Tetrahedron Letters,Vol.24,No.10,pp 1101-1104,1983 0040-4039/83/101101-04$03.00/0
Printed in Great Britain

THERMAL [$_{\pi}2_{s}+_{\pi}2_{s}+_{\pi}2_{s}$]-CYCLOADDITION OF THIOBENZOPHENONE TO SUBSTITUTED PHENYLALLENES.

HAMMETT CORRELATION OF RATES AND IONIZATION ENERGIES

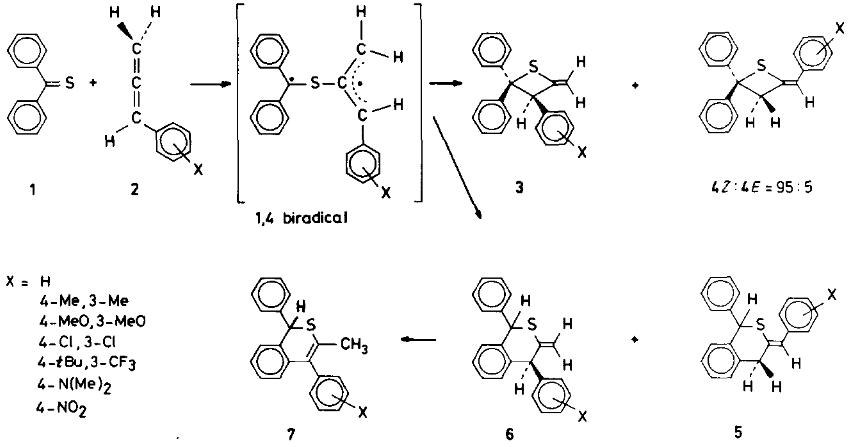
*J. Kamphuis, P.D.J. Grootenhuis and H.J.T. Bos**

Laboratory of Organic Chemistry, University at Utrecht

Croesestraat 79, 3522 AD Utrecht, The Netherlands

Abstract: Thiobenzophenone reacts as an electrophile in the thermal [$_{\pi}2_{s}+_{\pi}2_{s}+_{\pi}2_{s}$]-cycloaddition reaction with substituted phenylallenes, as was deduced from a linear free energy correlation of the reaction rates with σ^+ ($\rho^+ = -0.36 \pm 0.03$ (n=9, r=0.97)) and with the first ionization energies IE_a ($\log(k_X/k_H) = -0.55\ IE_a + 4.57$ (r=0.92)) of the substituted phenylallenes. Additional evidence for the mechanism is given.

A number of investigations on the thermal[1] and photochemical[2] cycloaddition reactions of aromatic thiones with cumulated systems have been carried out in this laboratory. We found that the thermal reaction shows typical features of an orbitally concerted but energetically non concerted (two step) mechanism, resulting in the formation of two (2+2)- and two (4+2)-cycloadducts *via* a biradical intermediate[1].



The $[_{\pi}2_s+_{\pi}2_s+_{\pi}2_s]$-type mechanism has received considerable interest during the last decade[3]. No Hammett evaluation of substituent effects on the $[_{\pi}2_s+_{\pi}2_s+_{\pi}2_s]$-type mechanism have been reported thus far however. Although *correlation analyses* of substituent effects in cumulated systems have been reported, there is still a lack of data on allenes, as mentioned by W. Runge in a recent review[4]. We therefore studied the influence of a wide range of *para* and *meta* substituents on the rate of the reaction of phenylallene with thiobenzophenone, in order to investigate linear free energy correlations. The reactions show clean second order kinetics as measured by UV spectroscopy (solvents dichloromethane and acetonitrile). For the reaction with phenylallene the rate constant k_H (298 K) amounts to $1.50 \cdot 10^{-3}$ $dm^3 \cdot mol^{-1} \cdot s^{-1}$ (CH_2Cl_2); $\Delta G^{\neq} = 89$ kJ $\cdot$ mol^{-1}, $\Delta H^{\neq} = 31$ kJ $\cdot$ mol^{-1} and $\Delta S^{\neq} = -195$ J $\cdot$ $mol^{-1} \cdot K^{-1}$.

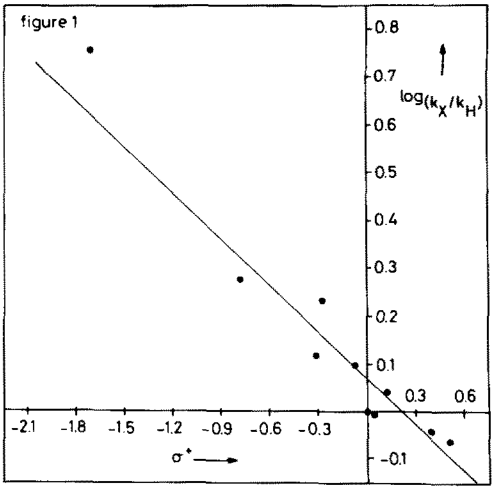
Table Relative rates and the first ionization energies of ten substituted phenylallenes at 40°C in acetonitrile.

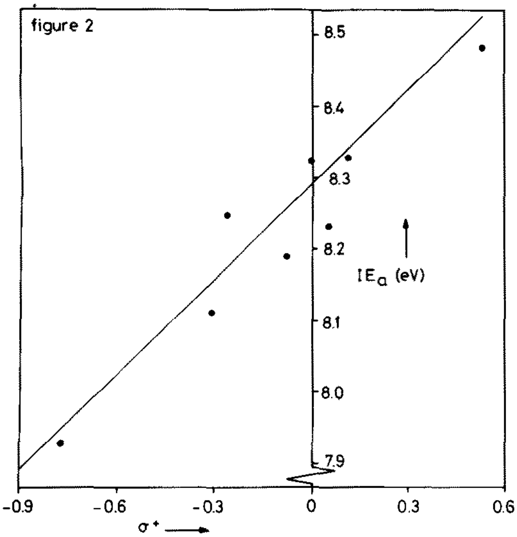
Subst. X	k_X/k_H	$IE_a(eV)$ [6]	σ^+	σ [7,8]	E_R [9]
4-N(Me)$_2$	5.69	5b	-1.7	-0.83	0.24
4-OMe	1.88	7.93	-0.78	-0.27	0.11
4-t-Bu	1.70	8.25	-0.26	-0.20	0.03
4-Me	1.30	8.11	-0.31	-0.17	0.03
3-Me	1.25	8.19	-0.07	-0.07	0.03
4-Cl	1.11	8.35	0.11	0.23	0.10
H	1.00[5a]	8.32	0	0	0
3-OMe	0.98	8.23	0.05	0.12	0.09
3-Cl	0.91	8.48	0.40	0.37	0.08
3-CF$_3$	0.87	5b	0.52	0.43	0.11
4-NO$_2$	5c	5b	0.79	0.78	0.41

As shown in figure 1 the thermal cycloaddition reactions obey the Hammett relationship, where for a correlation with σ^+: $\rho^+ = -0.36 \pm 0.03$ (n=9, r=0.97). For a correlation with σ a ρ-value of -0.61 ± 0.08 (n=9, r=0.95) is found. If we adhere strictly to the Hammett equation as advocated by Taft[10], the ρ^+ value does not change significantly ($\rho^+ = -0.39 \pm 0.05$, r=0.93) but the correlation for σ is diminished ($\rho = -0.65 \pm 0.1$, r=0.86) drastically.

Of all known dual substituent[8] parameter relations, the Yamamoto-Otsu relationship[11] gave the best fit to our data set, $\log(k_X/k_H) = -0.52\sigma + 1.16E_R + 0.03$ (r=.991) or $\log(k_X/k_H) = -0.51\sigma + 1.39E_R$ (r=0.986). From the relation found we conclude that some resonance interaction with X occurs in the transition state.

The negative ρ-value is in accordance with the observation that the less electrophilic 4,4'-dimethoxythiobenzophenone reacts with phenylallene 4.6 times as slow as thiobenzophenone does (40°C, acetonitrile).





The relative rates could also be correlated with the (first) adiabatic ionization energies of the conjugated double bond of the arylallenes (log $(k_X/k_H = -0.54\ IE_a + 4.56$, n=7, r=0.92), indicating that reaction occurs at the conjugated double bond of the arylallene. The IE_a could well be correlated to σ^+ where $IE_a = 0.44\sigma^+ + 8.3$(r=0.95); see fig. 2.

Both the relative rates in the Table and the sign of ρ indicate that in the transition state, positive charge develops to some extent in the allenic moiety of the transition state. The magnitude of the ρ-value is much smaller than those observed for an ionic process[12]. On the other hand, this ρ-value is fully in agreement with a biradical intermediated $[_\pi 2_s + _\pi 2_s + _\pi 2_s]$-mechanism,which implicates a transition state which is somewhat polar.

The low solvent effect, k(acetonitrile)/k(dichloromethane) = 1.6, found for phenylallene and the highly negative activation entropy of this cycloaddition reaction indicate a tight transition statewith little charge separation in the rate determining step.

A further confirmation of the postulated mechanism is found in the reaction of 1,3-diphenylallene with thiobenzophenone which appears to be 5.8 times as fast as the reaction with phenylallene,quite more than a statistical factor of 2. This is indicative for an additional stabilization of the transition state by the second phenylgroup.

Acknowledgement: This investigation was supported by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We thank Mr. H.S. Kiliaan and Ms. M.M.G. Wijdeveld for their enthusiastic cooperation.

References

1.a) J. Kamphuis, R.G. Visser and H.J.T. Bos, Tetrahedron Lett. 23, 3603 (1982); b) R.G. Visser, E.A. Oostveen and H.J.T. Bos, Tetrahedron Lett. 22, 1139 (1981).

2.a) J. Kamphuis, J.G. Hupkes, R.G. Visser and H.J.T. Bos, Recl. Trav. Chim. Pays-Bas, 101, 114 (1982); b) R.G. Visser and H.J.T. Bos, Tetrahedron Lett. 4857 (1979); c) see 1b); d) R.G. Visser, J.P.B. Baaij, A.C. Brouwer and H.J.T. Bos, Tetrahedron Lett. 4343 (1977).

3.a) J.E. Baldwin and U.V. Roy, J. Chem. Soc. D, 521 (1969); b) J.L. Gras et M. Betrand, Nouv. J. Chim. 5, 521 (1981); c)D.J. Pasto, P.F. Heid, S.E. Warren, J. Am. Chem. Soc. 104, 13 (1982); d) D.J. Pasto and S.E. Warren, J. Am. Chem. Soc. 101, 13 (1982); e) see 1a); f) R.A. Firestone Tetrahedron 33, 3009 (1977); g) D.J. Pasto, Tetrahedron Lett. 21, 4787 (1980).

4. W. Runge, Substituent Effects in Allenes and Cumulenes, Chapter 5 in: "Progress in Physical Organic Chemistry", Vol. 13, 315-484 (1981).

5.a) corresponding to a rate constant of $2.46 \cdot 10^{-3}$ $dm^3.mol^{-1}.s^{-1}$; b) not yet measured; c) a redox reaction occurs.

6. R.J. C. Koster, Thesis,University of Utrecht, 1975.

7. C.D. Ritchie and W.F. Sager, An Examination of Structure-Reactivity Relationships, Chapter 6 in: "Progress in Physical Organic Chemistry" Vol. 2, New York, 323-400 (1964).

8. N.B. Chapman and J. Shorter, "Correlation Analysis in Chemistry",Plenum Press, New York-London,1978.

9. C. Hansch and R. Kerley, Chem.&Ind. 294 (1969).

10. R.W. Taft, A generalized treatment of substituent effects in the benzene series. A statistical analysis by the dual substituent parameter equation; Chapter 1 in "Progress in Physical Organic Chemistry" Vol. 10, 1-80 (1973).

11. I. Yamamoto and T. Otsu, Chem.&Ind. 787 (1967).

12.a) H.C. Brown and Y. Ikamoto, J. Am. Chem. Soc., 80, 4979 (1958); b) R. Huisgen, Angew. Chem., Int. Ed. Engl. 2, 633 (1963).

13. L. Ghosez and M.J. O'Donnell, Pericyclic Reactions of Cumulenes, Org. Chem. (N.Y.), 35, part 2, 79-140 (1977).

(Received in UK 20 December 1983)