Hz), 7.20 (1 H, d, J = 8 Hz), 10.48 (1 H, broad, >NH) ppm; $\lambda_{max}^{H_2O}$ 257 nm (ϵ 6600), $\lambda_{max}^{HO^-}$ 287 nm (ϵ 10,000).

Anal. Calcd for $C_8H_{12}N_2O_2$: C, 57.13; H, 7.19; N, 16.65. Found: C, 56.94; H, 7.04; N, 16.43.

Registry No.—**1**, 34314-62-0; **4**, 34314-63-1; **12a**, 34314-64-2; **12b**, 24314-65-3; **15**, 34314-66-4; **16**, 34314-67-5; **17**, 34314-68-6; **18** (R = Ph; R′ = H), 34314-69-7; **20**, 27396-39-0; **21**, 34314-71-1; **22**, 28-289-95-4; trimethylsilyl *cis*-2-isocyanoatocyclohexanecarboxylate, 34314-733; trimethylsilyl β-isocyanatopropionate, 21655-05-0; trimethylsilyl butyrate, 16844-99-8; TMSA, 4648-54-8.

Acknowledgments.—This research was aided by an institutional grant to Temple University from the American Cancer Society. We thank Dr. Robert Suhadolnik for gifts of chemicals.

Dichloromaleimide Chemistry. I. Substituent Effects on Carbon-13 Nuclear Magnetic Resonance and Mass Spectra

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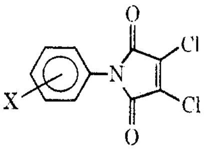
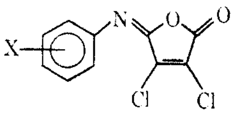
Eight N-aryldichloromaleimides (aryl = p-MeOC$_6$H$_4$, p-PhOC$_6$H$_4$, p-MeC$_6$H$_4$, p-PhC$_6$H$_4$, Ph, p-ClC$_6$H$_4$, m-ClC$_6$H$_4$, p-NCC$_6$H$_4$) were prepared from the appropriate aniline derivative and dichloromaleic andydride in HOAc.

Depending on the reaction conditions used, *N*-arylmaleimides or *N*-arylisomaleimides can be prepared from substituted anilines and maleic anhydride *via* the corresponding maleamic acids.[1]

Several authors have reported that the analogous reaction of substituted anilines with dichloromaleic anhydride produced *N*-aryldichloromaleimides **1**.[2] However, no evidence was presented to firmly establish that the products obtained were indeed the dichloromaleimides **1** and not the corresponding dichloroisomaleimides **2**.



1



2

a, X = p-OCH$_3$ **e**, X = H

b, X = p-OC$_6$H$_5$ **f**, X = p-Cl

c, X = p-CH$_3$ **g**, X = m-Cl

d, X = p-C$_6$H$_5$ **h**, X = p-CN

We have prepared a series of eight such imides from the appropriate aniline derivatives and dichloromaleic anhydride in acetic acid. It was not possible to make definitive structural assignments for the members (**a–h**) of this series using proton-nmr and mass spectrometry, elemental analysis, or ir spectroscopy, although the latter did favor **1a–h** over **2a–h**. Further structural proof was therefore sought using Fourier-transform, ^{13}C nmr spectroscopy. One would expect to find only *two* kinds of carbon atoms in the imide rings of **1** while *four* kinds would be expected in the isoimide rings of **2**.

It was found that each ^{13}C nmr spectrum showed two kinds of carbon atoms for the imide ring and the appropriate number and kind of carbon atoms in the *N*-aryl substituent (Table I). The C—Cl and C=O carbon atoms are little affected by remote substituents in the *N*-aryl ring and thus occur within very narrow ranges, 133.1–134.2 and 162.9–163.4 ppm, respectively. The former were readily distinguishable from nearby aromatic peaks because of their relatively low intensity resulting from a diminished nuclear Overhauser effect and the chlorine quadrupole broadening effect. It should be noted that these ranges are very close to the values for the corresponding kinds of carbon atoms in dichloromaleic anhydride, 135.9 and 159.7 ppm, respectively. These spectra leave little doubt that the correct structures are **1a–h**.

A most interesting substituent effect was observed for the aromatic carbon atoms attached to the imide nitrogens. An excellent correlation was found by plotting the ^{13}C chemical shifts of these carbon atoms against σ^+ for the substituents on the aromatic ring[3] (see Figure 1 and Table I); the correlation coefficient was 0.985.

It has recently been shown[4] that ^{13}C chemical shifts for aromatic ring carbon atoms do correlate quite well with calculated electron densities which, to some extent, are reflected by substituent parameters. It should be pointed out that a similar plot in the present example *vs.* σ gave a correlation coefficient of only 0.895. A similar difference in σ^+ and σ correlation coefficients was reported for the para carbons in monosubstituted benzenes.[4]

A study of the mass spectral rearrangements and cleavages of **1a–h** also proved to be very interesting. Reports have appeared in recent years indicating that a major path in the electron impact induced cleavage of N-substituted phthalimides and *N*-phenylmaleimide involved the loss of carbon dioxide from the molecular

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[1] (a) M. K. Hargreaves, J. G. Pritchard, and H. R. Dave, *Chem. Rev.*, **70**, 439 (1970), and references cited therein; (b) E. Hedaya, R. L. Hinman, and S. Theodoropulos, *J. Org. Chem.*, **31**, 1311, 1317 (1966); (c) C. K. Sauers, *ibid.*, **34**, 2275 (1969); (d) G. V. Boyd, *Chem. Commun.*, 1147 (1969); (e) T. M. Pyriadi and H. J. Harwood, *J. Org. Chem.*, **36**, 821 (1971).

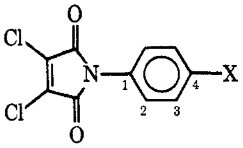
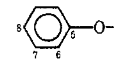
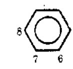
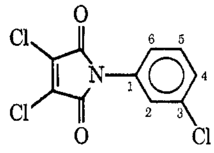
[2] (a) E. L. Martin, C. L. Dickinson, and J. R. Roland, *ibid.*, **26**, 2032 (1961); (b) G. H. F. Walker and F. R. Bradbury, U. S. Patent 2,962,504 (1960); (c) S. L. Shapiro, L. Freedman, and M. J. Karten, U. S. Patent 3,129,225 (1964); (d) M. J. Karten, S. L. Shapiro, E. S. Isaacs, and L. Freedman, *J. Org. Chem.*, **30**, 2657 (1965).

[3] Values for σ^+ taken from H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

[4] G. C. Levy, G. L. Nelson, and J. D. Cargioli, *Chem. Commun.*, 506 (1971).

TABLE I

ANALYTICAL DATA

Compd	X	^{13}C nmr chemical shifts[a] (probable assignments[b]) C-1	Other carbons	Mp, °C[c]	Lit. mp, °C
					
1a	$\overset{5}{C}H_3O-$	124.0	129.3 (2); 115.0 (3); 160.2 (4); 56.2 (5)	212–212.5	209–210[d]
1b		126.6	129.8, 130.9 (2, 7[e]); 119.3, 119.9 (3, 6[e]); 156.8, 157.8 (4, 5[e]); 124.8 (8)	183–183.5	f
1c	$\overset{5}{C}H_3-$	129.1	130.4 (2); 127.6 (3); 139.0 (4); 21.6 (5)	191–192	193–194[g]
1d		129.6	127.5, 128.0, 128.4 (2–8[e])	186.5–187	f
1e	H-	131.7	127.8, 129.4, 129.8 (2, 3, 4[e])	205–206	208[d]
1f	Cl-	134.0	129.5, 130.0, 130.8 (2, 3, 4[e])	214.5–215	210–216[d]
1h	$-\overset{5}{C}N$	136.3	128.2 (2); 134.6 (3); 111.8 (4); 119.1 (5)	229–230.5	f
					
1g	(Cl–)	134.0	126.5, 127.5, 129.5, 131.6, 133.7 (2, 3, 4, 5, 6[e])	181–182	183[d]

[a] Parts per million downfield from external TMS using DMSO-d_6 as solvent and internal standard. ^{13}C chemical shift of DMSO-d_6 from internal TMS was taken as 40.5 ppm. [b] Personal communications with G. C. Levy. [c] Recrystallization solvents: **1a**, chloroform + cyclohexane; **1b**, benzene + cyclohexane; **1c**, cyclohexane; **1d**, chloroform; **1e**, chloroform; **1f**, chloroform + hexane; **1h**, acetic acid; **1g**, acetic acid. [d] See ref 2c. [e] Not definite assignments. [f] A new compound for which satisfactory analytical data (±0.4% for C, H, and either N or Cl, or both) were reported. [g] See ref 2b.

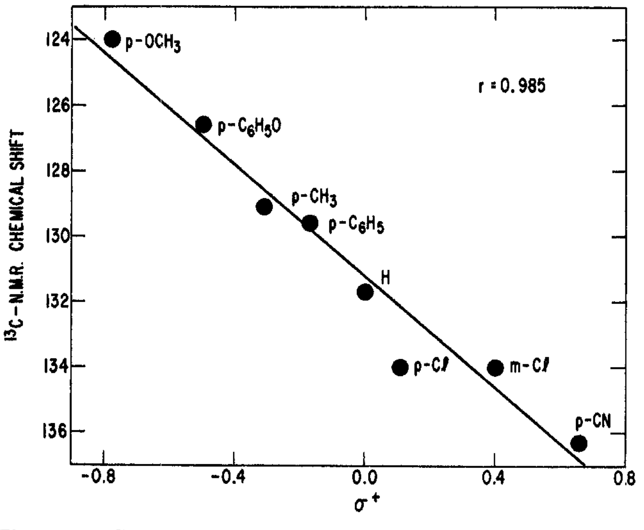


Figure 1.—Correlation of ^{13}C nmr chemical shift for the carbon bearing the imide nitrogen in **1a–h** with substituent parameters.

ions.[5] In view of these findings, we were surprised to find that the mass spectra of the N-aryldichloromaleimides (**1a–h**) showed no such $(M - CO_2)^+$ peaks at all (see Figure 2). On the other hand, each showed peaks representing the loss of CO_2 + Cl. This loss does not follow a regular pattern with respect to any substituent parameter (see Table II) and no Cl-, CO_2-, or CO_2-Cl-positive ions were present in any of these spectra. These facts are consistent with the rearrangement–cleavage mechanism proposed in Scheme I. Implied in the last decomposition step of this scheme is that the

TABLE II

SELECTED MASS SPECTRAL PEAK INTENSITIES FOR SUBSTITUTED N-PHENYLDICHLOROMALEIMIDES[a]

Substituent	Molecular ion	$(M - CO_2 - Cl)^+$	$(M - C_3Cl_2O)^+$	$(C_3Cl_2O)^+$	$\frac{(M - C_3Cl_2O)^+_{total}}{(C_3Cl_2O)^+_{total}}$[b]
p-OCH_3	100.0 (3)	9.9 (2)	53.0	3.6 (3)	8.41
	100.0 (3)	11.5 (2)	59.3	3.7 (3)	9.12
p-OC_6H_5	100.0 (3)	9.4 (2)	43.8	4.2 (3)	5.92
p-CH_3	100.0 (3)	24.4 (2)	67.0	7.1 (3)	5.40
	100.0 (3)	32.3 (2)	74.0	8.7 (3)	4.87
p-C_6H_5	100.0 (3)	13.7 (2)	72.0	2.2 (3)	18.45
	100.0 (3)	14.7 (2)	67.1	2.0 (3)	19.19
H	100.0 (3)	45.4 (2)	78.5	22.4 (3)	2.00
	100.0 (3)	79.2 (2)	87.5	28.3 (3)	1.77
p-Cl	100.0 (4)	35.6 (3)	81.0 (2)	32.5 (3)	1.91
	100.0 (4)	42.3 (3)	84.1 (2)	31.6 (3)	2.01
m-Cl	100.0 (4)	35.6 (3)	35.3 (2)	32.7 (3)	0.82
p-CN	100.0 (3)	38.9 (2)	30.9	38.9 (3)	0.45

[a] The number in parentheses next to intensity values indicates the number of peaks associated with the chlorine isotopic clusters (if present) for each ion. Intensities given are for the *all-^{35}Cl* peak of each cluster. Differences in the intensity values in two different spectra of a single compound are due to differences of as much as 50–100° in the source temperature of the mass spectrometer and to the use of two different source configurations during the course of this work. It should be noted that, when two ratios (last column) for the same compound were determined, they differed only slightly compared with those values for other compounds. [b] Total intensity for all peaks of $(M - C_3Cl_2O)^+$ cluster (when present) divided by total intensity for all peaks of $(C_3Cl_2O)^+$ cluster.

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[5] (a) R. A. W. Johnstone, B. J. Millard, and D. S. Millington, *ibid.*, 600 (1966); (b) J. L. Cotter and R. A. Dine-Hart, *ibid.*, 809 (1966); (c) C. M. Anderson, R. N. Warrener, and C. S. Barnes, *ibid.*, 166 (1968); (d) T. W. Bentley and R. A. W. Johnstone, *J. Chem. Soc. C*, 2354 (1968); (e) J. L. Cotter and R. A. Dine-Hart, *Org. Mass Spectrom.*, **1**, 915 (1968).

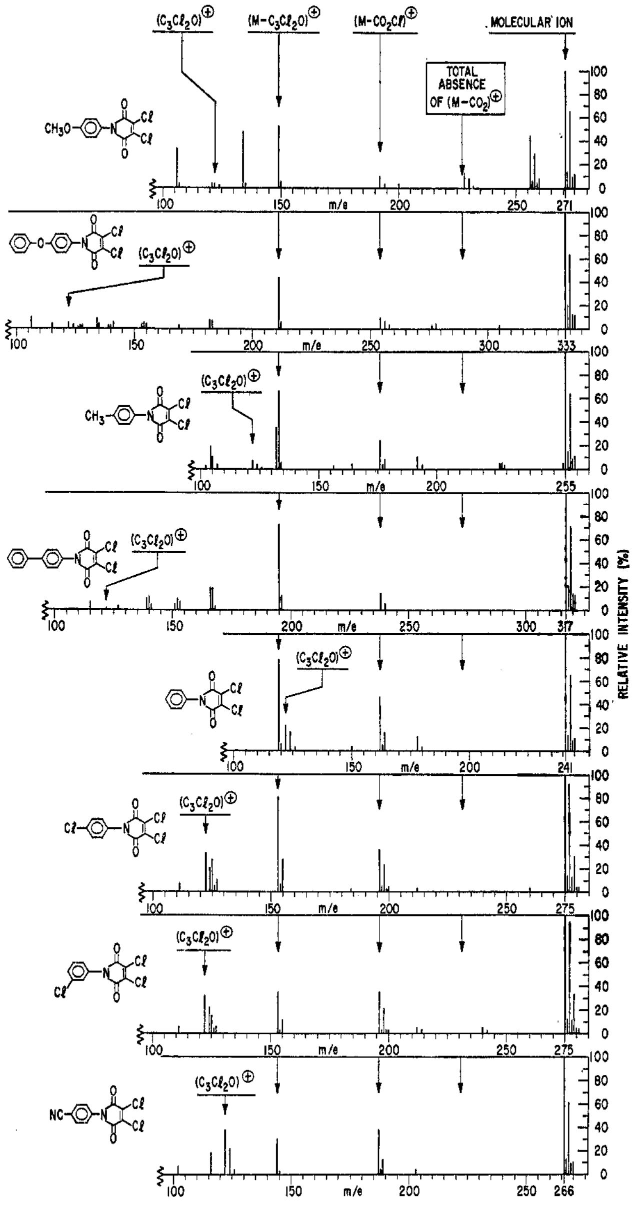
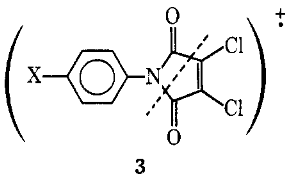


Figure 2.—Mass spectra of **1a–h**.

loss of CO_2 and Cl are either concerted or so nearly so that no substantial amount of the $(M - CO_2)^+$ ion [or $M - Cl)^+$ ion] is formed.

The other most prominent cleavage observed in the mass spectra is shown by the dotted line in **3**. Both



3

the $(M - C_3Cl_2O)^+$ and the $(C_3Cl_2O)^+$ ions are observed in all cases and as the expected isotopic clusters (see Table II). The relative intensities of these two ions varied in a regular way depending on the nature of the substituent on the *N*-aryl group. Plotting the log of this ratio *vs.* σ^+ values gives a good straight line with a correlation coefficient of 0.982 (see Figure 3). Thus, the tendency for the charge to remain in the isocyanate half on cleavage depends on the electron-donating (or electron-withdrawing) effect of the ring substituent.

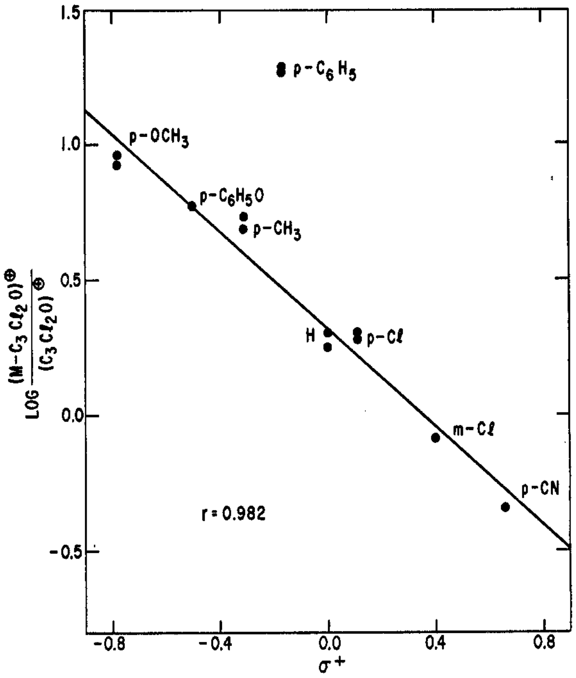
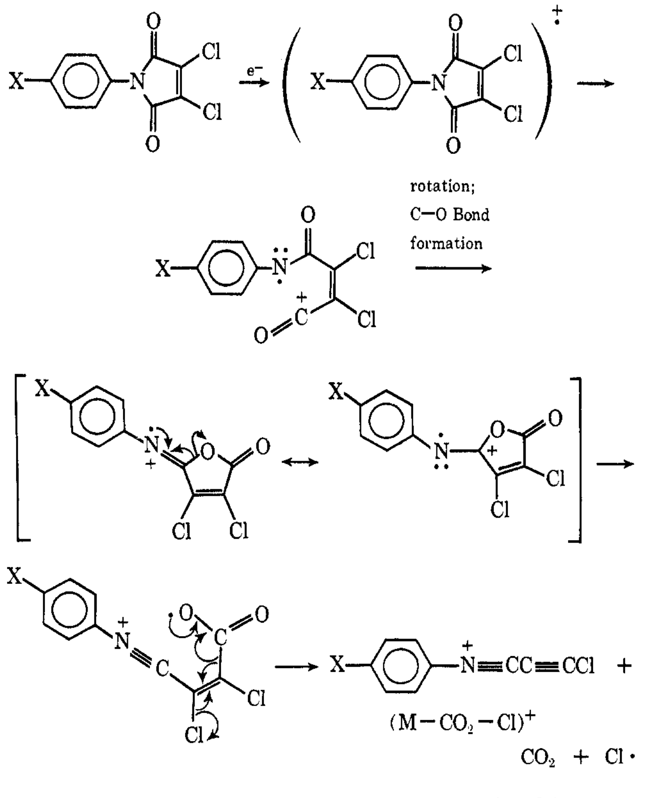


Figure 3.—Relation between the intensities of the $(M - C_3Cl_2O)^+$ and $(C_3Cl_2O)^+$ ions and the substituent parameters.

SCHEME I



(Substituent effects on relative ratios obtained in other mass spectral cleavages have been reported by several authors.[6]) The *p*-phenyl substituent of **1d** is quite unique, however, and apparently gives much more $(M - C_3Cl_2O)^+$ ions than would have been predicted. This may be the result of the formation of an unusually more stable ion than would have been expected from the σ^+ value of p-C_6H_5, a different ion from that pro-

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(6) See, for example, (a) F. W. McLafferty and M. M. Bursey, *J. Amer. Chem. Soc.*, **90**, 5299 (1968), and references cited therein; (b) M. M. Bursey, *Org. Mass Spectrom.*, **1**, 31 (1968).

duced in the rest of the series, or other effects such as a different mode of cleavage for **1d**.[7] Indeed, considering these possible differences, it is remarkable that the other seven compounds gave as good a correlation as they did.

Experimental Section

All ^{13}C nmr spectra were recorded with a Varian Associates XL-100-15 nmr spectrometer utilizing complete ^{1}H decoupling at 100 MHz with simultaneous ^{13}C observation at 25.2 MHz. Mass spectra were recorded on a CEC 21-104 analytical mass spectrometer.

Each imide, **1a–h**, was prepared by adding the appropriate aniline derivative slowly (at ~25°) to an excess of the dichloromaleic anhydride in glacial acetic acid. After several hours of stirring at 25°, each system was refluxed for 1 hr and cooled. The products crystallized from the solution on cooling and were readily isolated and purified. Each gave the expected ^{1}H and ^{13}C nmr spectra and mass spectra and showed strong C=O absorption in the ir at ~1725 cm^{-1}. Other analytical data are given in Table I.

Registry No.—**1a**, 34379-53-8; **1b**, 34281-45-3; **1c**, 29244-55-1; **1d**, 34281-46-4; **1e**, 3876-05-9; **1f**, 29236-09-7; **1g**, 34281-49-7; **1h**, 34281-50-0.

Acknowledgments.—The authors are indebted to Dr. G. C. Levy and J. D. Cargioli for their assistance in interpreting the ^{13}C nmr spectra.

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[7] Analogous behavior of the *p*-phenyl substituent has been noted before in another kind of correlation: M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 529 (1966).

Deuterium and Sulfur-34 Isotope Effects in the Thermal Decomposition of Some Cyclic Sulfones

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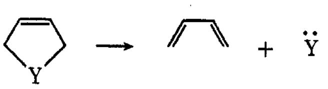
Received October 6, 1971

The k_H/k_D ratios in the decomposition of 2,5-dihydrothiophene-*2,2,5,5-d*$_4$ 1,1-dioxide (II) at 120° and 2,4-dimethyl-2,5-dihydrothiophene-*5,5-d*$_2$ 1,1-dioxide (IV) at 105° have been determined in the melt to be 1.094 ± 0.014 and 1.054 ± 0.019, respectively. The sulfur-34 isotope effect in the decomposition of the undeuterated analog of II has also been measured in the melt and in the diethylene glycol diethyl ether solution and $^{32}k/^{34}k$ ratio found to be 1.009 at 99.5°. Both deuterium and sulfur-34 isotope effects can well be accommodated by a concerted mechanism. The deuterium isotope effects are unusually small (about 3.3% per atom D extrapolated to room temperature). Possible explanations of this observation are mentioned.

The mechanism of addition of sulfur dioxide to conjugated acyclic dienes and the retro reaction, the thermal decomposition of cyclic sulfones, has been extensively studied. The two-step mechanism involving dipolar or diradical intermediates has been suggested mainly in earlier work,[1-5] though a concerted mechanism taking place in disrotatory manner has been also proposed.[6]

Woodward and Hoffman[7] predicted on the basis of orbital symmetry arguments that the concerted five-membered ring thermal fragmentation of the type

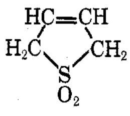


(Y can be SO_2, CO, NH, $\overset{+}{N}{=}\overset{-}{N}$, N–N=O) should be a disrotatory process. Experimental support for this prediction has been presented.[8,9] On the other hand, the photochemical SO_2 extrusion from sulfones occurs by concerted fragmentation[10] in a conrotatory manner, as also predicted by Woodward–Hoffman rules.[7]

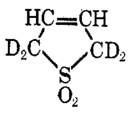
We studied the effect of deuteration on the rate of thermal decomposition of sulfolene I (II) and its 2,4-dimethyl analog III (IV). The kinetic sulfur-34 isotope effect in the reaction of I has also been measured. The intent of this work was to gain additional information about the mechanism of these reactions with respect to the timing of the bond-breaking processes and the structure of the transition state.

Results

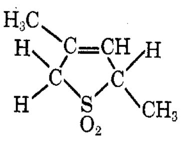
The kinetics of the thermal decomposition of I were previously studied.[2] We determined energy of activation, frequency factor, and entropy of activation as 33.2 kcal mol^{-1}, 7.1 × 10^{14} sec^{-1}, and 7.0 eu, which is in good agreement with published data (33.6 kcal mol^{-1}, 7.0 × 10^{14} sec^{-1}, and 8.9 eu).[2a,b] Using the sealed tube technique for the kinetic measurements, the rates of decomposition of I, of its tetradeuterated analog II, of 2,4-dimethyl-2,5-dihydrothiophene 1,1-dioxide (III) and of its deuterated analog IV, were determined.



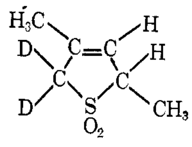
I



II



III



IV

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[1] L. R. Drake, S. C. Stowe, and A. M. Partansky, *J. Amer. Chem. Soc.*, **68**, 2521 (1946).

[2] (a) O. Grummitt, A. E. Ardis, and J. Fick, *ibid.*, **72**, 5167 (1950); (b) O. Grummitt and H. Leaver, *ibid.*, **74**, 1595 (1952); (c) O. Grummitt and J. Splitter, *ibid.*, **74**, 3924 (1952); (d) O. Grummitt and A. L. Endrey, *ibid.*, **82**, 3614 (1960).

[3] R. C. Krug and J. A. Rignay, *J. Org. Chem.*, **27**, 1305 (1962).

[4] (a) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964); (b) P. D. Bartlett, G. E. H. Wallbillick, and L. K. Montgomery, *J. Org. Chem.*, **32**, 290 (1967).

[5] T. J. Wallace, J. E. Hofmann, and A. Schriesheim, *J. Amer. Chem. Soc.*, **85**, 2739 (1963).

[6] W. L. Bailey and E. W. Cummins, *ibid.*, **76**, 1936, 1940 (1954).

[7] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

[8] (a) W. L. Mock, *ibid.*, **88**, 2857 (1966); (b) W. L. Mock, *ibid.*, **92**, 7610 (1970).

[9] D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

[10] J. Saltiel and L. Metts, *ibid.*, **89**, 2232 (1967).