The Thermal Cycloaddition of Substituted Thiobenzophenones with Phenylallene: Mechanism and Linear Free Energy Relationships of Reaction Rates

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The reaction rates for the thermal cycloadditions of substituted thiobenzophenones with phenylallene in CH_3CN at 40 °C were determined and analysed by linear free energy correlations. Using a Hammett-type relationship, the best correlations were obtained with the σ^--parameter ($\rho^- = 1.09 \pm 0.06$) indicating that, in the transition state, mesomeric interaction occurs between $-M$ substituents and an electron-releasing reaction centre. The small ρ^--value is in agreement with a 1,4-diradical intermediate in a $({}_{\pi}2_S + {}_{\pi}2_S + {}_{\pi}2_S)$-cycloaddition.

Separate correlation of electron-donating and electron-withdrawing substituents gives rise to two lines with different slopes, each with a much better correlation coefficient and ψ. This observation indicates that the thione system is relatively more sensitive to electron-donating substituents than to electron-withdrawing substituents *i.e.* a π-repulsive saturation interaction occurs with the π-acceptor thiocarbonyl function. Additional analysis with Charton's DSP-equation ($\rho_R/\rho_I = 1.82$) shows that the contribution of resonance effect is 69% and the contribution of inductive effect is 31%. Bromilow's DSP–non-linear resonance effect equation yields a value of $+0.38 \pm 0.01$ for the 'electron demand parameter,' indicating the enhanced resonance interaction of electron-acceptor substituents with the thione system in the transition state. An inverse secondary isotope effect on the rate constant of disappearance of thione during the reaction with PhCH=C=CH_2, PhCD=C=CH_2, and PhCD=C=CD_2 was observed; $k_2(H_\alpha)/k_2(D_\alpha) = 0.91 \pm 0.02$ and $k_2(2H_\gamma)/k_2(2D_\gamma) = 0.75 \pm 0.01$. These values are less than unity and consistent with attack at C-β and indicative for a change in hybridization at C-α and C-γ. The observed isotope effect when using D_3CO–CH=C=CH_2 instead of H_3CO–CH=C=CH_2, $k_2(H)/k_2(D) = 1.20 \pm 0.02$ represents a rotational isotope effect arising from an increase in mass on substitution of hydrogen by deuterium. Experiments with an optically active allene (+)-PhC(H)=C=CHBu^t yielded products which were optically inactive, which points to a non-chiral intermediate *i.e.* the allylic diradical. We observed also a low solvent effect which is in agreement with the reaction mechanism *i.e.* a 1,4-diradical-mediated $({}_{\pi}2_S + {}_{\pi}2_S + {}_{\pi}2_S)$-cycloaddition.

For some time now, our interest has been focused on the thermal[1,2] and photochemical reaction[3-9] of thiocarbonyl compounds with cumulative polyenes (*cf.*[10]). Thermal reactions occurred only with allenes and pentatetraenes and generally not with alkenes and butatrienes.[1] The thermal reaction was thought to follow a $({}_{\pi}2_S + {}_{\pi}2_S + {}_{\pi}2_S)$ pathway with a 1,4-diradical as an intermediate.[1] The cycloaddition gives rise to the formation of two [2 + 2]-cycloaddition products (**3**) and (**4**), though occasionally [4 + 2]-cycloaddition products (**5**) and (**6**) are also isolated[2,11,12] (see Scheme).

The $({}_{\pi}2_S + {}_{\pi}2_S + {}_{\pi}2_S)$-type mechanism has received considerable interest from other research groups during the last years.[1,13-17] Our previous studies[1,2] have shown that the reaction rates of thiobenzophenone with substituted phenylallenes XC_6H_4CH=C=CH_2 show a Hammett relationship with σ^+-constants;

$$\log\{k_2(X)/k_2(H)\} = (-0.36 \pm 0.03)\sigma^+ + 0.03$$
$$(r = 0.978, n = 10, f = 0.07).$$

Of all known dual substituent parameter equations the Yamamoto–Otsu relationship appeared to give the best fit to our data;

$$\log\{k_2(X)/k_2(H)\} = -0.52\sigma + 1.16\,E_R + 0.03$$
$$(r = 0.991, f = 0.001).$$

From these relationships we conclude that thiobenzophenone reacts as an electrophile and that some resonance interaction with the substituent occurs in the transition state. The relatively small value of $|\rho^+|$ is in agreement with a diradical-mediated reaction mechanism.

The relative rates can also be correlated to the first adiabatic ionization energies of the conjugated and the most electron-rich double bond of the substituted phenylallenes:

$$\log\{k_2(X)/k_2(H)\} = -0.65\,EI_X(1) + 0.08$$
$$(r = 0.950, f = 0.15)$$

also indicating that the reaction occurs at the aryl-conjugated double bond of the allenic system and that in the transition state only little electron-charge transfer takes place from the allenic system to the reaction centre. In order to gain further insight into the $({}_{\pi}2_S + {}_{\pi}2_S + {}_{\pi}2_S)$-type mechanism, linear free energy correlations of substituent effects in the thione system on the reaction rate of the thermal reaction were investigated as well as solvent and isotope substitution effects. Furthermore, an optically active allene was used to gain some information on the chirality of the reaction intermediate.

Results and Discussion

Substituent Effects.—The thermal cycloadditions of thirteen mono- and di-*para*-substituted thiobenzophenones with phenylallene were studied by measuring the decrease of absorption at 590—605 nm at 40.0 °C in acetonitrile (see

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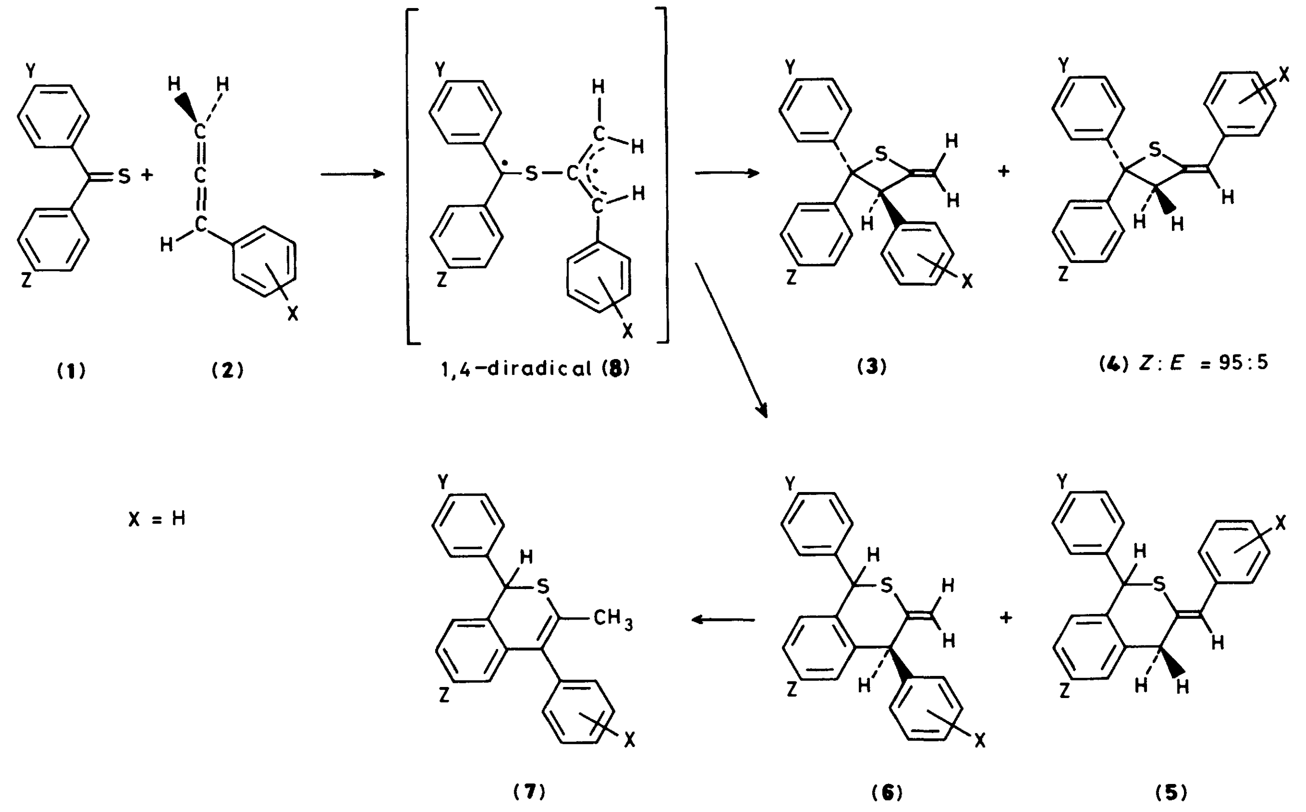

Scheme.

Table 1. Reaction rates for the thermal reaction of mono- and di-*para*-substituted thiobenzophenones with phenylallene at 40 °C in acetonitrile; values of some substituent constants σ_p, σ_p^-, $\sigma_R(BA)$, and σ_I are also given[18–21]

Substituent	$10^3k_2(Y,Z)^a$/ dm^3 mol^{-1} s^{-1}	σ_p	σ_p^-	$\sigma_R(BA)$	σ_I
4,4'-Dimethoxy	0.537 ± 0.004	−0.54	−0.54	−1.26	0.54
4-Methoxy	0.977 ± 0.004	−0.27	−0.27	−0.63	0.27
4,4'-Dimethyl	1.02 ± 0.02	−0.28	−0.28	−0.22	−0.10
4-Methyl	1.63 ± 0.02	−0.14	−0.14	−0.11	−0.05
4,4'-Difluoro	1.990 ± 0.007	0.12	−0.04	−0.9	1.00
4-Fluoro	2.34 ± 0.03	0.06	−0.02	−0.45	0.50
Hydrogen	2.46 ± 0.03	0	0	0	0
4-Phenyl	3.89 ± 0.02	−0.01	0.11	−0.11	0.10
4-Chloro	4.79 ± 0.03	0.23	0.23	−0.23	0.46
4-Bromo	5.25 ± 0.02	0.23	0.26	−0.2	0.44
4,4'-Dichloro	7.08 ± 0.04	0.45	0.45	−0.46	0.92
4-Cyano	18.6 ± 0.6	0.66	0.88	0.13	0.59
4-Nitro	39.8 ± 0.1	0.78	1.27	0.15	0.65

[a] $T = 313.0 \pm 0.2$ K.

Experimental section). Clean second-order reaction kinetics are observed, leading to the reaction rates as given in Table 1.

Linear Free Energy Relationships.—Figure 1 illustrates that using a Hammett-type relationship, the best results were obtained when using σ_p^--constants;

$$\log k_2(Y,Z) = \log k_2(H,H) + \rho^- \sigma_p^-$$
$$= (1.09 \pm 0.06)\sigma_p^- - 2.67 \quad (1)$$
$$(r = 0.982,\ \psi = 0.20).$$

while there exists a poor correlation with σ_p^+ [$\rho^+ = 0.79 \pm 0.09$, $r = 0.928$, $\psi = 0.40$, $\log k_2(H,H) = -2.39$] and with σ_p [$\rho = 1.32 \pm 0.10$, $r = 0.971$, $\psi = 0.25$, $\log k_2(H,H) = -2.61$]. The positive sign of ρ^- in equation (1) is in accordance with the electrophilic nature of the thiocarbonyl group in the reaction. The correlation with σ_p^- indicates that mesomeric interaction occurs between the acceptor substituents and an electron-releasing reaction centre in the transition state.[19] It is worthy of note, however, that when the electron-donating and -withdrawing substituents of thiobenzophenone are treated separately, two lines with different slopes are obtained, each with a much better correlation coefficient and ψ.

$$\log k_2(Y,Z) = (1.31 \pm 0.07)\sigma_p^- - 2.61$$
$$(r = 0.992,\ \psi = 0.14) \quad (2)$$
$$(\sigma = -0.54\text{—}0.11)$$

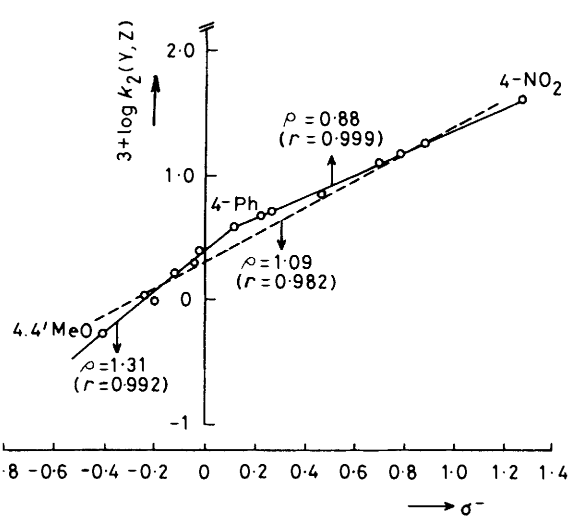

Figure 1. The logarithm of the reaction rates for the thermal cycloaddition of substituted thiobenzophenones with phenylallene as a function of σ^--constants

$$\log k_2(\mathrm{Y,Z}) = (0.88 \pm 0.02)\sigma_p^- - 2.51 \quad (r = 0.999,\ \psi = 0.05) \quad (3)$$
$$(\sigma_p^- = 0.11\text{—}1.27)$$

Both lines have the amphielectronic phenyl substituent in common. The different slopes can be explained by the electron-demanding property of the thiocarbonyl group[22] (*i.e.* its electrophilic nature). It seems to be more sensitive than expected for electron-donating substituents than for electron-withdrawing substituents. In comparison with equation (1), equation (2) shows an enhancement of ρ due to enhanced conjugation between the thiocarbonyl group and the π-donor substituent ($\sigma_p = \sigma_p^-$). The lower value of ρ in equation (3) with respect to that in equation (1) demonstrates that a π-repulsive saturation interaction occurs with the π-acceptor thiocarbonyl function.[22,23]

The magnitude of ρ is considered as being too small to be indicative of a dipolar intermediate (*cf* ref. 9), but is more in agreement with the 1,4-diradical-mediated (${}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s$)-mechanism. Dual substituent parameter analysis of the data in Table 1 shows for the Yukawa–Tsuno equation:[24a]

$$\log k_2(\mathrm{Y,Z}) = (1.21 \pm 0.06)[\sigma_p + 0.69(\sigma_p^- - \sigma_p)] - 2.65 \quad (4)$$
$$(r = 0.990,\ \psi = 0.16)$$

The factor r^- = (0.69 ± 0.16) indicates also that there is a decreased resonance effect of $-M$ substituents with respect to equation (1). The bend in the line observed in Figure 1 is, however, still present when using equation (4). The line becomes straight when correlating $\log k_2(\mathrm{Y,Z})$ with ($\sigma_p + 0.6\sigma_p^-$); (*cf.* ref. 24*b*).

$$\log k_2(\mathrm{Y,Z}) = 0.75(\sigma_p + 0.6\sigma_p^-) - 2.02 \quad (5)$$
$$(r = 0.992,\ \psi = 0.11)$$

This is illustrated in Figure 2.

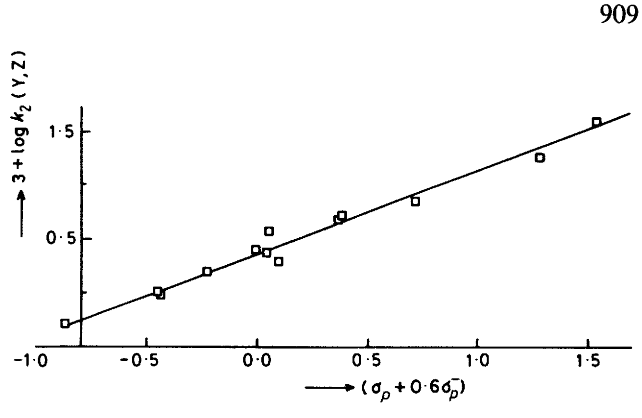

Figure 2. Correlation of $\log\{k_2(\mathrm{Y,Z})\}$ with (σ_p + 0.6 σ_p^-) for the thermal reaction of substituted thiobenzophenones with phenylallene

This correlation illustrates that a π-repulsive saturation interaction between π-acceptor substituents and the thiocarbonyl function occurs.[24b] Charton's extended Hammett equation[25,26] reveals

$$\log k_2(\mathrm{Y,Z}) = (0.91 \pm 0.11)\sigma_I + (1.65 \pm 0.13)\sigma_R - 2.43 \quad (6)$$
$$(r = 0.973,\ \psi = 0.25)$$

A good *overall* assessment of the resonance effect with respect to the inductive effect is calculated by a procedure based on weighting each regression coefficient by the standard deviation of the corresponding explanatory variables.[20] In our case, the weighting factors are $a = \{\Sigma(\sigma_I - \bar{\sigma}_I)^2/(n-1)\}^{\frac{1}{2}}$ and $b = \{\Sigma(\sigma_R - \bar{\sigma}_R)^2/(n-1)\}^{\frac{1}{2}}$, wherein $\bar{\sigma}_R$ and $\bar{\sigma}_I$ are the mean values of σ_R and σ_I, respectively, giving values of a = 0.34, b = 0.37. This overall percentage contribution from the resonance effect is the ratio $100(b \times \rho_R)/(b \times \rho_R + a \times \rho_I)$ which amounts to 69%.

The non-linear resonance equation[27] recently developed by Bromilow *et al.*[26] which introduces an 'electron demand' parameter, X, supports the foregoing conclusions:

$$\log k_2(\mathrm{Y,Z}) = \log k_2(\mathrm{H,H}) + \rho_I\sigma_I + \rho_R\tilde{\sigma}_R \quad (7)$$

wherein $\tilde{\sigma}_R = \sigma_R(1 - \varepsilon\sigma_R)$; see Table 1 for σ_R.

In the case of the reaction of substituted thiobenzophenones with phenylallene we find:

$$\log k_2(\mathrm{Y,Z}) = (1.07 \pm 0.09)\sigma_I + (1.69 \pm 0.11)\tilde{\sigma}_R - 2.49$$
$$(r = 0.984,\ \psi = 0.19;\ \varepsilon = +0.38 \pm 0.01).$$

The positive value of ε indicates the charge transfer to some extent from the reaction centre to the substituents in the transition state. In this equation the absolute value $|\tilde{\sigma}_R|$ increases with increasing values of σ_R for π-acceptor substituents (X = NO_2) and $|\tilde{\sigma}_R|$ decreases with decreasing values of σ_R for π-donors (X = OCH_3), indicating the enhanced resonance interactions with the thione system in the transition state in the case of acceptor substituents.

Isotope Effects.[28]—Comparison of the reaction rate of α-deuteriated phenylallene ($PhCD{=}C{=}CH_2$) with thiobenzophenone in acetonitrile with respect to the rate for the reaction of thiobenzophenone with phenylallene ($Ph\overset{\alpha}{C}H{=}\overset{\beta}{C}{=}\overset{\gamma}{C}H_2$) revealed a value of:

$$\frac{k_2(\mathrm{H}_\alpha)}{k_2(\mathrm{D}_\alpha)} = 0.91 \pm 0.02$$

and for ($PhCH{=}C{=}CH_2$) *versus* $PhCD{=}C{=}CD_2$:

$$\frac{k_2(2\mathrm{H}_\gamma)}{k_2(2\mathrm{D}_\gamma)} = 0.75 \pm 0.01$$

which is consistent with attack at C-β (*cf.* ref. 15) and indicative for a change in hybridization at C-α and C-γ.[15,29]

Table 2. Rate constants[a] for the thermal reaction of unsubstituted thiobenzophenone with phenylallene at 40 °C in different solvents compared with the solvent parameters E_T[31,32]

Solvent	10^3k_2(H,H)	E_T
Propan-1-ol	4.67 ± 0.06	50.7
Butan-1-ol	3.55 ± 0.04	50.2
Pentan-1-ol	3.23 ± 0.04	47.4
Acetonitrile	2.45 ± 0.03	46.0
Dichloromethane	1.70 ± 0.02	41.1
o-Dichlorobenzene	2.57 ± 0.03	38.1
Benzene	3.07 ± 0.04	34.5
Tetrachloromethane	3.08 ± 0.05	32.5
Hexane	2.29 ± 0.03	30.9

[a] $dm^3\ mol^{-1}\ s^{-1}$.

The isotope effect when using $D_3CO{-}CH{=}C{=}CH_3$ with respect to $H_3CO{-}CH{=}C{=}CH_2$ is found to be

$$\frac{k_2(H)}{k_2(X)} = 1.20 \pm 0.20$$

and is associated with a rotation of the OCH_3 group around the O–C(α) bond during the reactions.[15] These effects are significant and reproducible (see Experimental section).

Optically Active Allenes.—In accordance with the presence of the intermediate allylic 1,4-diradical, we found that by treating xanthene-9-thione with an excess of the optically active allene[30] (+)-PhC(H)=C=CHBu^t (28% enantiomeric excess), the mixture of reaction products (**3**), (**4**), and (**5**) isolated in this reaction showed no measurable optical activity and is undoubtedly a racemic mixture, while the unchanged optically active allene showed no loss in optical rotation. This proves that the cycloaddition reaction mechanism involves a non-chiral intermediate, such as the allylic 1,4-diradical (**8**). Furthermore, this intermediate undergoes ring closure much faster than disproportionation (see the Scheme) (*cf.* ref. 9).

Solvent Effects.—In our previous publication[1] reaction addition rates of xanthenethione to phenylallene were measured in only three solvents. Owing to the better solubility of thiobenzophenone it was possible to study the rate of reaction of thiobenzophenone with phenylallene in nine different solvents (see Table 2). As summarized in Table 2, the reaction rate is only slightly dependent on the solvent polarity, which is pointing to only small charge development in the transition state. On the other hand the low solvent effect is in agreement with a 1,4-diradical-mediated ($_{\pi}2_S + {}_{\pi}2_S + {}_{\pi}2_S$) reaction mechanism (Scheme). Although this lack of solvent effect might result from the difficulty in solvating the charge in a fairly congested transition state or from the short lifetime of a dipolar intermediate, we consider the possibility of a dipolar intermediate very unlikely. It appears that the same products are formed in the photochemical reaction,[9] in which we have trapped the intermediate diradical.[10d]

Conclusions

Analysis of the measured reaction rates of the thermal cycloaddition of substituted thiobenzophenones with phenylallene by linear free energy relationships shows that the reaction undoubtedly proceeds *via* a 1,4-diradical-mediated ($_{\pi}2_S + {}_{\pi}2_S + {}_{\pi}2_S$)-mechanism. Mesomeric interaction is found to occur in the transition state between acceptor substituents and the electron-releasing reaction centre. This is substantiated by the value of the constants ρ^- and r^- and the positive value of electron-demand parameter ε.

Results of experiments with deuterium-labelled allenes are consistent with attack of the thione at C-β of the allenic system and the experiment with an optically active allene supports the presence of a non-chiral intermediate *i.e.* the allylic diradical (**8**). The weak solvent effect is in accordance with our mechanism as depicted in the Scheme.

Experimental

General.—Kinetic data were subjected to the least-squares program 'POLGRAF' on an Apple II/e microcomputer. Multiple regression analysis was carried out using 'NIPREGER' run on a Cyber 170-100 computer.

U.v. spectra were recorded on a Perkin–Elmer 555 spectrophotometer with a thermostatted cell holder. H.p.l.c. separation experiments were performed on a JOBIN-YVON Miniprep (40 cm column, internal diameter = 2 cm, using Kieselgel 60, Merck 230—400 mesh, eluting with CH_2Cl_2). Optical rotations were determined with a Perkin–Elmer 241 polarimeter. The solvents were dried and distilled before use: CH_2Cl_2 from $CaCl_2$(solid) and CH_3CN from P_2O_5(solid), other solvents were all Uvasol (Merck) quality.

Starting Materials.—Thiones: Thiobenzophenones[33] and xanthene-9-thione[33,34] were prepared from their corresponding ketones. *p*-Cyanothiobenzophenone was prepared from *p*-cyanobenzoic acid as follows:[35] *p*-cyanobenzoic acid (7.5 g, 0.05 mol) was treated with thionyl chloride (25 ml) at 60—70 °C until the evolution of SO_2 gas had ceased.[36] The excess of thionyl chloride was distilled off at normal pressure. The acid chloride was used without further purification. To a well stirred solution of *p*-cyanobenzoyl chloride (5 mmol) in dry ether (100 ml) was added phenylmagnesium bromide solution (0.90M in ether; 80 ml) at −5 °C. Stirring was continued for another 15 min at −5 °C and for 1 h at room temperature. The reaction mixture was poured into saturated aqueous NH_4Cl and extracted four times with ether. Drying ($MgSO_4$) and concentration under reduced pressure (12 mmHg) yielded crude *p*-cyanobenzophenone (9.0 g). Purification by column chromatography on silica gel with CH_2Cl_2 as the eluant yielded pure *p*-cyanobenzophenone (8.0 g, 70%), m.p. 102—103 °C; $\nu_{max.}$(KBr) 1 650 (C=O) and 2 125 cm^{-1} (C≡N); δ_C ($CDCl_3$) 194.8 (C=O) and 117.8 (C≡N).

p-Cyanothiobenzophenone was prepared according to ref. 33. Phenylallene was prepared by a 1,3-substitution reaction of phenylmagnesium bromide with 3-methoxyprop-1-yne as described by Brandsma *et al.*[36] using CuBr (2 mol %). The α-deuteriated allene was prepared as described.[3] $D_3COCH_2C{\equiv}CH$ was prepared from $HOCH_2C{\equiv}CH$ using perdeuteriated dimethyl sulphate;[36] subsequently base-catalysed isomerization[36] with KOBu^t gave $D_3COCH{=}C{=}CH_2$ (70%) containing t-butyl alcohol (4%).

The optically active allene (+)-PhCH=C=CHBu^t was prepared by Mr. P. Wijkens from the methanesulphinate ester of optically active (+)-2,2-dimethylpent-4-yn-3-ol using a phenylcopper reagent.[30]

Thermal Reactions.—Typical experiment. A u.v. cell containing an acetonitrile solution of thiobenzophenone (2.25mM; 4.00 ± 0.5 ml) under nitrogen was thermostatted at 40.0 ± 0.2 °C until the absorbance at λ 600 nm remained constant. Phenylallene (40 mol equiv.) was added to the solution. The reaction was followed by the change of absorption at λ 600 nm with time. The data of the recorded spectra were subjected to a linear regression program on an Apple II computer. Dual substituent parameter correlations were

Table 3.

Allene	10^3k_2/ $dm^3\ mol^{-1}\ s^{-1}$	$k_2(H)/k_2(D)$
$H_3COCH{=}C{=}CH_2$	8.82 ± 0.08	1.20 ± 0.02
$D_3COCH{=}C{=}CH_2$	7.35 ± 0.07	
1:1 Mixture	8.04 ± 0.07	1.21 ± 0.02
$PhCH{=}C{=}CH_2$	2.46 ± 0.03	0.91 ± 0.02
$PhCD{=}C{=}CH_2$	2.70 ± 0.03	
1:1 Mixture	2.59 ± 0.03	0.92 ± 0.02
$PhCD{=}C{=}CD_2$	3.61 ± 0.04	0.75 ± 0.01

performed with program NIPREGER on a Cyber model 170-100 computer.

Thermal reaction of xanthene-9-thione with the optically active allene[37] (+)-$PhC(H){=}C{=}CHBu^t$. A solution of xanthene-9-thione (150.1 mg, 0.708 mmol) in dichloromethane (10 ml) was treated with an excess of the optically active allene {395 mg, 2.30 mmol; $[\alpha]^{20}$ 12.1 ± 1°; c = 0.401M (CH_2Cl_2); 28% enantiomeric excess}. The reaction was allowed to proceed for 6 h at 40 °C, when the excess of the allene and the cycloaddition products (**3**), (**4**), and (**5**) were separated by preparative h.p.l.c. (Kieselgel 60, 230—240 mesh) with hexane–dichloromethane (1:3) as the eluant. The optical activity of the unchanged allene was determined: $[\alpha]_D^{20}$ 11.8 ± 1°; c = 0.104M (CH_2Cl_2). The product mixture showed no optical rotation: $[\alpha]_D^{20}$ 0.0 ± 0.5°; c = 0.70M (CH_2Cl_2).

Reactions with Deuterium-labelled Compounds.—The isotope purity of the allenes were always > 98% (by n.m.r. spectroscopy). The reactions were performed as described above under the heading thermal reactions by treating deuteriated allenes as well as a 1:1 mixture of deuteriated and non-deuteriated allenes with thiobenzophenone. The results are given in Table 3. A set of three experiments was performed in one day; rate constants are the mean of three values.

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