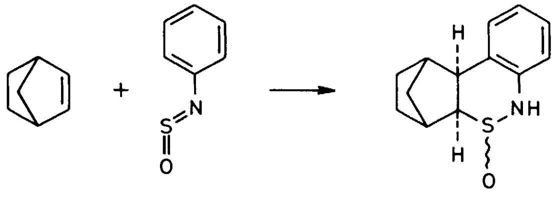
1,2-Thiazines and Related Heterocycles. Part 1. An Investigation of the Cycloadditions of *N*-Sulphinylanilines with 1,4-Epoxy-1,4-dihydronaphthalene and Other Alkenes

Peter Hanson,* Robin J. Lewis, and Thomas W. Stone
Department of Chemistry, University of York, Heslington, York YO1 5DD

Evidence is adduced from the character of the alkenes which cycloadd to *N*-sulphinylanilines and from a kinetic investigation of the reactions of *N*-sulphinylanilines with 1,4-epoxy-1,4-dihydronaphthalene, examining the effects upon reaction rate of solvent polarity, temperature, and substitution in the *N*-sulphinylanilines, that the cycloadditions are pericyclic reactions of Diels–Alder type with inverse electron demand. A degree of charge separation in the transition state is indicated but this is small and confined essentially to the sulphinylaniline moiety.

The chemistry of 1,2-thiazines has been relatively neglected particularly that where sulphur occurs in lower states of oxidation than in the six-membered, irreducible sultams which have received most attention.[1] The reactions of *N*-sulphinylamino-compounds, RN=S=O, offer interesting potential for the synthesis of 1,2-thiazine *S*-oxides. The reactivity of these heterocumulenes as dienophiles and the fundamental properties of their thiazine adducts with simple dienes have been reviewed by Kresze and Wucherpfennig.[2] Of particular relevance for the present work, however, are the reports that *N*-sulphinylaniline (1) cycloadds to bicyclo[2.2.1]heptene and its derivatives, also to form 1,2-thiazine oxides.[3,4] Here the heterocumulene ostensibly acts as a ' diene ', one half of which comprises the N=S double bond whilst a Kekulé ' double ' bond of the phenyl ring comprises the rest (Scheme 1). This type of reaction has been neither developed synthetically nor investigated mechanistically.

Collins [3] reported the failure of *N*-sulphinylanilines to cycloadd to alkenes other than bicyclo[2.2.1]heptene without specifying which particular alkenes failed to react. Soviet workers [5] did list unreactive dienophiles but all, with the exception of methyl vinyl ether, were electron-deficient. Since this work was published, understanding of pericyclic addition has undergone a revolution; we felt, therefore, that further study would be worthwhile, particularly since a theoretical analysis [6] of the electronic properties of *N*-sulphinylaniline in terms of frontier electron densities had concluded that cycloaddition would be expected to be a two-step ionic process. Before reporting, in subsequent Parts, the synthetic applications of analogues of the cycloaddition where *N*-sulphinylanilines react with hetero-bridged bicyclic alkenes, we here describe an investigation of the reactivity of *N*-sulphinylanilines towards alkenes, in general, and their reaction with 1,4-epoxy-1,4-dihydronaphthalene in particular.

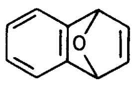


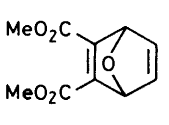
(1)

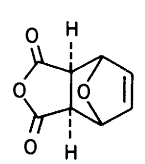
Scheme 1.

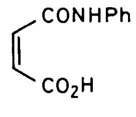
Results and Discussion

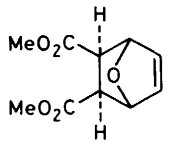
(a) *Alkene Reactivity*.—On the assumption that the cycloaddition of *N*-sulphinylamines to alkene bonds *is* pericyclic, frontier orbital considerations lead to the expectation that the reaction will be of Diels–Alder type with inverse electron demand: [7] the frontier orbitals of the ' diene ' are no doubt low in energy on account of its electronegative heteroatom content and aromatic stabilisation; consequently, an electron-rich dienophile will be required. Support for this reasoning is provided by Collins' observation [3] that electron-donating (4-MeO) substitution in *N*-sulphinylaniline inhibits its reactivity with bicyclo[2.2.1]heptene and by Beecken's [8] observation that the electron-rich dienophile, ethoxyacetylene, cycloadds to certain 5-sulphinylamino-1,2,4-thiadiazoles. We have consequently attempted to react *N*-sulphinylaniline with a wide range of alkenes exhibiting various frontier orbital energies and steric properties. Styrene, ω-nitrostyrene, indene, *N*-phenylmaleimide, maleic esters, tetracyanoethylene, but-2-enes, cyclohexene, cyclopentene, 3-sulpholene, 2,5-dihydrofuran, 2,3-dihydrofuran, and ethyl vinyl ether all failed to yield cycloadducts and unchanged dienophile was recovered. 1-(Cyclohex-1-enyl)pyrrolidine appeared to react, on the evidence of an immediate darkening of colour on mixing reagents. However, only tarry products resulted. The failure of the electron-deficient dienophiles to react confirms the results of Kataev and his co-workers; [5] the failure of electron-rich dienophiles other than bicyclic alkenes is at first sight surprising. Even forcing conditions of temperature and attempted Lewis acid catalysis did not elicit the reaction of compounds whose highest occupied molecular orbitals (HOMO) have energies comparable with that of the bicyclo[2.2.1]heptene π-orbital. If first ionisation potentials are taken as indicative of the energy of the HOMO (Koopmans' theorem [9]) the unreactivity of the simple alkenes, butenes (I_p 9.32 eV [10]), cyclopentene (I_p 9.18 eV [11]), and cyclohexene (I_p 9.12 eV [12]) is understandable as the first ionisation potentials of bicyclo[2.2.1]heptene and bicyclo[2.2.1]hepta-2,5-diene are 8.97 and 8.69 eV, respectively.[12] But the vinyl ethers [13,14] and enamine [15] have first ionisation potentials in the range 7.1—8.95 and would, on this basis, be expected to be more reactive than the bicyclic alkenes. We note at this point, however, that vinyl ethers and enamines are highly polarised dienophiles owing to the mesomeric interaction of the heteroatom with the alkene moiety whereas, by contrast, the reactive bicyclic alkenes are symmetrical in charge distribution. Their high *exo*-reactivity has been ascribed, in part, to a deviation from the trigonal configuration of the alkene carbons which results in a ' nonequivalent orbital extension ' of the π-molecular orbital on the *exo*-face by comparison with the *endo*-face; [16]

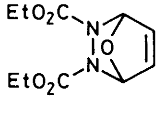

(2)

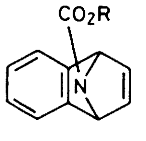

(3)

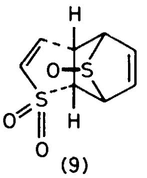

(4)

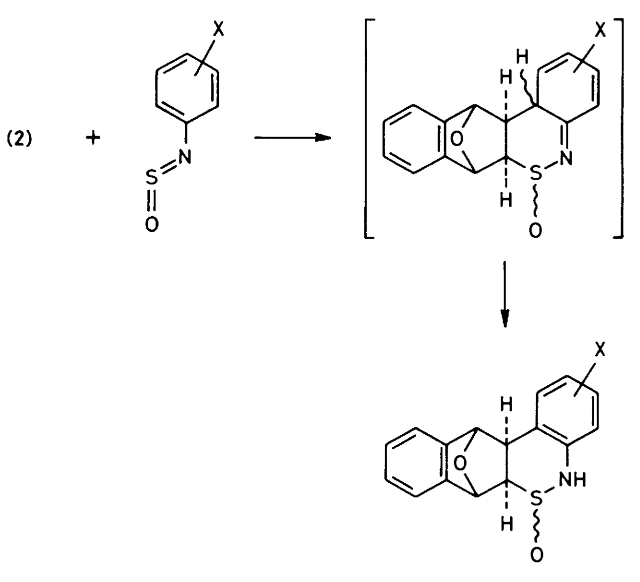

(5)


(6)


(7)


(8) a; R = Et
b; R = Bu^t


(9)



Scheme 2.

Table 1. Second-order rate constants for the cycloaddition of 1,4-epoxy-1,4-dihydronaphthalene and *N*-sulphinylaniline in various solvents at 363 K

Solvent	Dielectric constant at 293 K	10^5k/ dm^3 mol^{-1} s^{-1}
Cyclohexane	2.023 [a]	4.7
Chlorobenzene	5.708 [a]	8.3
Acetonitrile	37.5 [b]	10.9

[a] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, Chemical Rubber Co., Ohio, 58th edn., 1978. [b] 'American Institute Handbook of Physics,' ed. D. E. Gray, McGraw-Hill, New York, 2nd edn., 1963.

Table 2. Variation of second-order rate constants with temperature and activation parameters for the cycloaddition of 1,4-epoxy-1,4-dihydronaphthalene and *N*-sulphinylaniline in chlorobenzene

T/K	10^5k/ dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J mol^{-1} K^{-1}	$\Delta G^\ddagger$/ kJ mol^{-1}
353	3.61	80.2	−104.3	111.3
363	8.31			
373	14.72			
384	37.74			

experimental evidence has been found in support of this concept.[17]

In order to widen the range of alkenes which do cycloadd to *N*-sulphinylanilines we have investigated various analogues of bicyclo[2.2.1]heptene and have found some to react. The chemistry of the adducts produced will be described in later Parts; here we restrict ourselves to identifying the systems which do and do not react.

The Diels–Alder reaction of furan with various dienophiles leads to cycloadducts which are derivatives of 7-oxabicyclo[2.2.1]heptene. Thus the trapping of benzyne by furan gives 1,4-epoxy-1,4-dihydronaphthalene (2);[18,19] the cycloadduct of furan with dimethyl acetylenedicarboxylate is (3)[20,21] and that with maleic anhydride is (4).[22] We find that (2) and (3) react to give thiazine oxide adducts with *N*-sulphinylaniline. The anhydride (4) gave no thiazine oxide but, from an attempted cycloaddition, *N*-phenylmaleamic acid (5) was isolated, arising, presumably, from reaction of *N*-sulphinylaniline with the carboxylic anhydride function of (4), for which there is precedent,[23] followed by a loss of furan by retro-Diels–Alder reaction. However, conversion of (4) into the corresponding bicyclic dimethyl ester (6)[24] by treatment with acidified methanol yielded a 7-oxabicyclo[2.2.1]heptene derivative which does yield thiazine oxide adducts with *N*-sulphinylanilines. By contrast with (2), (3), and (6) diethyl 7-oxa-5,6-diazabicyclo[2.2.1]heptene-5,6-dicarboxylate (7)[25] failed to react with (1). The 1,4-dihydro-1,4-iminonaphthalene-*N*-carboxylates[26,27] (8a and b) both react with *N*-sulphinylaniline with formation of thiazine oxide adducts but the uncarboxylated imine gave tarry products and its hydrochloride failed to react. Failure to react was also noted for α-pinene and for the thiophene oxidation product (9).[28]

(b) *Kinetics*.—A kinetic investigation of the reactions of (1) and various 3- and 4-substituted *N*-sulphinylanilines with 1,4-epoxy-1,4-dihydronaphthalene (2) was carried out. The reactions were found to be of second order overall and, when both reactants were amenable to analysis (g.l.c.), consistent rates were found by measurement of the rate of disappearance of each. The products usually precipitated and their formation did not impede measurement; they were formed according to Scheme 2 and were fully characterized.[29] It should be noted that, in fact, parallel reactions occurred in each case: all *N*-sulphinylanilines may give diastereoisomeric products depending on the configuration at sulphur relative to the bridging oxygen; 3-substituted *N*-sulphinylanilines, in addition, yield products which are constitutional isomers. Details of the assignment of stereochemistry and structure will be published subsequently; current concern is with the rates of disappearance of reactants to give, by similar parallel reactions, their various products.

(i) *Influence of solvent*. The rate constant for the reaction between (1) and (2) was determined at 363 K in three solvents, cyclohexane, chlorobenzene, and acetonitrile (Table 1). The reaction is only slightly affected by change in solvent, a two- to three-fold increase in rate being observed for a large change in solvent polarity. It appears unlikely, therefore, that there is any high degree of charge separation in the transition state.

Table 3. Second-order rate constants for the cycloaddition of 1,4-epoxy-1,4-dihydronaphthalene to various 3- and 4-substituted *N*-sulphinylanilines and substituent constants for the substituents

Substituent	10^5k/ $dm^3\ mol^{-1}\ s^{-1}$	log*k*	σ_I [a]	$\sigma_R{}^+$ [a]	$\sigma_R{}^\circ$ [a]	$\bar{\sigma}$
3-MeO	76.05	−3.119	0.27	−1.02		2.803
3-Cl	23.28	−3.633	0.46	−0.36		1.354
3-Me	11.42	−3.942	−0.04	−0.25		0.581
3-NO_2	9.53	−4.021	0.65	0.15		0.278
H	8.31	−4.080	0.00	0.00	0.00	0.000
4-MeO	4.97	−4.034	0.27		−0.45	1.254
4-Cl	5.44	−4.264	0.46		−0.23	0.963
4-Me	7.19	−4.143	−0.04		−0.11	0.200
4-MeO_2C [b]	(18.17)	(−3.741)				
4-NO_2 [b]	(5.81)	(−4.236)				

[a] Ref. 30. [b] Non-correlated values.

(ii) *Influence of temperature.* The rate constants for reaction of (1) and (2) in chlorobenzene were determined at four temperatures; this enabled the calculation of apparent activation parameters for the reaction. The results are given in Table 2. The relatively low enthalpy of activation and the strongly negative entropy of activation are consistent with a highly ordered transition state in which bond reorganisation is synchronous. The results noted in (i) and here militate against a two-step ionic addition mechanism.

(iii) *Substituent effects.* The rate constants for the reaction of (2) with a series of 3- and 4-substituted *N*-sulphinylanilines in chlorobenzene at 363 K were determined. It was intended to use a wide range of substituent types, varying in character from MeO ($+M$) to NO_2 ($-M$). It was found, however, that reaction of (2) with 4-nitro-*N*-sulphinylaniline gave reaction solutions which were brown and tarry and no rate constant which could be treated meaningfully with others was obtained. 4-Methoxycarbonyl-*N*-sulphinylaniline was tried as a reactant with an alternative $-M$ substituent and likewise discolouration and failure to obtain a meaningful rate constant occurred. The 4-substituted *N*-sulphinylanilines thus lack representatives of $-M$ character. The second-order rate constants for substituted *N*-sulphinylanilines are given in Table 3.

Qualitative trends are immediately apparent from the data: the reaction rate increases with increasing mesomeric donation from the 3-position in the *N*-sulphinylaniline and decreases with such substitution in the 4-position, the relative effect of a 3-substitution being greater. It is apparent that this relative effect is electronic and not merely statistical for a 3-methoxy-substitution accelerates the rate of reaction of *N*-sulphinylaniline almost ten-fold whereas the same substitution in the 4-position merely halves the rate. In attempting to assess more quantitatively the electronic influence of substituents on rate we find that the simple Hammett relationship fails to correlate the data. For example, a simple linear regression of $\log k_3$ upon σ_m has a correlation coefficient of only 0.128 and that of $\log k_4$ upon σ_p only 0.204. We find, however, that the results are amenable to analysis in terms of a dual substituent parameter regression utilizing the σ_I and σ_R values of Taft and his co-workers.[30] Equations (1) and (2) give the correlations for the 3- and 4-series, respectively; standard errors are given for the regression coefficients and constant term.

$$\log k_3 = -(4.112 \pm 0.028) + (0.352 \pm 0.065)\sigma_I - (0.874 \pm 0.043)\sigma_R{}^+ \quad (1)$$

R_3 0.998; F_3 273.1, probability 0.0036

$$\log k_4 = -(4.093 \pm 0.019) - (0.171 \pm 0.077)\sigma_I + (0.379 \pm 0.094)\sigma_R{}^\circ \quad (2)$$

R_4 0.993; F_4 35.18, probability 0.1184

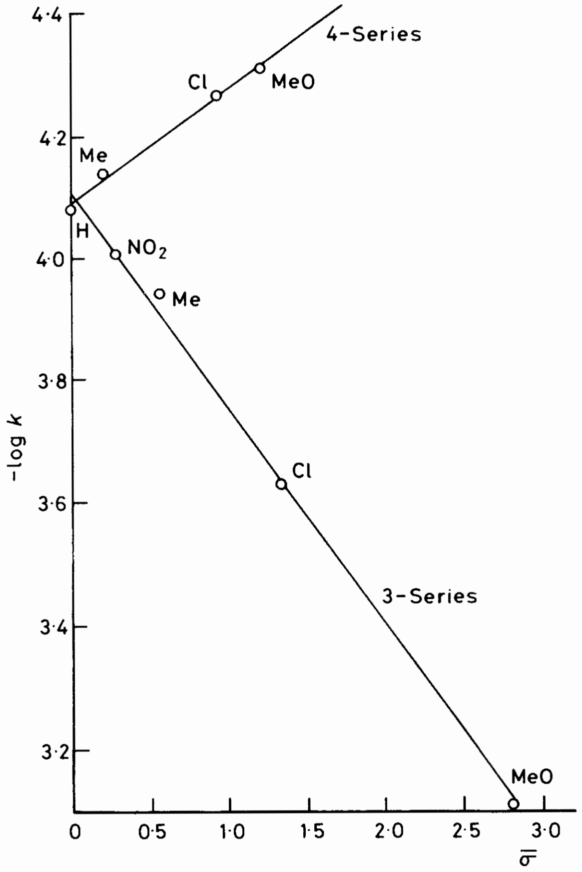
The multiple correlation coefficient R_3 indicates that 99.64% of the variance in the data for the 3-series is correlated by equation (1) and the *F*-test indicates a <0.5% probability that the observed data could have come from an uncorrelated parent population. The multiple correlation coefficient R_4 indicates that 98.6% of the variation in the data for the 4-series is correlated by equation (2); here the number of data is fewer and the *F*-test indicates a 12% probability that they could arise from an uncorrelated parent population. Recasting equations (1) and (2) in the form $\log k = a + \rho_I(\sigma_I + \lambda\sigma_R)$ where $\lambda = \rho_R/\rho_I$ gives equations (3) and (4). If, to facilitate

$$\log k_3 = -4.112 + 0.352(\sigma_I - 2.483\sigma_R{}^+) \quad (3)$$

$$\log k_4 = -4.093 - 0.171(\sigma_I - 2.216\sigma_R{}^\circ) \quad (4)$$

graphical display, the parenthetical terms in equations (3) and (4) are called $\bar{\sigma}$, literature values of σ_I, $\sigma_R{}^+$, and $\sigma_R{}^\circ$ [30] may be used to evaluate $\bar{\sigma}$ values for the 3- and 4-series (Table 3).

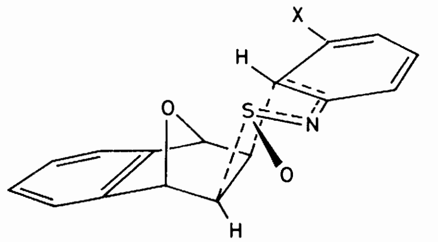
The Figure shows the plots of log*k* *versus* $\bar{\sigma}$ for both series. The good linearity indicates that, over the range of substituents examined, the cycloaddition of the *N*-sulphinylanilines to (2) can be expressed quantitatively in terms of the electronic character of the substituents despite the fact that the reaction rates measured are composite, summing the rates of parallel reactions leading to isomeric thiazine oxide adducts. This is particularly remarkable for the 3-substituted series where one of the modes of addition involves C(2) of the *N*-sulphinylaniline which position is *ortho* both to the NSO function and to the substituent, and for this reason might be expected to suffer steric hindrance specific to the substituent. Were this the case, however, a linear correlation of $\log k_3$ would not have been found. Evidently, the geometry of the transition state is such that specific steric effects are minimised. This might occur if the approach of the reactants were mutually suprafacial as in (10). Interaction of the π-systems would plausibly commence at a separation of *ca.* 0.3 nm as occurs in molecular π-complexes,[31] at which point steric interactions would be small; as rehybridisation of appropriate trigonal centres to tetrahedral progresses in the transition state, that at C(2) of the sulphinylaniline moiety would ensure the rotation of the potentially hindering 3-substituent X away from H(1) of the 1,4-epoxy-1,4-dihydronaphthalene moiety.



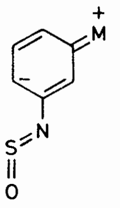
Variation of log*k* with $\bar{\sigma}$ for 3- and 4-substituted *N*-sulphinylanilines

(c) *Conclusions*.—Overall, the evidence favours a concerted cycloaddition mechanism. The large magnitude and negative sign of the entropy of activation are characteristic of pericyclic addition, *e.g.* for dimerisation of cyclopentadiene at 298 K,[32] $\Delta S^\ddagger$ is -111 J K^{-1} mol^{-1}. The enthalpy change represents 72% of the free energy of activation, which is a somewhat high proportion in cycloaddition, but it does indicate a relatively late transition state and consequently a large measure of rehybridisation of the interacting centres; thus ensuring the minimal steric effects from 3-substituents discussed above. The small magnitudes of the solvent and substituent effects, less than ten-fold variation in rate over the ranges studied, are consistent with only a small degree of charge-separation in the transition state and strong evidence against an ionic mechanism. The failure of 4-substituted *N*-sulphinylanilines with $-M$ substituents to react in a manner comparable with the remainder of the *N*-sulphinylanilines may betoken a change of mechanism from pericyclic to ionic, where the sulphinylamino-function effects an electrophilic attack on the alkene. The reaction, noted in section (a), of *N*-sulphinylaniline itself with an enamine to give tarry products may represent, similarly, a change of mechanism from pericyclic to ionic, this time facilitated by the availability of the amino-nitrogen of the enamine to stabilise the cationic charge resulting from an electrophilic attack by the sulphinylamino-sulphur.

The correlation of the majority of reaction rates in a dual-parameter analysis also predicates a pericyclic mechanism. Mesomeric effects dominate the small substituent effect in both series of reactions *i.e.* $|\lambda| > 1$. This is to be expected for [4 + 2] cycloaddition involving π-electrons. Other features of the correlation find ready explanation. The reactivity of the 3-series is best correlated using $\sigma_R{}^+$. This is the resonance parameter most appropriate for expressing direct conjugation between $+M$ substituents and the reaction site.[30] Thus we envisage the small charge separation that does occur in the transition state to be distributed mainly as shown in (11). Such a distribution increases electron density at C(2) of the sulphinylaniline moiety and makes for a better match of the orbital coefficients of its LUMO with the symmetrical coefficients of the HOMO of the dienophile.[7] The signs of the coefficients ρ_I and ρ_R in equation (1) also agree with the roles of substituents in supplying or withdrawing electron density from C(2) of the *N*-sulphinylaniline.



(10)



(11)

Since the data for the 4-substituted series are few, we attach less significance to the correlation indicated by equation (2), but, nevertheless, the signs of the coefficients are consistent with the rate-enhancing effect of electron withdrawal by 4-substituents, presumably by increase in the electrophilicity of the sulphinyl sulphur, but the degree to which this may occur without a change of mechanism is, seemingly, limited.

Experimental

(a) N-*Sulphinylanilines*.—*N*-Sulphinylanilines were prepared from thionyl chloride and the appropriate aniline according to the method described by Kresze *et al.*[33] Most *N*-sulphinylanilines were purified by distillation at reduced pressure; the solid 3- and 4-nitro-*N*-sulphinylanilines were recrystallised from light petroleum. B.p.s and m.p.s were consistent with values recorded in the literature.[34-36]

(b) 1,4-*Epoxy*-1,4-*dihydronaphthalene*.—The dienophile used for kinetic work was prepared by trapping benzyne[19] with furan after the method of Stiles and Miller.[18] It was purified by chromatography on alumina eluting first with light petroleum (b.p. 40—60 °C) followed by diethyl ether. Recrystallisation from light petroleum (b.p. 40—60 °C) gave material, m.p. 55—56 °C (lit.,[37] 55—56 °C).

(c) *Kinetics*.—(i) *Solvents*. Cyclohexane and chlorobenzene were fractionated before use; acetonitrile was refluxed with P_4O_{10}, distilled, and refractionated.

(ii) *Method*. Duplicate solutions were made up separately at room temperature, in the chosen solvent, each containing equimolar 1,4-epoxy-1,4-dihydronaphthalene and the appropriate *N*-sulphinylaniline (1.500 mol dm^{-3}). For each solution six 1 cm^3 portions were transferred to separate tubes and frozen by immersion in liquid nitrogen. Whilst frozen, the tubes were evacuated and sealed. The sealed tubes were then placed in a thermostatted bath at the desired temperature ($\geqslant 90$ °C). Timing was started from the moment of immersion in the high-temperature bath. Pairs of tubes, one from each series, were withdrawn at convenient intervals over periods of up to 5 h after initiation of reaction, depending on the temperature. Reaction was quenched by rapid cooling to 0 °C. The tubes were opened and the contents diluted to known convenient volumes with a solution of an internal standard (4-

bromotoluene, 0.01 mmol dm^{-3}) in cyclohexane. (For reaction in acetonitrile the dilution was carried out with an acetone solution of the internal standard.)

The resultant mixtures were then analysed in duplicate by g.l.c. for remaining reactants: column, 1.5 m, Apiezon L 10% on 60—80 mesh Celite; oven temperature 150 °C; nitrogen carrier-gas, flow *ca.* 50 cm^3 min^{-1}. The quantity of reactant remaining was determined by triangulation and comparison of the peak area with that of the internal standard, response factors having been determined previously under these conditions. The rate constants were obtained graphically by plotting $x/a(a - x)$ *versus* time where a is the initial concentration of reactant and $(a - x)$ the measured remaining concentration; slopes of the graphs, equal to the second-order rate constants, were obtained by a least-mean-squares treatment of the plots. The rate constants presented in Tables 1—3 are averages of the duplicate analyses of the duplicate runs. Where possible, each reactant was analysed; the constants have an estimated error of *ca.* 6%.

Acknowledgements

We are grateful to the S.E.R.C. for a research studentship (T. W. S.).

References

1 J. G. Lombardino and D. E. Kuhla, *Adv. Heterocycl. Chem.*, 1981, **28**, 73.
2 G. Kresze and W. Wucherpfennig, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 149.
3 G. R. Collins, *J. Org. Chem.*, 1964, **29**, 1688.
4 A. Macaluso and J. Hamer, *J. Org. Chem.*, 1967, **32**, 506.
5 E. G. Kataev, V. V. Plemenkov, and V. K. Pluzhnov, *Zh. Org. Khim.*, 1967, **3**, 336.
6 V. V. Plemenkov and E. G. Kataev, *Str. Mol. Kvantovaya Khim.*, (*Kiev*), 1970, 146 (*Chem. Abstr.*, 1971, **74**, 87103).
7 I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley-Interscience, New York, 1976, ch. 4.
8 H. Beecken, *Chem. Ber.*, 1967, **100**, 2159.
9 T. Koopmans, *Physica* (*Utrecht*), 1934, **1**, 104.
10 M. B. Robin, G. N. Taylor, N. A. Kuebler, and R. D. Bach, *J. Org. Chem.*, 1973, **38**, 1049.
11 P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, 1970, **53**, 1677.
12 P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, 1969, **52**, 1745.
13 P. Huisgen and H. Mayr, *Tetrahedron Lett.*, 1975, 2965.
14 P. Caramella, G. Cellerino, A. Corsico Coda, A. Gamba Invernizzi, P. Grunanger, K. N. Houk, and F. Marinoni Albini, *J. Org. Chem.*, 1976, **41**, 3349.
15 F. P. Colonna, G. Distefano, S. Pignataro, G. Pitacco, and E. Valentin, *J. Chem. Soc., Faraday Trans. 2*, 1975, **71**, 1572.
16 S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.*, 1976, **98**, 4054.
17 R. Huisgen, P. H. J. Ooms, M. Mingin, and N. L. Allinger, *J. Am. Chem. Soc.*, 1980, **102**, 3951.
18 M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, 1960, **82**, 3802.
19 F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, 1968, **48**, 12.
20 T. Sakai, K. Kanematsu, and K. Hayakawa, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1951.
21 H. Prinzbach, M. Arguelles, and E. Druckrey, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 1039.
22 R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, 1948, **70**, 1161.
23 S. Nishizaki and T. Toshimoto, *Kobunshi Ronbunshu*, 1975, **32**, 566 (*Chem. Abstr.*, 1976, **84**, 106110k).
24 J. Jolivet, *Ann. Chim.* (*Paris*), 1960, **5**, 1165 (*Chem. Abstr.*, 1961, **55**, 13403i).
25 Y. Yur'ev and N. Zefirov, *Zh. Obshch. Khim.*, 1959, **29**, 2954.
26 L. A. Carpino and D. E. Barr, *J. Org. Chem.*, 1966, **31**, 764.
27 M. J. O. Anteunis, F. A. M. Borremans, J. Gelan, A. P. Marchand, and R. W. Allen, *J. Am. Chem. Soc.*, 1978, **100**, 4050.
28 R. E. Merrill and G. Sherwood, *J. Heterocycl. Chem.*, 1977, **14**, 1251.
29 P. Hanson and T. W. Stone, work in preparation.
30 S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, 1973, **10**, 1.
31 R. Foster, 'Organic Charge Transfer Complexes,' Academic Press, London, 1969, p. 233.
32 J. Sauer, H. Weist, and A. Meilert, *Chem. Ber.*, 1964, **97**, 3183.
33 G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede, *Angew. Chem., Int. Ed. Engl.*, 1962, **1**, 89.
34 G. Butt, M. Davies, Y. T. Pang, R. D. Topsom, and A. R. Katritzky, *J. Chem. Soc., Perkin Trans. 2*, 1974, 260.
35 G. Leandri and A. Mangini, *Ric. Sci.*, 1957, **27**, 1920.
36 H. Sugihara, M. Sasaki, Y. Kawamatsu, and H. Morimoto, *Liebigs Ann. Chem.*, 1972, **763**, 121.
37 G. Wittig and L. Pohmer, *Chem. Ber.*, 1956, **89**, 1334.

Received 11*th March* 1983; *Paper* 3/384