a mixture of dichloromethane (150 m*l*) and cyclohexene (50 m*l*) was irradiated with LP or HP lamp. The decomposition rate was determined by following the decrease of II using glc.

Quenching Experiments. a) Quenching with Piperylene: The thiatriazole (I) (2.00 g, 12.3 mmol), cyclohexene (20 m*l*), and piperylene (6.8 g, 100 mmol) were dissolved in dichloro-

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[13] Attempts to trap Ph-C(=S)-N fragment with maleic anhydride were unsuccessful.

[14] S. O. Jones and E. E. Reid, *J. Amer. Chem. Soc.*, **60**, 2452 (1938).

[15] K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, **4**, 1349 (1950).

[16] E. Lieber, E. Oftedahl, C. N. Pillai, and R. D. Hites, *J. Org. Chem.*, **22**, 441 (1957).

[17] E. E. van Tamelen, "Organic Syntheses," Coll. Vol. IV, p. 232 (1963).

[18] M. A. Youtz and P. P. Perkins, *J. Amer. Chem. Soc.*, **51**, 3508 (1929).

methane (60 m*l*), and the solution was irradiated with HP lamp for 18 hr. After similar work-up to that in the other experiments for (I), product analyses were made by glc.

b) Quenching with Naphthalene: The thiatriazole (I) (5.00 g, 30.7 mmol), cyclohexene (50 m*l*), and naphthalene (3.85 g, 30.1 mmol) were dissolved in dichloromethane (150 m*l*) and the solution was irradiated with LP lamp for 10 hr. Product analyses were performed similarly.

Thermal Decomposition of the Thiatriazole (I) or (III) in the Presence of Cyclohexene. The thiatriazole (I) (5.00 g, 30.7 mmol) in a cyclohexene(90 m*l*)-toluene(100 m*l*) mixture was heated at about 100°C for 20 hr. After usual work-up, no cyclohexene episulfide was formed. The thiatriazole (III) (2.70 g, 26.5 mmol) and cyclohexene (50 m*l*) were dissolved in methanol (150 m*l*), and the solution was refluxed for 7 hr. No formation of II was observed.