and error bars drawn on both sides (Figure 1) to reflect the error in k_d. The sensitizers and their triplet energies, rates of deactivation (k_d), and quantum yields for intersystem crossing are listed in Table III.

Table III. Data on Sensitizers

Sensitizer	E_T,[a] kcal/mol	ϕ_{ST} [d]	10^4k_d,[g] sec^{-1}
β-Acetonaphthone	59.3	0.84	0.33 ± 0.03
Phenanthrene	61.8[b]	0.76	0.90 ± 0.08
Thioxanthone	65.5	1.0[e]	1.3 ± 0.1
Benzophenone	68.5	1.0	5.0 ± 2.0[f]
Acetophenone	73.6	1.0	100.0 ± 200.0[f]
Cyclopropyl phenyl ketone	74.4[c]	1.0	500.0 ± 200.0[f]

[a] Except where otherwise noted, from W. G. Herkstroeter, A. A. Lamola, and G. F. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964). [b] E. Clar and M. Zander, *Chem. Ber.*, **89**, 749 (1956). [c] Reference 25. [d] Reference 7 except where otherwise noted. [e] This research. [f] Reference 25. [g] Reference 6 except where otherwise noted.

Control Experiments on Quenching Rates. To test the validity of our methods and the purities of our sensitizers and solvents, we determined quenching rates for a number of sensitizer triplets by *trans*-stilbene, and compared the results with those of Herkstroeter and Hammond.[6] The procedure was identical with that above, except that the quantum yield of *cis*-stilbene was determined by glpc. The rates obtained were: anthracene, 2.3 × 10^5 M^{-1} sec^{-1} (lit.[6] 1.1 × 10^5); acridine, 1.6 × 10^6 (lit.[6] 5.8 × 10^6); and 1,2-benzanthracene, 7.1 × 10^7 (lit.[6] 3.3 × 10^8). The error in all three cases is less than that reported[26] for k_d of the sensitizer.

Intersystem Crossing Ratios. The method of Lamola and Hammond,[7] was used to determine intersystem crossing ratios (ϕ_{ST}) for several sensitizers. The values obtained were 1,2-benzanthracene, 0.87 ± 0.05; pyrene, 0.10 ± 0.05; and thioxanthone, 1.00 ± 0.05.

Molecular Orbital Calculations. The extended Hückel theory program described by Hoffmann[15] was adapted for use on our IBM 7074 computer. Bond lengths in methyl azide were those determined by Livingston and Rao.[13] Values for the Slater exponents were: hydrogen, 1.00; carbon, 1.625; nitrogen, 1.95.[28] Valence-state ionization potentials were those of Skinner and Pritchard.[29] In one series of calculations the $N_1N_2N_3$ bond angle (θ) was varied from 110 to 250° keeping other bond lengths and bond angles constant. In another, θ was held constant at 140° and the effect of varying the $MeN_1N_2N_3$ dihedral angle determined (Me and N_3 had been kept coplanar in the first series of calculations).

Acknowledgment. We are especially indebted to Dr. C. D. DeBoer for numerous helpful discussions and suggestions.

---

(28) K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964, p 471.

(29) H. H. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953); H. O. Pritchard and H. H. Skinner, *Chem. Rev.*, **55**, 745 (1955).

Photocycloaddition of Thiocarbonyl Compounds to Olefins. The Reaction of Thiobenzophenone with Styrene and Substituted Styrenes

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

Contribution from the Sagami Chemical Research Center,
Onuma, Sagamihara-shi, Kanagawa, 229, Japan. *Received May 20, 1968*

Abstract: Thiobenzophenone reacts with styrene, on irradiation with ultraviolet or visible light to give 2,2,3,3,5-pentaphenyl-1,4-dithiane. The mechanism of this reaction has been studied kinetically. It is shown that the reaction proceeds through the addition of the n → π* triplet state of thiobenzophenone, which behaves like a thiyl radical, to styrene. The characteristic difference between the photocycloaddition of thiobenzophenone affording 1,4-dithianes and that of benzophenone to give oxetanes is discussed in terms of the reactivities of carbon radicals toward a thiocarbonyl sulfur and a carbonyl oxygen. The high reactivity of the intermediate composite radical toward the thioketone leads to 1,4-dithianes from thiobenzophenone. It is suggested that the use of photoexcited thiobenzophenone as a model of thiyl radicals simplifies the study of the addition reactions of thiyl radicals to olefins. From this viewpoint, the relative rates of the addition reactions of thiobenzophenone with unsubstituted and various *para-* and *meta*-substituted styrenes have been examined. Based on the absence of a substituent effect, it is proposed that the sulfur atom β to the radical center stabilizes it by forming a sulfur-bridged radical. The stabilizing effect of this type is strong enough to overshadow the effects of substituents in styrenes.

Photocycloaddition reactions of ketones to olefins to give oxetanes are well documented.[1] On the other hand, little is known[2-4] about the photochemistry of thioketones. A recent study on the photocycloaddition reactions of thiobenzophenone with various olefins, by irradiation with a high-pressure mercury lamp, has shown that the only isolable products are 1,4-dithianes.[5] Thus, reactions of thiobenzophenone with cyclohexene, 2,3-dihydropyran, ethyl vinyl ether, and styrene afford 3,3,4,4-tetraphenyl-2,5-dithiabicyclo[4.4.0]decane (I), 3,3,4,4-tetraphenyl-7-oxa-2,5-dithiabicyclo[4.4.0]decane (II), 2,2,3,3-tetraphenyl-5-ethoxy-1,4-dithiane (III), and 2,2,3,3,5-pentaphenyl-1,4-dithiane (IV), respectively. We have found that the same

---

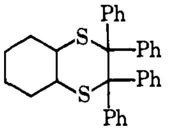
(1) For example (a) J. N. Pitts, Jr., and J. K. S. Wan, in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1966, Chapter 16; (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 208-211.

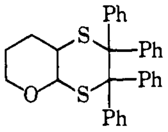
(2) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 275 (1943).

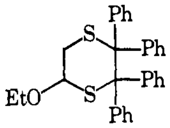
(3) G. Oster, L. Citarel, and M. Goodman, *J. Amer. Chem. Soc.*, **84**, 703 (1962).

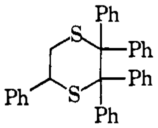
(4) E. T. Kaiser and T. F. Wulfers, *ibid.*, **86**, 1897 (1964).

(5) G. Tsuchihashi, M. Yamauchi, and M. Fukuyama, *Tetrahedron Lett.*, 1971 (1967).


I


II


III


IV

reactions also take place by irradiation with visible light giving the products I–IV in more than 90% yields[6] (better than uv irradiation). Each of these products consists of only one isomer: *trans*-ring junctions for I and II, axial-ethoxy group in III, and equatorial-phenyl group in IV.

That the photocycloaddition of thioketone proceeds quite stereospecifically giving only one isomeric product in a remarkably high yield is in sharp contrast to the photocycloaddition of carbonyl compounds, the Paterno–Büchi reaction,[1] where a mixture of oxetanes is obtained in fair yield. This has stimulated us to study the mechanism of the reaction.

Furthermore, in the course of the study, it has been found that the photoexcited thiobenzophenone can be regarded as a kind of thiyl radical (*vide infra*). An analogous relationship is observed in a pair of photoexcited benzophenone and *t*-butoxy radical for hydrogen-abstraction reactions.[7]

Thus, the study of photoexcited thiobenzophenone may shed light on the behavior of thiyl radicals in their addition to olefins, because this approach will eliminate ambiguities caused by ionic reactions, polymerization of olefins, and uncertainty of the rate-determining step, which are always complications when thiols are used as thiyl radical sources.[8,9]

The mechanism and relative rates of the addition reactions of photoexcited thiobenzophenone with styrene and various substituted styrenes have accordingly been investigated.

Results

The reaction of styrene affords IV in yields of 68% by a high-pressure mercury lamp and 94% by a photoreflector lamp. The reactions of *p*-methoxy-, *p*-chloro-, *p*-cyano-, *m*-methoxy-, *m*-methyl-, *m*-chloro-, and *m*-cyanostyrenes also gave compounds of type IV on irradiation with a high-pressure mercury lamp, in average yields of around 65%. Structures of products were confirmed by nmr spectroscopy. The rate of the reaction at 25° was followed by recording the decrease of 609-mμ absorption of thiobenzophenone in the solution by a Cary-14 spectrophotometer. The reaction was found to be zero order in thiobenzophenone to more than 80% of complete reaction as illustrated in Figure 1. For the reactions with substituted styrenes the light intensity was monitored by reference to the rate of reaction in a standard cell containing both thiobenzophenone and styrene at the specified concentrations. The observed rate constant remains constant with change of the initial concentration of thiobenzophenone, whereas it increases with increasing concentration of styrene. Since thiobenzophenone itself is known to react to give 3,3,5,5-tetraphenyl-1,2,4-trithiacyclopentane by ultraviolet irradiation,[10] the rate of this reaction was also studied. A cyclohexane solution of thiobenzophenone containing benzene instead of styrene was irradiated under the same conditions, and the zero-order rate constant was found to be 3.40×10^{-8} M sec^{-1}. The true observed rate constant, k_{obsd}, was derived by subtracting this minor value from each observed rate constant. The absorption spectrum of thiobenzophenone does not change whether styrene ($\lambda_{\max}$ 605 mμ (ϵ 180)) or cyclohexane ($\lambda_{\max}$ 609 mμ (ϵ 180)) is used as a solvent and thus the possibility of the formation of a charge-transfer complex of thiobenzophenone with styrene prior to irradiation is ruled out. The results for styrene are summarized in Table I and those for substituted styrenes are listed in the second column of Table II.

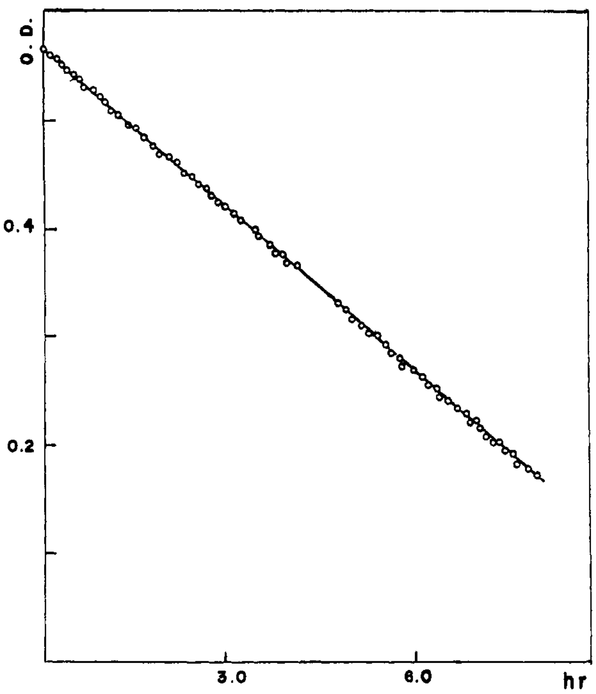


Figure 1. Pseudo-zero-order kinetics for the reaction of thiobenzophenone with styrene.

Discussion

Mechanism of the Reaction. In view of the facts that the product consists of two molecules of thiobenzophenone and one molecule of styrene and that photoexcitation is zero order with respect to excited species in the present system, it is quite reasonable to propose the mechanism shown in the following scheme (eq 1). In this mechanism, *i* is the rate for the formation of

---

(6) A. Ohno, Y. Ohnishi, M. Yamauchi, and G. Tsuchihashi, Abstracts, 21st National Meeting of the Chemical Society of Japan, Suita, Osaka, Japan, April 2, 1968, p 2084.

(7) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **86**, 3902 (1964); **87**, 3361 (1965).

(8) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp 313–326.

(9) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 16–93.

(10) A. Schönberg, O. Schütz, and S. Nickel, *Chem. Ber.*, **61**, 2175 (1928).

Table I. Kinetic Data for the Reaction of Thiobenzophenone with Styrene in Various Conditions

[S], M	$[S]^{-1}$, M^{-1}	$[V]_0$, M	$k_{obsd} \times 10^3$, M hr^{-1}	$1/k_{obsd} \times 10^{-3}$, M^{-1} hr
1.296	0.772	0.127	0.459	2.16
1.683	0.594	0.134	0.490	2.04
1.923	0.520	0.143	0.537	1.86
2.897	0.345	0.140	0.706	1.40
2.899	0.345	0.138	0.638	1.57
5.095	0.196	0.161	0.898	1.10
3.947[a]	0.253	0.132	1.23	
3.947[a]	0.253	0.069	1.13	
3.947[a,b]	0.253	0.133	1.13	

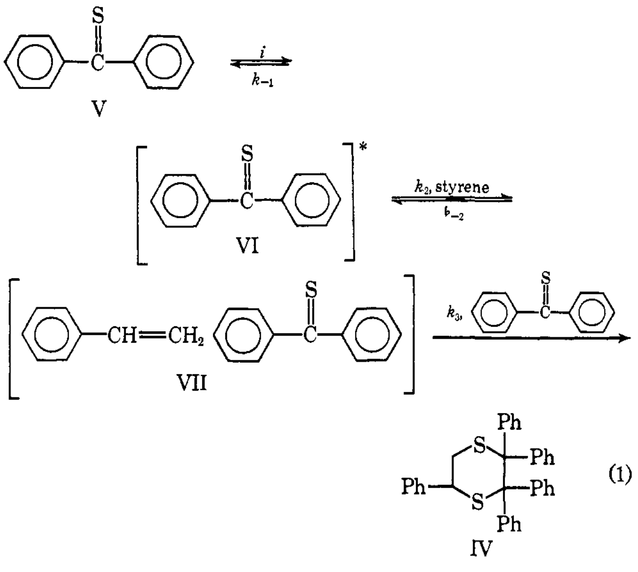
[a] The reaction vessel is different from that used for the other runs. [b] 0.014 M of benzophenone was added to the solution.

Table II.[a] Kinetic Data for the Reaction of Thiobenzophenone with Substituted Styrenes

X	$k_{obsd} \times 10^3$, M hr^{-1}	[S], M	Log xy[b]	Log (k_2^X/k_2^H)
p-CH$_3$O	0.694	2.875	−0.346	0.02
m-CH$_3$	0.627	3.038	−0.465	−0.10
m-CH$_3$O	0.526	2.387	−0.505	−0.14
p-Cl	0.706	2.897	−0.332	0.03
m-Cl	0.664	2.788	−0.376	0.01
m-CN	0.687	2.498	−0.295	0.07
p-CN	0.626	2.143	−0.315	0.05
H			−0.362[c]	0.00

[a] 0.13 M of thiobenzophenone was used. [b] $x = k_{obsd}/[S]$; $y = 1/(2i - k_{obsd})$. [c] Average value.

photoexcited thiobenzophenone[11] and mainly depends on the intensity of incident light. By the assumption



(1)

of steady states for VI and VII, eq 2 is obtained

$$t = \frac{k_{-1} + k_2[S]}{2ik_2[S]}([V]_0 - [V]) + \frac{k_{-1}\,k_{-2}}{2ik_2k_3[S]} \ln \frac{[V]_0}{[V]} \quad (2)$$

where [V] and $[V]_0$ are concentrations of thiobenzophenone at the time t and at time 0, respectively, and [S] is the concentration of styrene, which remains almost constant throughout the reaction under the conditions employed. Since the kinetics is zero order in thiobenzophenone over a wide range of concentrations, the second term of the right-hand side in eq 2 can be neglected and the rate expression is simplified to

$$t = \frac{k_{-1} + k_2[S]}{2ik_2[S]}([V]_0 - [V]) \quad (3)$$

Therefore

$$k_{obsd} = \frac{2ik_2[S]}{k_{-1} + k_2[S]} \quad (4)$$

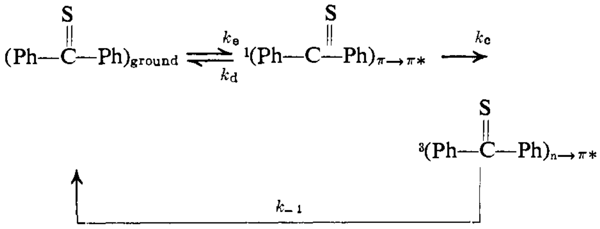
or

$$\frac{1}{k_{obsd}} = \frac{1}{2i} + \left(\frac{k_{-1}}{2ik_2}\right)\left(\frac{1}{[S]}\right) \quad (5)$$

By plotting $1/k_{obsd}$ against $1/[S]$, values for k_{-1}/k_2 and i should be obtained from the slope and the intercept of the line. This treatment is applied to the actual system as shown in Figure 2. Since a nice straight line is obtained by this treatment, the proposed mechanism is plausible.

A recent esr study on an alkaline solution of thiobenzophenone has shown that irradiation with 3660-Å light (π → π* band) produces a thioketyl radical identical with that produced by the irradiation of 5770-Å light (n → π* band).[13] Our results have shown that the compound IV is obtained in a better yield with visible light than with ultraviolet irradiation. These facts imply, as suggested by Heller,[13] that the n → π* excited state of thiobenzophenone is responsible for the photochemical reaction, even in case of ultraviolet irradiation where the π → π* excited state of thiobenzophenone is formed. Therefore, the intermediate VI in eq 1 is assumed to be n → π* triplet state of thiobenzophenone.

The i value calculated by least-squares method is 1.71×10^{-7} M sec^{-1}. Since the mechanism of photoexcitation is



$$(\mathrm{Ph{-}C({=}S){-}Ph})_{\text{ground}} \underset{k_d}{\overset{k_e}{\rightleftharpoons}} {}^1(\mathrm{Ph{-}C({=}S){-}Ph})_{\pi\to\pi*} \xrightarrow{k_c} {}^3(\mathrm{Ph{-}C({=}S){-}Ph})_{n\to\pi*} \xrightarrow{k_{-1}} (\mathrm{Ph{-}C({=}S){-}Ph})_{\text{ground}} \quad (6)$$

i in eq 1 is then expressed as

$$i = \frac{k_e k_c}{k_d + k_c} \quad (7)$$

where k_e is determined to be 3.0×10^{-5} M sec^{-1} by the actinometry[14] of the system (see Experimental Section). From eq 7, the value of k_d/k_c is calculated to be 1.8×10^2.

An alternative mechanism, that photoexcited thiobenzophenone might attack another molecule of ground-state thiobenzophenone prior to attack on styrene is discarded because, if this were the case, the kinetics must be first order in thiobenzophenone,

---

(11) Though the irradiation by a high-pressure mercury lamp promotes π → π* transitions (at around 310 mμ) of the thioketone,[12] the n → π* triplet state of the thioketone will be referred to as "photoexcited thioketone," because the latter is considered to be the reacting species in the photocycloaddition reaction (*vide infra*).

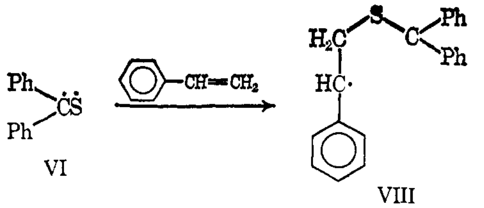
(12) O. Korver, J. U. Veenland, and Th. J. de Boer, *Rec. Trav. Chim. Pays-Bas*, **84**, 289 (1965).

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

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

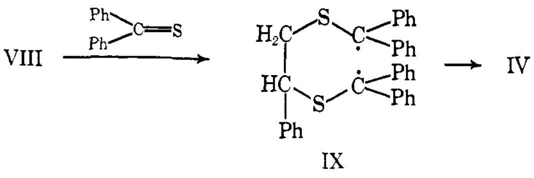
contrary to observation. Dimerization of two molecules of photoexcited thiobenzophenone followed by the reaction with styrene is also improbable from the viewpoint of their concentrations.

On the basis of stabilization of the composite radical, it seems quite reasonable that the photoexcited thiobenzophenone initially attacks the β-carbon of styrene giving the intermediate diradical VIII, designated VII in eq 1. Since the radical center on the benzhydryl position in VIII is highly stabilized by two phenyl groups



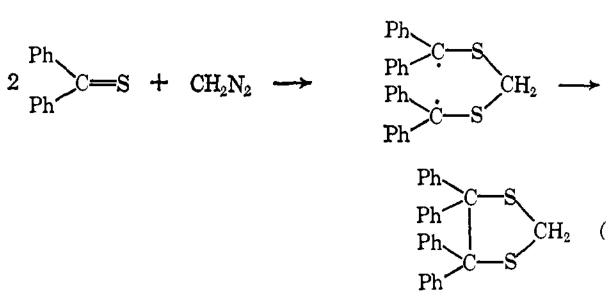
(8)

and a sulfur atom, the next reaction of VIII with thiobenzophenone should involve attack by the radical center on the benzyl position to form the second diradical IX. The two radical centers in IX subsequently recombine to form the final product, IV.

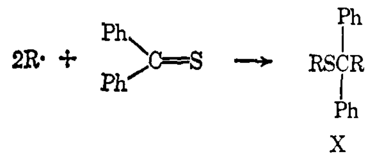


(9)

An analogous intermediate diradical is proposed for the reaction of thiobenzophenone with diazomethane.[15] The present scheme is also in accord with our finding that thiobenzophenone reacts quite rapidly with carbon radicals such as 2-cyano-2-propyl[16] and 1-phenylethyl[17] radicals affording compounds such as X, containing new carbon–sulfur bonds according to eq 11.



(10)



$$2R\cdot + Ph_2C{=}S \longrightarrow RSC(Ph)_2R$$

(11)

X

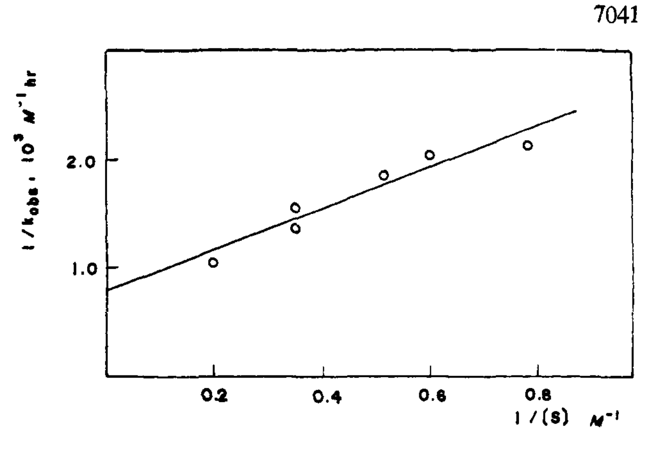
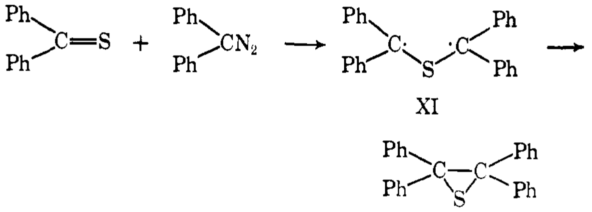


Figure 2. A plot of $1/k_{obsd}$ against $1/[S]$.

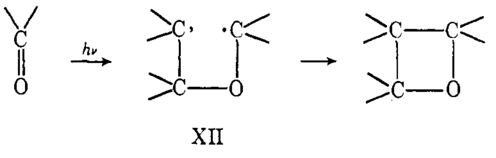
Formation of a thiirane derivative by the reaction of thiobenzophenone with diphenyl diazomethane[18] is accounted for again by the inertness of the benzhydryl-type radical in intermediate XI toward thiobenzophenone.[19]



(12)

A few examples of the reaction of oxygen atoms in carbonyl groups with carbon radicals are known. One of these is the reaction of perfluoroacetone with trifluoromethyl radical in the gas phase to give perfluoro-*t*-butyl trifluoromethyl ether in a low yield.[20] Another example is the reaction of quinones.[21–25] Thus, except for these atypical ketones, it appears that an oxygen atom in a carbonyl group has little tendency, if any, to react with carbon radicals.

Now the difference between photochemical behaviors of ketones and thioketones becomes clear; the intermediate of reaction 13, XII,[26] forms an oxetane by a simple recombination of radical centers without



(13)

capturing another molecule of ketone, whereas the high reactivity of thioketone to the composite radical, VIII, results in the formation of 1,4-dithiane.

The Reaction with Substituted Styrenes. Since *i* and k_{-1} in eq 4 can be regarded as independent of

---

[15] E. Campaine, in ref 1a, p 946.

[16] M. Yamauchi, A. Ohno, M. Fukuyama, and G. Tsuchihashi, Abstracts, 21st National Meeting of the Chemical Society of Japan, Suita, Osaka, Japan, April 4, 1968, p 1568.

[17] G. Tsuchihashi, M. Yamauchi, A. Ohno, and M. Fukuyama, unpublished data.

[18] (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).

[19] For an alternative mechanism, see ref 18.

[20] A. S. Gordon, *J. Chem. Phys.*, **36**, 1330 (1962). Although the yield is not described on this product, the authors estimate it to be less than 10% from the data of gas chromatography.

[21] K. Ziegler, W. Deparade, and W. Meye, *Justus Liebigs Ann. Chem.*, **567**, 141 (1950).

[22] A. F. Bickel and W. A. Waters, *J. Chem. Soc.*, 1764 (1950).

[23] F. J. L. Aparicio and W. A. Waters, *ibid.*, 4666 (1952).

[24] G. S. Hammond and G. B. Lucas, *J. Amer. Chem. Soc.*, **77**, 3249 (1955).

[25] B. A. Gingras and W. A. Waters, *J. Chem. Soc.*, 1920 (1954).

[26] (a) G. Büchi, C. G. Inman, and E. S, Lipinsky, *J. Amer. Chem. Soc.*, **76**, 4327 (1954); (b) G. Büchi, J. T. Kofron, E. Koller, and D. Rosenthal, *ibid.*, **78**, 876 (1956); (c) G. Büchi and N. C. Yang, *ibid.*, **79**, 2318 (1957).

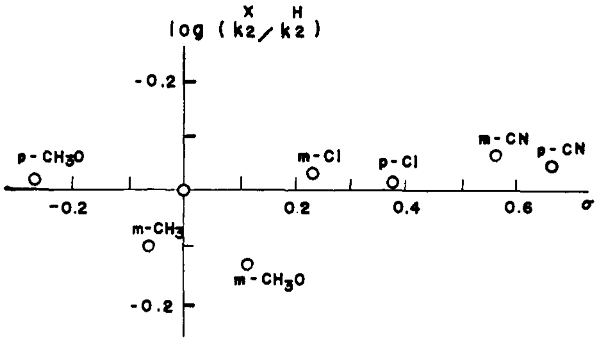


Figure 3. Hammett relationship for the addition of thiobenzophenone to various substituted styrenes.

substituents in styrenes (*ca.* 2 *M*), we obtain

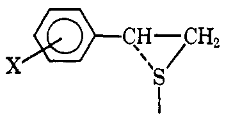
$$\log \frac{k_2^{\mathrm{X}}}{k_2^{\mathrm{H}}} = \log \frac{k_{\mathrm{obsd}}^{\mathrm{X}}}{[\mathrm{S}]^{\mathrm{X}}} - \log \frac{k_{\mathrm{obsd}}^{\mathrm{H}}}{[\mathrm{S}]^{\mathrm{H}}} + \log \frac{2i - k_{\mathrm{obsd}}^{\mathrm{H}}}{2i - k_{\mathrm{obsd}}^{\mathrm{X}}} \tag{14}$$

where superscripts X and H are for substituted and unsubstituted styrenes, respectively. The relative rate constants for the addition of photoexcited thiobenzophenone to styrenes are, therefore, simply calculated from eq 14. The results are summarized in Table II and the Hammett relationship of the system is shown in Figure 3.

The results reveal that substituents exert no effect on the rate constant of the addition step.

Substituent effects on addition reaction of free radicals to styrene have been observed in several cases reported so far.

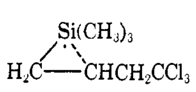
Both Walling and Imoto,[27] in the study of copolymerization of substituted styrenes, have found a polar effect on the reaction of styryl radicals. The ρ value for the addition of trichloromethyl radical to substituted styrenes is -0.43.[28] Polar effects are also observed with the thiyl radical derived from thioglycollic acid in the addition to *para*-substituted α-methylstyrenes.[29] Thus, the complete lack of substituent effect in the present case is unique. To account for this, the authors would like to suggest that the extensive stabilization of the radical center by participation of sulfur atom in the β position, a likely representation being XIII, plays an important role,[30] namely,



XIII

the stabilizing effect is so large that it overcomes the effect of substituents on the benzene ring.

This kind of overshadowing effect has been proposed by Russell for the hydrogen-abstraction reaction of peroxy radical with benzyl phenyl ether.[31] Based on the stereochemistry of addition reaction of thiyl radicals, Skell[32,33] and Ford[34] proposed sulfur-bridged radicals. d orbital participation of an atom β to the radical center, XIV, is also proposed in the addition reaction of trichloromethyl radical with trimethyl ω-alkenylsilane (XV) where the compound with $n = 1$ has abnormally higher reactivity than the others.[35]



XIV

$(CH_3)_3Si(CH_2)_nCH{=}CH_2$

($n = 0{\sim}4$)

XV

It will be interesting to compare the behavior of a thiyl radical from thioglycollic acid,[29] or its ester[29] and that of photoexcited thiobenzophenone. The polar observed in the reaction with the former radical might be attributable to the electron-withdrawing character of the carboxylic substituent.

A question still remains whether the lack of substituent effect observed here is characteristic only of the reaction with the photoexcited thiobenzophenone. In this connection, the reactions of excited thiobenzophenone with various types of vinyl monomers, such as butyl vinyl ether, butyl vinyl sulfide, methyl acrylate, and acrylonitrile, have been studied[36] and it appears that the substituent on vinyl compounds does exert a considerable effect on the rate of the addition as was found in the reaction with alkylthio radicals.[37]

As to the stereochemistry of the addition process, a *trans* addition is proved by the fact that the reaction with 2,3-dihydropyran solely affords *trans*-3,3,4,4-tetraphenyl-7-oxa-2,5-dithiabicyclo[4.4.0]decane.[5] This *trans* addition is also in accord with our proposal of a sulfur-bridged radical. However, the overshadowing effect gives stronger evidence than an analysis of stereochemistry, because the latter is always open to the question that the preferential *trans* addition comes merely from the result of steric hindrance to the entering group.

Experimental Section

Materials. Thiobenzophenone was prepared by treatment of an ethanolic solution of benzophenone with H_2S in the presence of HCl.[38] Recrystallizations were carried out in a drybox filled with CO_2. Thiobenzophenone used for the reaction did not show the C=O stretching absorption of benzophenone at 1670 cm^{-1}.

Styrene and *p*- and *m*-chlorostyrenes are commercially available (Tokyokasei Co.). They were dried over Drierite and redistilled just before use, and center cuts were used. *m*-Methylstyrene was prepared by dehydrochlorination[39] from *m*-(1-chloroethyl)-toluene which was synthesized by chlorination of *m*-methyl-α-methylbenzyl alcohol.[40] The latter compound was obtained by

---

[27] (a) C. Walling, E. R. Briggs, K. B. Wolfstirn, and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1537 (1948); (b) M. Imoto, M. Kinoshita, and M. Nishigaki, *Makromol. Chem.*, **86**, 217 (1965).

[28] H. Sakurai, A. Hosomi, and S. Hayashi, Abstracts, 21st National Meeting of the Chemical Society of Japan, Suita, Osaka, Japan, April 1, 1968, p 2060.

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

[30] For electron-sharing conjugative effects of sulfur, see C. C. Price, and S. Oae, "Sulfur Bonding," The Ronald Press, Co., New York, N. Y., 1962, pp 26–55.

[31] G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.*, **86**, 2357 (1964).

[32] P. S. Skell and R. G. Allen, *ibid.*, **82**, 1511 (1960).

[33] P. D. Readio and P. S. Skell, *J. Org. Chem.*, 31, 759 (1966).

[34] J. F. Ford, R. C. Pitkethly, and V. O. Young, *Tetrahedron*, 4, 325 (1958).

[35] H. Sakurai and A. Hosomi, Abstracts, Symposium on Organic Reaction Mechanisms, Oct 10, 1967, Kyoto, Japan, pp 51–52.

[36] A. Ohno, Y. Ohnishi, and G. Tsuchihashi, Abstracts, 21st National Meeting of the Chemical Society of Japan, Suita, Osaka, Japan, April 2, 1968, p 2083.

[37] (a) C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, **81**, 1144 (1959); (b) N. P. Petukhova and E. N. Prilenzhaeva, *J. Org. Chem. USSR*, **2**, 1914 (1966).

[38] B. F. Gofton and E. A. Braude in "Organic Syntheses," N. Rabjohn, Ed., Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 927.

[39] A. Klages, *Chem. Ber.*, **35**, 2245 (1902).

Table III. Pseudo-Zero-Order Kinetics for the Reaction of Thiobenzophenone with Styrene[a]

Time, hr	OD	($[V]_0 - [V]$) × 10^2, *M*
0.0	0.656	0.0
1.5	0.645	0.2140
3.0	0.630	0.505
4.0	0.625	0.603
5.0	0.624	0.622
6.0	0.613	0.836
7.0	0.613	0.836
8.0	0.610	0.894
9.0	0.602	1.050
10.0	0.600	1.089
11.0	0.595	1.186
12.0	0.590	1.283
13.0	0.585	1.380
14.0	0.570	1.575
24.0	0.543	2.197
25.0	0.537	2.313
26.0	0.534	2.372
27.0	0.530	2.449
28.0	0.525	2.547
29.0	0.524	2.566
30.5	0.510	2.838
32.0	0.506	2.916
33.0	0.499	3.052
34.0	0.498	3.072
35.0	0.494	3.149
36.5	0.483	3.363
37.5	0.480	3.421
47.5	0.441	4.180

[a] $[V]_0 = 0.140\,M$; $[S] = 2.897\,M$; $k_{obsd} = 0.706 \times 10^{-3}\,M\,hr^{-1}$.

Grignard reaction of *m*-bromotoluene with acetaldehyde.[41] *m*-Methoxystyrene was prepared by dehydration[42] with $NaHSO_4$ of *m*-methoxy-α-methylbenzyl alcohol which was synthesized by Grignard reaction of *m*-bromoanisole with acetaldehyde. On the other hand, pure *p*-methoxystyrene was simply obtained by vacuum distillation of *p*-methoxy-α-methylbenzyl alcohol[42,43] in 80% yield. *p*-Cyanostyrene was prepared by dehydration[44,45] of the corresponding alcohol which was synthesized by reduction of *p*-cyanoacetophenone with $NaBH_4$.[46] *p*-Cyanoacetophenone was obtained by Sandmeyer reaction of *p*-aminoacetophenone.[44] *m*-Cyanostyrene[47] was prepared by the same procedures as described for the *para* isomer.

Vacuum distillations of styrenes were carried out in the presence of hydroquinone and in an atmosphere of nitrogen. All physical constants, nmr and ir spectra, and vpc confirmed the purity of the materials used.

Kinetics. Preparations of reaction solutions were carried out in a drybox under an atmosphere of CO_2. The photoreactions were carried out by external irradiation method, using a high-pressure mercury lamp (Riko-Kagakusangyo, 100 W) and a Pyrex reaction vessel (Figure 4) placed at fixed positions. The reaction temperature was maintained at 25.0 ± 0.3° by circulating water from a thermostat through the vessel. At appropriate intervals, 80-μl aliquots were pipetted by a Hamilton 100-μl microsyringe, equipped with a spacer, through a silicon-rubber stopper and were diluted by 3.00 ml of cyclohexane in a uv cell in order to obtain a suitable concentration for the measurement. The optical density at the absorption maximum (609 mμ) of the resulting solution was measured by a Cary 14 spectrophotometer. A typical run is shown in Table III. The light intensity was monitored by reference to the rate of the reaction in a standard cell which contains the specified concentrations of thiobenzophenone and styrene. The *i* value of the reaction was determined at a moment when the number of protons absorbed by the system was 3 × 10^{19} sec^{-1}. In order to obtain a rate constant, more than 20 points were treated by the least-squares method.

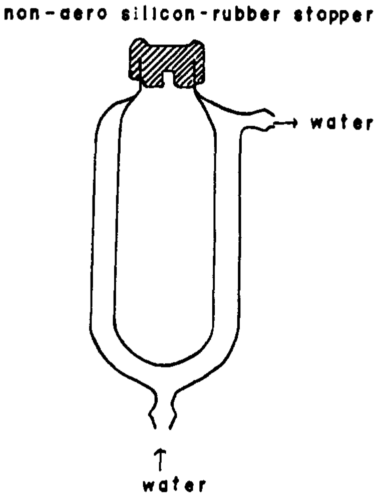


Figure 4. A figure of the reaction vessel.

Product of the Reaction of Thiobenzophenone with Styrene. In a Pyrex reaction vessel similar to that shown in Figure 4, 4 g of thiobenzophenone and 40 ml of styrene were irradiated by a 400-W high-pressure mercury lamp (Toshiba H-400 P) or by a photoreflector lamp (Toshiba). The irradiation was continued until the blue color of thiobenzophenone had completely disappeared (*ca.* 30 hr with the former and *ca.* 3 days with the latter). In the case of the irradiation with a high-pressure mercury lamp, styrene was removed from the reaction mixture under reduced pressure, and the residue was chromatographed on neutral alumina (Woelm, activity grade 1) with a benzene-petroleum ether (bp 30–60°) mixture as eluent. A crystalline material (3.2 g) was obtained in 65% yield and it gave, on recrystallization from benzene, crystals of IV, mp 154° (*Anal.* Calcd for $C_{34}H_{28}S_2$: C, 81.56; H, 5.64. Found: C, 81.89; H, 5.56); ir (KBr) 3080, 3050, 3020, 2945, 2915, 2900, 735, 720, and 695 cm^{-1}; nmr (in $CDCl_3$, δ from TMS) 7.89–7.05 multiplet (25 H), 4.86 quartet (1 H), 3.21 triplet (1 H), and 2.90 quartet (1 H). On the other hand, with visible-light irradiation almost pure crystals of IV appear during the irradiation. The crystals were removed from the reaction mixture, giving 4.8 g of IV, 94% yield. The identity of the products in both cases was further confirmed by spectroscopic data and by a mixture melting point. The same product was obtained in similar yields by uv and visible-light irradiations of 2 g of thiobenzophenone with 20 ml of styrene in 40 ml of cyclohexane, which is the standard composition of kinetic runs.

The reaction with substituted styrenes gave the products of the same type as IV. Structures were confirmed by nmr and ir spectra.

Actinometry. According to Parker,[14] the potassium ferrioxalate (XVI) system was employed. The zero-order rate constant of the decrease of XVI, which was spectrophotometrically followed by using *o*-phenanthroline as an indicator, was 3.3 × 10^{-5} *M* sec^{-1}.

---

(40) R. L. Burwell, Jr., A. D. Shields, and H. Hart, *J. Amer. Chem. Soc.*, **76**, 908 (1954).

(41) F. C. Whitmore, W. L. Evers, and H. S. Rothrock, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1948, p 408.

(42) R. L. Frank, C. E. Adams, R. E. Allen, R. Gander, and P. V. Smith, *J. Amer. Chem. Soc.*, **78**, 1365 (1946).

(43) D. T. Mowry, M. Renoll, and W. F. Huber, *ibid.*, **68**, 1105 (1946).

(44) C. S. Marvel and C. G. Overberger, *ibid.*, **67**, 2250 (1945).

(45) L. A. Brooks, *ibid.*, **66**, 1295 (1944).

(46) S. W. Chaikin and W. G. Brown, *ibid.*, **71**, 122 (1949).

(47) R. H. Wiley and N. R. Smith, *ibid.*, **70**, 1560 (1948).