Kinetics Runs. The apparatus used for the spectrophotometric runs may be described as follows. A Beckman Model DU-2-visible spectrophotometer, equipped with a Beckman 2180 dual thermospacer set, was also equipped with a specially built aluminum-block cell holder and a thermostated aluminum box cover for the cell compartment. From a constant-temperature bath, propylene glycol was pumped through the thermospacer set, cell block, and cell cover and returned to the bath. The temperature was monitored by the use of a calibrated thermister which was embedded in the bath liquid inside the cell block. Temperature control of ±0.05° was usually obtained with this thermostated assembly.

Except for the fact that the absorbance at 490 mμ due to BDPA was continually monitored, the kinetics runs were accomplished by methods which have been described.[3c]

Product Analysis. Peroxide vials were prepared in the previously described manner and decomposed for ten half-lives of the peroxide at 60°. Esters were analyzed by vpc methods analogous to those in paper II in this series.[3b] Columns used were (a) 5% Apiezon L on Chrom GAW DMCS, 3 ft × $^1/_8$ in.; (b) 2% QF-1 on Anakrom Abs, 10 ft × $^1/_8$ in.; (c) 10% methyl phenyl silicone oil on Chrom WAW HMDS. Column b at a column temperature of 120° and a flow rate of 30 ml/min was found to be the best for speed and reproducibility.

Acids from the decomposition of peroxides If and Ih were insoluble in the reaction mixture and were isolated and identified by melting point and mixture melting point. Acids from the decomposition of Ib, Ic, and Id were estimated by standard ir analysis of the reaction mixture.

Inversion products from peroxides Ib, If, Ih were isolated by decomposing 0.1 g of the respective peroxide in 25 ml of $CHCl_3$ under reflux for 1 hr. Extraction of the acid from the solution with bicarbonate, drying over anhydrous sodium sulfate, and removal of the solvent in a stream of nitrogen yielded fairly pure inversion product. The inversion product derived from Ih was the only solid, mp 50–55°. The only major impurity was ester which was corrected for in making up the standard solutions for determination of the yield of inversion product by ir.

Inversion products from peroxides Ic and Id were estimated by a barium hydroxide titration method which was patterned after a procedure used by Leffler.[6a]

Acknowledgment. We wish to thank the grant agencies whose support made this work possible.[2] We are especially indebted to Dr. David C. Lunney, who constructed the thermostated cell compartment for the spectrophotometer.

Photocycloaddition of Thiocarbonyl Compounds to Olefins. The Reaction of Thiobenzophenone with Various Types of Olefins[1,2]

A. Ohno, Y. Ohnishi, and G. Tsuchihashi

Contribution from the Sagami Chemical Research Center, Onuma, Sagamihara-shi, Kanagawa, 229, Japan. *Received February 20, 1969*

Abstract: The mechanism of photocycloaddition of thiobenzophenone to various types of olefins has been studied. Electron-rich olefins react with the n,π* triplet state of thiobenzophenone yielding either 1,4-dithiane or thietane derivatives depending on the structure of the olefin. Steric effect is an important factor in determining the reaction path. Electron-deficient olefins react with the π,π* singlet state of thiobenzophenone giving thietane derivatives. The kinetics and product analyses of the reactions show that the reaction with the former type of olefin proceeds *via* a radical mechanism, whereas that with the latter type of olefin takes place by a nucleophilic attack of excited thiobenzophenone on the olefins or through complexes between the olefins and the π,π* singlet state of thiobenzophenone. In the reactions that produce 1,4-dithiane derivatives, *trans* addition of two molecules of thiobenzophenone is verified. The structure and the configuration of the products have been determined both spectroscopically and chemically.

Thiobenzophenone is a unique compound in view of its absorption spectrum. The band of n → π* transition (λ_{max} 609 mμ (ε 180) in cyclohexane[3]) is completely separated from that of π → π* transition (λ_{max} 314.5 mμ (ε 15,500) in cyclohexane[3]). Therefore, by the irradiation with light of a suitable wavelength, it is possible to promote specifically only one of the transitions. Consequently, this compound lends itself easily to photochemical studies. Thiobenzophenone has other advantages over carbonyl compounds in the mechanistic study of the photoreaction with olefins: (i) since the olefins used in this study are transparent to 5890-Å light from a sodium lamp,[2c] there is no direct interaction between incident light and olefin; (ii) the energy of the n,π* triplet state of thiobenzophenone (40–43 kcal/mol[4]) is too low to be transferred to olefins. Therefore, the reaction of excited olefins need not be considered.

In previous papers,[2a–c] we have reported that olefins, in the photocycloaddition with thiobenzophenone, can be classified into three categories.

Case I olefins are those olefins which are substituted by electron-releasing groups. The reaction with this type of olefin, on irradiation with 5890 Å light, proceeds through the n,π* state of thiobenzophenone, resulting in the formation of 1,4-dithiane derivatives by the addition of two molecules of thiobenzophenone.[2c,d]

Case II olefins are those olefins which are substituted by electron-withdrawing groups. The reaction with

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(1) Part V of this series.

(2) (a) Part IV: A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Lett.*, 283 (1969); (b) part III: A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *ibid.*, 161 (1969); (c) part II: A. Ohno, Y. Ohnishi, M. Fukuyama, and G. Tsuchihashi, *J. Amer. Chem. Soc.*, 90, 7038 (1968); (d) part I: G. Tsuchihashi, M. Yamauchi, and M. Fukuyama, *Tetrahedron Lett.*, 1971 (1967).

(3) O. Korver, J. U. Veenland, and Th. de Boer, *Rec. Trav. Chim. Pays-Bas*, 84, 289 (1965).

(4) (a) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, 66, 2100 (1944); (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 132.

Table I.[a] Reactions with Cases I and III Olefins

Olefin	Thiobenzophenone/ olefin, g/g	Cyclohexane,[b] ml	Product	Yield, %	
				3660 Å	5890 Å
Cyclohexene	4.0/20.0		**1**	72	96
2,3-Dihydropyran	4.0/20.0		**2**	70	92
Ethyl vinyl ether	4.0/20.0		**3**	73	93
n-Butyl vinyl ether	1.0/12.0	40.0	**4**	47	
	3.0/8.0		**4**		95
n-Butyl vinyl sulfide	2.0/5.0	30.0	**5**	41	
	3.0/16.6		**5**		92
Styrene	4.0/20.0		**6**	65	94
1-Octene	3.5/15.0	25.0	**7**		47
trans-Propenylbenzene	3.2/10.0	10.0	*trans*-**10**		63
cis-Propenylbenzene	3.2/10.0	10.0	**10**[c]		63
1,3-Cyclooctadiene	2.0/7.0	10.0	**9**	60	60
α-Methylstyrene	3.6/12.0		**11**		90

[a] Reactions were carried out at the temperature of running water. [b] Used as a solvent. [c] A mixture of *cis* and *trans* isomers.

this type of olefin, on irradiation with 3660 Å light, proceeds through the π,π^* state of thiobenzophenone giving stereospecifically thietane derivatives.[2b]

Case III olefins are those olefins which are substituted by electron-releasing groups. The reaction with this type of olefin, on irradiation with 5890 Å light, results in the formation of thietane derivatives.[2a]

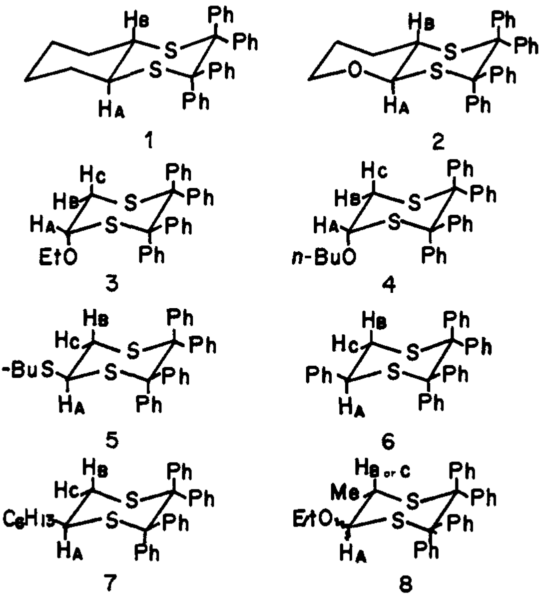
In this paper, we would like to present more detailed evidence on the mechanism of the reaction and to discuss the difference in reactivities of the n,π^* and the π,π^* state of thiobenzophenone.

Results and Discussion

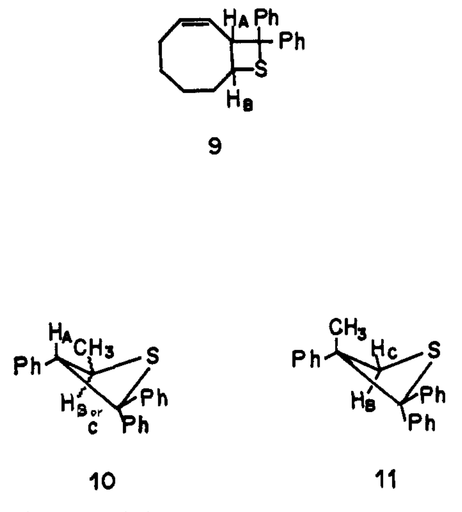
The Reaction with Case I and III Olefins. The reactions of cyclohexene, 2,3-dihydropyran, ethyl vinyl ether, *n*-butyl vinyl ether, *n*-butyl vinyl sulfide, styrene, 1-octene, and ethyl propenyl ether (*cis* and *trans*) yielded *trans*-3,3,4,4-tetraphenyl-2,5-dithiabicyclo[4.4.0]decane (**1**), *trans*-3,3,4,4-tetraphenyl-7-oxa-2,5-dithiabicyclo-[4.4.0]decane (**2**), 2,2,3,3-tetraphenyl-5-ethoxy-1,4-dithiane (**3**), 2,2,3,3-tetraphenyl-5-butoxy-1,4-dithiane (**4**), 2,2,3,3-tetraphenyl-5-butylthio-1,4-dithiane (**5**), 2,2,3,3,5-pentaphenyl-1,4-dithiane (**6**), 2,2,3,3-tetraphenyl-5-hexyl-1,4-dithiane (**7**), and a mixture of *cis*- and *trans*-2,2,3,3-tetraphenyl-5-ethoxy-6-methyl-1,4-dithianes (**8**), respectively, after irradiation with either 3660 Å light from a high-pressure mercury lamp or 5890 Å light from a sodium lamp[2c] (Scheme I). Reaction conditions and yields of products (based on thiobenzophenone) are summarized in Table I.

However, irradiation with either 3660 Å light or 5890 Å light of a mixture of thiobenzophenone and 1,3-cyclooctadiene, propenylbenzene (*cis* and *trans*), or α-methylstyrene resulted in the formation of 10,10-diphenyl-9-thiabicyclo[6.2.0]decene-2 (**9**),[5] a mixture of *cis*- and *trans*-2,2,3-triphenyl-4-methylthietanes (**10**), or 2,2,3-triphenyl-3-methylthietane (**11**), respectively, under the same condition in which case I olefins produced 1,4-dithiane derivatives[2a] (Scheme II).

Scheme I



Scheme II



In view of the facts that the reaction proceeds with 5890 Å light, that photoexcitation is zero order with respect to thiobenzophenone in the present system, and that *cis–trans* isomerization takes place during the reaction,[6] and further considering the esr study on an alkaline solution of thiobenzophenone,[7] it is evident that the reaction is initiated by the attack of the *n*,π^* *triplet state* of thiobenzophenone to case I or III olefins (eq 1) as previously proposed for the reaction with styrene.[2c] The very small energy difference between singlet and triplet states of n,π^* excited thiobenzophenone (ΔE_{ST}

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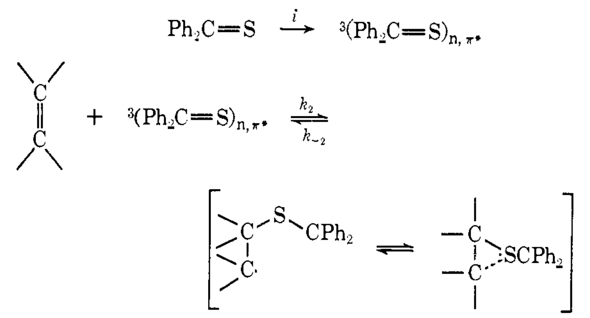
(5) The nmr spectrum of this compound is identical with that reported previously: K. Yamada, M. Yoshioka, and N. Sugiyama, *J. Org. Chem.*, **33**, 1240 (1968); also see ref 2a.

(6) A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Lett.*, 643 (1969).

(7) H. C. Heller, *J. Amer. Chem. Soc.*, **89**, 4288 (1967).

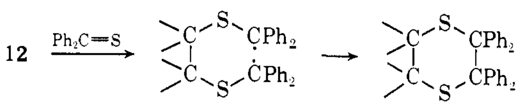


(1)

12a **12b**

≈ 0.8 kcal/mol[8]) as well as the heavy-atom effect of sulfur suggests fast intersystem crossing,[9,10] supporting the above mechanism.

In the reaction of case I olefins, the next step involves the attack of **12** on thiobenzophenone forming another composite diradical **13** and the two radical centers in **13** subsequently combining to form the final product (eq 2).

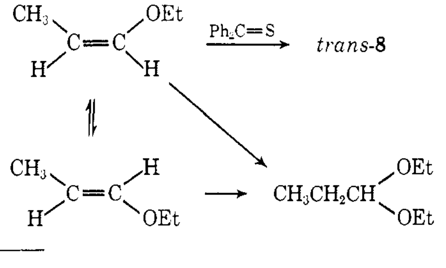


(2)

13

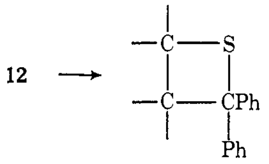
Since the radical centers on the benzhydryl positions in **12** and **13** are stabilized by two phenyl groups and a sulfur atom, they have little facility to react with thiobenzophenone. The reaction of thiobenzophenone with diazomethane[11] or with diphenyldiazomethane[12] as well as our findings on the reactivities of carbon radicals toward thiocarbonyl compounds[2c,13] support this mechanism.

It is difficult to elucidate the stereochemistry of the reaction since the addition reaction is accompanied by the isomerization of the olefin and the *cis*/*trans* ratio in the product does not correspond exactly to that of recovered olefin. However, we have established that the addition of thiobenzophenone molecules to case I olefins takes place in the *trans* manner. The use of 3660 Å light for the irradiation of ethyl propenyl ether provides a fortuitous situation. Since the *trans* isomer of this olefin is converted rapidly to 1,1-diethoxypropane, addition products with thiobenzophenone are not produced. Thus, only the reaction with the *cis*-olefin can be considered and this reaction has been found to give *trans*-**8** exclusively (eq 3). It should be noted that cyclohexene and 2,3-dihydropyran also give the *trans* adducts.



(3)

On the other hand, the two radical centers in **12** combine to give thietane derivative in the reaction of case III olefins (eq 4). It appears that steric effects play an important role in placing olefins into either case I or III category. The composite diradical derived from 1,3-cyclooctadiene has an allyl-type radical center, while that from styrene has a benzyl-type center. Since the stabilization energies or reactivities of both radicals are expected to be nearly the same,[14,15] it is not plausible for the electronic effect to be a key factor. This is also supported by the fact that propenylbenzene is a case III olefin in contrast to styrene (case I). Thus, the steric inhibition of substituent(s) to *trans* addition controls the reaction path. It is important to emphasize that cyclohexene is a case I olefin because the backside of the thiobenzophenone moiety in **12** is open, whereas the 1,3-cyclooctadiene-ring methylenes in **12**, by protecting the radical center, prevent this composite diradical from reaction with a second molecule of thiobenzophenone. Consequently, 1,3-cyclooctadiene belongs to case III.



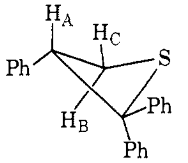
(4)

Thus, eq 2 and 4 are essentially competitive reactions, which makes it possible to expect that thietane derivatives would result from the reaction of case I olefins, provided the concentration of thiobenzophenone is low enough. Indeed, this postulation has been proved as illustrated in Table II. The major product changed from **6** to **14** when the concentration of thiobenzophenone was lowered in the reaction with styrene. However, even though similar concentrations of thiobenzophenone were used, the reaction with ethyl vinyl ether

Table II. The Effect of Concentrations of Thiobenzophenone

Olefin (ml)[a]	Solvent,[b] ml	Light, Å	Product 6	Product 14
Styrene (5.0)	None	3660	Major	Minor[c]
Styrene (5.0)	None	5890	Major	Minor[c]
Styrene (10.0)	25.0	3660	Minor[c]	Major
Styrene (10.0)	25.0	5890	Minor[c]	Major
Ethyl vinyl ether (10.0)	25.0	5890	Major	*d*

[a] 1 g of thiobenzophenone was used. [b] Cyclohexane. [c] Detected by thin layer chromatography. [d] 2,2-Diphenyl-3-ethoxythietane could not be detected.



14

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(8) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **67**, 994 (1945).

(9) F. Wilkinson, *Advan. Photochem.*, 3, 242 (1964).

(10) S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964).

(11) E. Campaine in "The Chemistry of Carbonyl Group," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1966, p 946.

(12) (a) H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, 3, 833 (1920); (b) A. Schönberg, D. Cernick, and W. Urban, *Chem. Ber.*, **64**, 2577 (1931).

(13) M. Yamauchi, A. Ohno, M. Fukuyama, and G. Tsuchihashi, Abstracts, 19th Symposium on Organic Reaction Mechanism, Yamagata, Japan, Oct 1968, p 132.

(14) (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 393; (b) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 50.

(15) J. A. Berson and E. J. Walsh, Jr., *J. Amer. Chem. Soc.*, **90**, 4730 (1968).

produced **3**. This fact suggests that the carbon radical substituted by an ethoxy group at the α position is more reactive toward the thiocarbonyl group than that substituted by a phenyl group.

The Reaction with Case II Olefins. Thiobenzophenone, under irradiation with 5890 Å light, does not react with olefins that are substituted by electron-withdrawing substituent(s). However, irradiation with 3660 Å light does initiate the reaction giving thietane derivatives.[2b] Thus, the reaction of acrylonitrile, methyl acrylate, vinyl acetate, dichloroethylene (*cis* and *trans*), dicyanoethylene (*trans*), and crotononitrile and isocrotononitrile yielded 2,2-diphenyl-3-cyanothietane (**15**), 2,2-diphenyl-3-methoxycarbonylthietane (**16**), 2,2-diphenyl-3-acetoxythietane (**17**), 2,2-diphenyl-3,4-dichlorothietane (**18**), *trans*-2,2-diphenyl-3,4-dicyanothietane (**19**), and 2,2-diphenyl-3-cyano-4-methylthietane (**20**) (with a small amount of 2,2-diphenyl-4-cyano-3-methylthietane (**21**)), respectively (Scheme III). The reaction proceeds stereospecifically and the configuration in the olefin is completely retained both in the product and in the recovered olefin. The results are summarized in Table III.

Scheme III

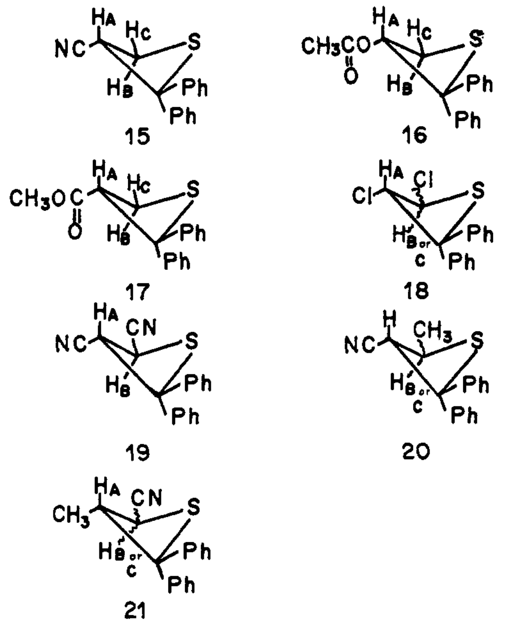


Table III.^{a} Reactions with Case II Olefins

Olefin	Thiobenzophenone/olefin, g/g	Cyclohexane,^{b} ml	Product	Yield,^{c} %
Acrylonitrile	1.3/8.0	40.0	**15**	93
Methyl acrylate	2.0/15.0	10.0	**16**	81
Vinyl acetate	4.3/20.0	40.0	**17**	50
trans-Dichloroethylene	1.5/8.5	15.0	*trans*-**18**	90
cis-Dichloroethylene	2.4/20.0	10.0	*cis*-**18**	83
trans-Dicyanoethylene	3.0/1.17	15.0^d	**19**	36
Crotononitrile	1.4/5.0	5.0	*trans*-**20**	60
			trans-**21**	30
Isocrotononitrile	2.4/7.0	10.0	*cis*-**20**	60
			cis-**21**	30

^{a} Reactions were carried out at the temperature of running water. ^{b} Used as a solvent. ^{c} Irradiation with 3660 Å light. ^{d} Tetrahydrofuran was used as a solvent.

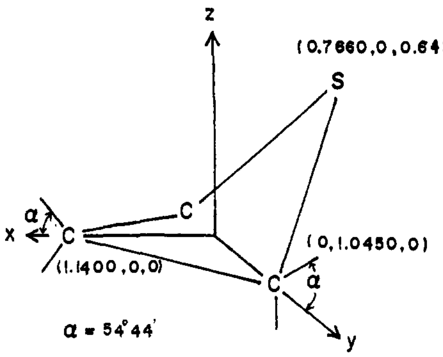


Figure 1. Direction cosines of atoms in thietane.

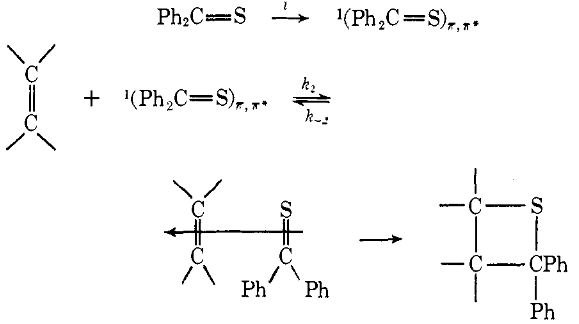
Dipole moments[16] have been employed to analyze the configurations of these compounds because coupling constants in the nmr spectra of ring protons in four-membered ring compounds have abnormal values[17] (almost identical values for *cis* and *trans* couplings) and cannot be useful tools for the determination of configurations. The results are summarized in Table IV, where the calculated values have been obtained, by assuming direction cosines shown in Figure 1 for each of the pertinent atoms.[18] The molecular refractivity value of 20.49 cc was used for the thietane ring.[19]

Table IV. Dipole Moments of Thietane Derivatives

Compd	Found	Calcd	Bond moments used for Calcns^a μ_{C_3-X}	μ_{C_4-X}
15	2.33	2.32	4.00	
trans-**18**	2.02	2.02	1.30	2.05
cis-**18**	2.16	2.16	1.40	2.15
19	3.84	3.92	4.00	4.00

^{a} Dipole moment of thietane was observed as 1.72 D (lit.[20] 1.78 D).

As previously proposed for the reaction of acetone,[20,21] the reaction with case II olefins should involve nucleophilic attack by the π,π* *singlet state* of thiobenzophenone or an electron transfer from the π,π* state of thiobenzophenone to the electron-deficient double bond (eq 5). This view is supported by considering



$$\mathrm{Ph_2C{=}S} \xrightarrow{i} {}^1(\mathrm{Ph_2C{=}S})_{\pi,\pi^*}$$

$$\mathrm{>C{=}C<} + {}^1(\mathrm{Ph_2C{=}S})_{\pi,\pi^*} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \quad (5)$$

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(16) We thank Professor T. Shimozawa of the Saitama University for the measurement of and useful discussions on dipole moments of thietane derivatives. Detailed discussions on this subject will be published elsewhere.

(17) V. Georgian and L. Georgian, *Tetrahedron*, **19**, 1219 (1963).

(18) M. S. White and E. L. Beeson, Jr., *J. Chem. Phys.*, **43**, 1839 (1965).

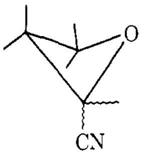
(19) C. W. N. Cumper and A. I. Vogel, *J. Chem. Soc.*, 3521 (1959).

(20) N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Grick, *J. Amer. Chem. Soc.*, **89**, 3950 (1967).

(21) Note that benzophenone does not react with case II olefins: D. R. Arnold, R. L. Hinman, and A. H. Grick, *Tetrahedron Lett.*, 1425 (1964).

the following; (i) the reaction does not proceed with irradiation of 5890 Å light; (ii) photoexcitation is zero order with respect to thiobenzophenone; (iii) thietane derivatives are the only detectable products; (iv) olefins are electron deficient; (v) stereochemical relationship in the initial olefin is completely retained both in the product and in the recovered olefin; and (vi) the possibility of intersystem crossing from $^1(\pi,\pi^*)$ state to $^3(\pi,\pi^*)$ state is very small.[22] The idea of the nucleophilic character of the *reacting* thiobenzophenone is also supported by the fact that the yield of **17** is fairly low.[23] This occurs because the double bond in vinyl acetate is relatively less electron deficient than other olefins in this group. In this connection, it is interesting to observe that the reaction with crotononitrile or isocrotononitrile, although completely stereospecific, results in the formation of a 2:1 mixture of **20** and **21**. Conceivably, the electron deficiency at the β-carbon in these olefins is somewhat weakened by the electron-releasing ability of the methyl group and, as a result, the orientational specificity observed in the reaction with acrylonitrile no longer holds. The uv spectra of thiobenzophenone in cyclohexane and in acrylonitrile (λ_{max} 320 mμ (ϵ 13,000)) does not suggest the presence of a charge-transfer complex between these olefins and thiobenzophenone in the ground state nor does it suggest an excitation of the π electron of thiobenzophenone into a charge-transfer orbital.

Recently, Barltrop and Carless have reported that oxetanes which are formed by photocycloaddition of aliphatic ketones with acrylonitrile or methacrylonitrile have structures represented by **22**.[24] Here, the direction of the attack of the heteroatom is in reverse direction to that in thiobenzophenone. We believe this is due to the difference in excitations, that is, the n,π^* excited state of a ketone has the resonance structure **23** and the nucleophilic site of the molecule exists on the carbonyl carbon as a result of the contribution of **23b**.[25] On the other hand, thiobenzophenone reacts in its π,π^* singlet state. Although it is difficult to predict a precise structure for this excited state,[25] the polarization of the thiocarbonyl group can be expected to be the same as that of the ground state, **24**. Therefore, the nucleophilic center in this state of thiobenzophenone is located on the sulfur atom.



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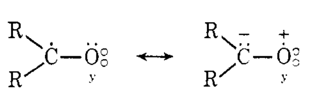
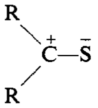


23a **23b**



24

Reactivities of Photoexcited Thiobenzophenone and Thiyl Radicals. Walling and Gibian have reported that the n,π^* triplet state of benzophenone behaves similarly to *t*-butoxy radicals[26] in hydrogen abstraction. Photocycloaddition of thiobenzophenone also resembles reactions of thiyl radicals.[27–29] In this context it will be useful to compare the relative reactivities of olefins with both photoexcited thiobenzophenone and thiyl radicals. Hence the relative rates of the addition of the n,π^* excited state of thiobenzophenone to various olefins have been studied. The procedure has been described in a previous paper.[2c] The observed rate constant, k_{obsd}, can be expressed as

$$\frac{1}{k_{obsd}} = \frac{1}{2i} + \frac{k_{-1}}{2ik_2}\frac{1}{[S]} \tag{6}$$

for reactions that yield 1,4-dithiane derivatives, and

$$\frac{1}{k_{obsd}} = \frac{1}{i} + \frac{k_{-1}}{ik_2}\frac{1}{[S]} \tag{7}$$

for reactions that yield thietane derivatives. In eq 6 and 7, i, k_{-1}, k_2, and [S] are the rate for the formation of *reacting* thiobenzophenone, the rate constant for the deactivation of the *reacting* thiobenzophenone to its ground state, the rate constant for the addition of the *reacting* thiobenzophenone to an olefin, and the concentration of the olefin, respectively.[2c] When it is assumed that the k_{-1} values are identical for all reactions if the electronic and spin states of thiobenzophenone are the same, then the k_2/k_{-1} ratios represent the relative reactivities of olefins toward the addition of thiobenzophenone. The results are summarized in Table V together with those obtained for reactions of olefins and thiyl radicals.

Table V. Relative Reactivities toward Electron-Releasing Activated Olefins

Olefin	^{3}(Ph$_2$-C=S)$_{n,\pi^*}$	$C_{12}H_{25}S\cdot$[a]	$CH_3O_2CCH_2S\cdot$[b]	$C_4H_9S\cdot$[c]
$CH_3(CH_2)_5CH=CH_2$	1.00	1.00	1.1	
$CH_2(CH_2)_3CH=CH$	2.00	0.25		
$O(CH_2)_3CH=CH$	4.00			
$C_6H_5CH=CH_2$	10.0	17		
n-$C_4H_9OCH=CH_2$	11.0	3.9	10	1.0
n-$C_4H_9SCH=CH_2$	>40			10

[a] Reference 28. [b] Reference 29. [c] Reference 30.

As seen in Table V, electron densities on carbon–carbon double bonds seem to play an important role in the reaction of the n,π^* triplet state of thiobenzophenone, whereas stabilities of composite radicals are important for the reaction of thiyl radicals. Thus, the relative reactivity of *n*-butyl vinyl ether is three times as large for thiobenzophenone than for dodecanethiyl radical. Although, according to the above discussion the n,π^* trip-

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[22] Reference 4b, pp 57–59.

[23] The yield of **19** is also low, but this is due to the difference of the reaction condition (See Table III).

[24] J. A. Barltrop and H. A. J. Carless, *Tetrahedron Lett.*, 3901 (1968).

[25] H. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

[26] (a) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **86**, 3902 (1964); (b) C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

[27] C. Walling and W. Helmreich, *ibid.*, 81, 1144 (1959).

[28] J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc.*, *B*, 1191 (1966).

[29] N. P. Petukhova and E. N. Prilezhaeva, *J. Org. Chem. USSR*, 2, 1914 (1966).

let state of thiobenzophenone should be regarded as electrophilic as a thiyl radical derived from methyl thioglycollate, we believe this is incidental and the former is less electrophilic than the latter. This is supported by the fact that no substituent effect was observed in the reaction of thiobenzophenone with substituted styrenes,[2c] while a polar effect was reported for the reaction of methyl thioglycollate with substituted α-methylstyrenes.[28]

The addition reaction with case II olefins has also been studied kinetically to determine whether or not the π,π^* singlet state of thiobenzophenone behaves like thiyl radicals. The procedure is the same as described above and relative rates are listed in Table VI together with the reactivity with a thiyl radical.

Table VI. Relative Reactivities toward Electron-Deficient Olefins

Olefin	$^1(Ph_2C{=}S)_{\pi,\pi^*}$	$C_{12}H_{25}S\cdot$[a]
$CH_3CO_2CH{=}CH_2$	1.00	1.00
cis-$ClCH{=}HCCl$	2.25	<0.25
$CH_3O_2CCH{=}CH_2$	3.00	2.52
$NCCH{=}CH_2$	5.30	[b]

[a] Reference 28. [b] The reaction does not proceed.

As seen in Table VI, the reactivity of these olefins with the π,π^* singlet state of thiobenzophene increases with the increasing electron deficiency of the carbon–carbon double bond and forms a different spectrum from that of the thiyl radical.

methylstyrene, acrylonitrile, methyl acrylate, vinyl acetate, *cis*- and *trans*-dichloroethylenes, *trans*-dicyanoethylene, crotononitrile, and isocrotononitrile are commercially available.

n-Butyl vinyl sulfide was prepared by dehydration[31] of 2-(*n*-butylthio)ethanol. The latter was synthesized by the reaction of sodium *n*-butylmercaptide with 2-chloroethanol.[32] A dropping funnel containing 68.6 g of 2-(*n*-butylthio)ethanol was attached to a Claisen flask containing 40 g of KOH. The alcohol was added dropwise while the flask was kept at 220° using an oil bath. The distillate (~130°) was collected in a flask and the upper layer separated and dried over $CaCl_2$. Distillation gave 43.2 g of the olefin (60%), bp 140–141° (lit.[33] 141°).

Ethyl propenyl ether was synthesized by the dehydrochlorination with pyridine of α-chloropropyl ethyl ether.[34] Fractional distillation of the product gave the *cis*- and *trans*-olefins, bp 69.0° (lit.[35] 69.0°) and 75.0° (lit.[35] 75.0°), respectively.

cis-Propenylbenzene was prepared by decarboxylation[36] of *trans*-2-methyl-3-phenylpropenoic acid which was obtained by a Perkin reaction;[37] bp 59° (19 mm) (lit.[38] 55° (15 mm)).

All olefins were purified by distillation through a heli-grid column of over 65 theoretical plates and the purity was confirmed by vpc.

Photocycloaddition. A 400-W high-pressure mercury lamp (Toshiba H-400P) or eight 60-W low-pressure sodium lamps (National SOI-60) arranged in a merry-go-round fashion were used for irradiation. The detailed procedure has been described previously.[2c] The irradiation was continued until the blue color of thiobenzophenone had completely disappeared. The reaction time depended on the concentration of thiobenzophenone. After the reaction, excess olefin was removed from the reaction mixture under reduced pressure, and the residue was chromatographed on neutral alumina (Woelm, grade 1) with a benzene–petroleum ether (bp 30–60°) mixture as an eluent. The solid product thus obtained was recrystallized from a benzene–*n*-hexane mixture and was analyzed. Some of the products were directly recrystallized after removal of excess olefin. Melting points and results of elemental analyses of products are listed in Table VII.

Table VII. Melting Points and Results of Elemental Analyses of Products

		Calcd, %				Found, %			
Compd[a]	Mp, °C	C	H	S	Other	C	H	S	Other
1	174	80.29	6.32	13.40		80.40	6.46	13.20	
2	147	77.46	5.87	13.34		77.62	5.83	13.40	
3	140	76.88	6.02	13.68		76.46	5.89	13.71	
4	132–133	77.38	6.42	12.90		77.68	6.42	12.73	
5[b]	116–117	74.95	6.29	18.76		74.93	6.08	18.82	
6	154	81.56	5.64	12.81		81.89	5.56	12.58	
7	115	80.26	7.13	12.61		80.06	7.34	12.50	
trans-**8**	78–79	77.13	6.27	13.29		77.66	6.24	13.27	
10	78–79	83.50	6.37	10.13		83.84	6.73	10.30	
11	112–113	83.50	6.37	10.13		83.72	6.38	10.20	
14	140	83.40	6.00	10.60		83.45	6.23	10.59	
15	84	76.46	5.21	12.75	N, 5.57	76.67	5.21	12.73	N, 5.73
16	84–85	71.80	5.67			71.16	5.64		
17[c]	180								
trans-**18**	72–73	61.02	4.10	10.86	Cl, 24.02	60.96	4.04	10.86	Cl, 23.91
cis-**18**	126–127	61.02	4.10	10.86	Cl, 24.02	61.29	4.07	10.77	Cl, 24.16
19	144	73.88	4.38	11.59	N, 10.14	73.84	4.60	11.66	N, 10.25
20	87	76.96	5.70	12.08	N, 5.28	77.26	5.56	12.08	N, 5.32

[a] Recrystallized from a benzene–*n*-hexane mixture. [b] Recrystallized from acetonitrile. [c] Recrystallized from benzene.

Consequently, we have concluded that the addition of the n,π^* triplet state of thiobenzophenone proceeds by a radical mechanism, while the π,π^* singlet state of thiobenzophenone attacks electron-deficient olefins as a nucleophile.

Experimental Section

Materials. Thiobenzophenone was prepared and purified as previously described.[2c,30]

Cyclohexene, 2,3-dihydropyran, ethyl vinyl ether, butyl vinyl ether, 1-octene, 1,3-cyclooctadiene, *trans*-propenylbenzene, α-

When a mixture of *trans*-ethyl propenyl ether and thiobenzophenone was irradiated with 3660 Å light, neither addition product nor recovered olefin was obtained. The only isolable compound was 1,1-diethoxypropane. A separate experiment confirmed that the acetal formation is much faster than the photocycloaddition

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(30) B. F. Gofton and E. A. Braude, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 927.

(31) L. A. Brooks, *J. Amer. Chem. Soc.*, **66**, 1295 (1944).

(32) T. C. Whitner, Jr., and E. E. Reid, *ibid.*, **43**, 636 (1921).

(33) W. Reppe, *et al.*, *Justus Liebigs Ann. Chem.*, 601, 81 (1956).

(34) L. C. Swallen and C. E. Boord, *J. Amer. Chem. Soc.*, **52**, 651 (1930).

(35) M. Farina, M. Peraldo, and G. Bressan, *Chem. Ind.* (Milan), **42**, 967 (1960); *Chem. Abstr.*, **55**, 11284*d* (1961).

(36) W. R. R. Park and G. F. Wright, *J. Org. Chem.*, **19**, 1435 (1954).

(37) W. H. Perkin, *J. Chem. Soc.*, **31**, 388 (1877).

(38) C. G. Overberger, D. Tanner, and E. M. Pearce, *J. Amer. Chem. Soc.*, **80**, 4566 (1958).

Table VIII. Chemical Shifts of Protons in Nmr Spectra of Products, δ[a]

Compd	H_A	H_B	H_C	Phenyl	Others	J, Hz		
						AB	AC	BC
1	3.09 (m)	3.09 (m)		6.8–7.6	1.1–2.0 (m)			
2	4.88 (d)	3.97 (bd)		7.0–7.7	3.50 (bt) 3.14 (bt) 1.68 (m)	10.0		
3	4.80 (t)	2.86 (qt)	2.66 (qt)	6.9–8.0	4.27 (qn) 3.50 (qn) 1.45 (t)	3.0	3.0	15.4
4	4.75 (t)	2.82 (qt)	2.62 (qt)	6.8–8.1	4.10 (sx) 3.39 (sx) 1.02 (t) 1.4–1.9 (m)	3.0	3.0	14.8
5	4.40 (qt)	3.03 (qt)	3.05 (qt)	6.9–7.7	2.52 (m) 1.34 (m) 0.84 (m)	10.6	5.8	23.0
6	4.86 (qt)	2.90 (qt)	3.21 (qt)	7.0–7.9		11.8	4.2	14.0
7	3.43 (m)	2.75 (qt)	2.76 (qt)	6.8–7.7	1.0–1.6 (m) 0.86 (t)	8.8	6.4	15.1
trans-**8**	4.50 (d)	3.59 (m)		6.8–7.7	3.38 (m) 1.22 (d) 1.09 (t)	10.6		
cis-**8**	4.59 (d)		~3.6 (m)		1.44 (t) 1.16 (d)		3.2	
9	4.54 (dd)	3.30 (sx)		6.8–7.6	5.35 (m) 0.80–2.50 (m)	10.0		
trans-**10**	4.86 (d)	3.97 (dq)		6.7–7.4	1.38 (d)	10.0		
cis-**10**[b]	4.95 (d)		4.04 (dq)	6.6–7.6	1.03 (d)		8.6	
11		2.92 (d)	4.05 (d)	6.9–7.6	1.68 (s)			9.2
14	5.40 (t)	3.21 (t)	3.53 (t)	6.6–7.6		8.5	8.5	8.5
15	4.93 (t)	3.23 (t)	3.50 (t)	7.1–7.7		9.0	9.0	9.0
16[b]	4.80 (t)	2.92 (t)	3.73 (t)	7.0–7.5	3.22 (s)	9.6	9.6	9.6
17	6.45 (t)	3.21 (t)	3.36 (t)	7.1–7.6	1.85 (s)	9.0	9.0	9.0
trans-**18**	5.75 (d)	5.36 (d)		7.0–7.6		7.8		
cis-**18**	6.17 (d)		5.66 (d)	7.0–7.7			6.7	
19	5.17 (d)	4.40 (d)		7.0–7.7		10.0		
trans-**20**[b]	4.30 (d)	3.82 (dq)		6.8–7.8	1.48 (d)	10.0		
cis-**20**[b]	4.80 (d)		3.62 (dq)	6.9–7.8	1.45 (d)		8.6	
cis-**20**	4.94 (d)		3.80 (dq)	7.1–7.6	1.54 (d)		8.6	
trans-**21**	3.82 (dq)	3.60 (d)		6.8–7.7	0.79 (d)	10.0		
cis-**21**	4.17 (dq)		3.92 (d)	6.9–7.8	0.98 (d)		8.6	

[a] In $CDCl_3$ with internal standard of TMS. Abbreviations are: s = singlet; d = doublet; t = triplet; qt = quartet; qn = quintet; sx = sextet; m = multiplet; bd = broad doublet; bt = broad triplet; dd = doublet of doublets; dq = doublet of quartets. All phenyl protons appear as multiplets. [b] In CCl_4 with internal standard of TMS.

under the reaction conditions. Thus, when the neat olefin was irradiated with 3660 Å light for 10 hr, the olefin was entirely consumed giving 1,1-diethoxypropane.[39] The nmr, ir, and mass spectra, refractive index, and the boiling point of the product were identical with those of the authentic compound.

Oxidation of Thietane Derivatives. For example, 0.2 g of **15** was oxidized to 2,2-diphenyl-3-cyanothietane 1,1-dioxide (**25**) by keeping it in 50 ml of acetic acid containing 0.5 ml of 30% hydrogen peroxide at room temperature for a week. Crystals that appeared, on neutralization of the solution with K_2CO_3, were recrystallized from 95% ethanol yielding a pure material, mp 157–158.5°.

Characterization of Products. a. 1,4-Dithiane Derivatives Structures and configurations of products were determined mainly by spectroscopic methods. Chemical shifts of protons in nmr spectra of products are listed in Table VIII. The results on the spin-decoupling study of the adduct from *n*-butyl vinyl sulfide are in agreement with the structure **5**. Thus, protons A and B are coupled with J = 10.6 Hz, while the coupling constant for protons A and C is 5.8 Hz. This suggests that protons A and B are in the axial positions. The situation is the same, as seen in Table VIII, for compounds **2**, **6**, **7**, and *trans*-**8**. On the other hand, the adduct **4** has an abnormal nmr spectrum. A signal corresponding to the proton A appears as a triplet at δ 4.75 and those to protons B and C appear as quartets at δ 2.82 and 2.62, respectively. The coupling constants, J_{AB} and J_{BC}, were found to be 3.0 Hz, suggesting that the proton A is in the equatorial position. When **4** was warmed for several minutes at 60–70°, the intensities of the signals at δ 4.10 and 3.39 in the nmr spectrum of **4** decreased and new signals appeared

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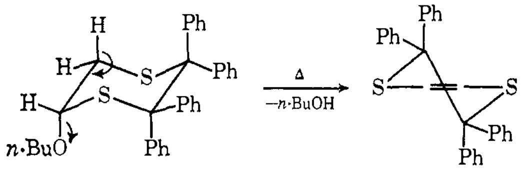
[39] The reaction may proceed by disproportionation yielding methylacetylene as another product. However, effort was not made to isolate the gaseous products. An alternative possibility is the presence of undetectable amount of catalyst such as proton. Further studies are in progress.

at δ 6.17 (singlet) and 3.58 (triplet). This indicates that a butanol can be easily eliminated from **4** according to the equation



and supports the proposal that the butoxy group is situated axially, consequently favoring the elimination.

It is interesting to note that methylene protons next to the oxygen atom in the butoxy group of **4** have quite a different chemical shift ($\Delta\delta = 0.71$) due to asymmetric induction by C_5 and the anisotropy of the axial phenyl group at C_3. This implies that the butoxy group is highly hindered to rotation around the C–O bonds. All of these facts are in accord with the axial assignment of the butoxy group in **4**. This is also true for **3**.[2d]

The configurational analysis of **8** should be mentioned. The product obtained by the irradiation with 3660 Å light of a mixture of thiobenzophenone and *cis*-ethyl propenyl ether has nmr signals which are in accord with the structure of the *trans*-**8**, with methyl and ethoxy groups at equatorial positions. However, the nmr spectrum of the product obtained by the irradiation with 5890 Å light of the same mixture has a doublet at δ 4.59 ($J = 3.2$ Hz) in addition to signals for *trans*-**8**. Since it has been established that axial protons are more shielded than equatorial protons due to the anisotropy of axial phenyl group(s) (see Table VIII), the doublet can be tentatively assigned to H_A in *cis*-**8**. It is implied that *cis*-**8** has an equatorial methyl group and an axial ethoxy group, since the multiplet at δ ~3.6, corresponding to H_C, appears almost identical with that of H_B in the *trans* isomer. The chemical shift of H_A in *cis*-**8** is close to that of H_B in **3** and, as seen in Table VIII, the coupling constants of these signals are consistent with the assigned configuration.

b. Thietane Derivatives. With thietane derivatives, the mass spectrum is indicative of the structure. For example, in the mass spectrum of **15**, the presence of peaks at *m/e* 45 and 205 corresponding to ions $(CH{\equiv}S)^+$ and $(NCCH{=}CPh_2)\cdot^+$, respectively, and the absence of a peak at *m/e* 71 corresponding to the ion $(NCCHS)\cdot^+$ clearly suggest that C_3 is substituted by a cyano group. In the nmr spectrum of **25**, signals originally corresponding to three triplets in **15** appeared at δ 4.50–4.14 as an ABC multiplet. This fact again supports the structure.

Based on the defined structures and configurations of **15**, *cis*- and *trans*-**18**, and **19**, the structures of **16**, **17**, **20**, and **21** have been elucidated by analyzing chemical shifts in nmr spectra of these compounds.

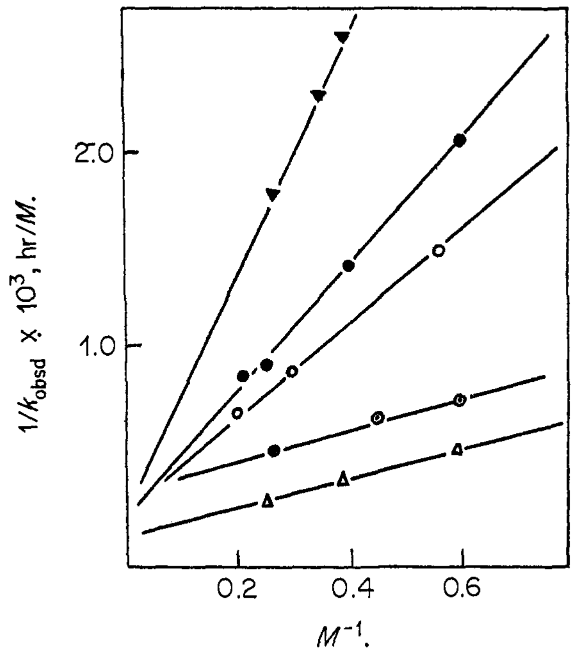


Figure 2. Plot of $1/k_{obsd}$ *vs.* 1/[S] for the reaction of thiobenzophenone with various olefins: ○, cyclohexene; ⊙, *n*-butyl vinyl ether; ▼, 1-octene; △, methyl acrylate; ●, vinyl acetate.

Kinetics. The procedure and conditions were the same as described previously.[2c] The light intensity was monitored by referring to the rate of the reaction in a standard cell which contained the specified concentrations of thiobenzophenone and styrene. The i values of reactions were determined from intercepts of lines shown in Figure 2. The number of photons absorbed by the system was 3×10^{19} sec^{-1}.

Actinometry. Parker's method[40] was employed as previously described.

Spectrometry. A Varian HA-100 nmr spectrometer and a Hitachi RMU-6E mass spectrometer were respectively employed for nmr and mass spectrometry.

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(40) C. A. Parker, *Proc. Roy. Soc., Ser. A*, 220, 104 (1953).