amounts of NaOH and Br_2 was thermostated at 25°. The reaction was started by addition of α-phenylbenzoin. At appropriate time intervals, aliquots were taken out and extracted with benzene. The contents of α-phenylbenzoin and benzophenone were measured by glc with a column packed with SE-30 as stated above. The plot of log ([substrate]$_0$/[substrate]) against time gives a straight line up to 50–75% conversion. The data were reproducible to within 5%.

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Registry No.—Bromine, 7726-95-6; dioxane, 123-91-1; hypobromous acid, 13517-11-8.

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Homoconjugation Effects in the Diels–Alder Reaction of 1-(Substituted phenyl)-3,4-dimethylenepyrrolidines

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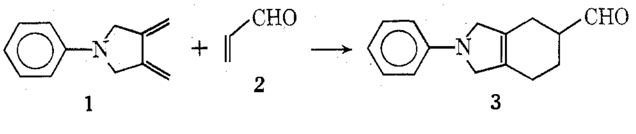
A kinetic study of the substituent effect on the diene reactivity of 1-(substituted phenyl)-3,4-dimethylenepyrrolidines in the Diels–Alder reaction was carried out. It was found that electron-withdrawing groups increased the rate of reaction and electron-donating groups decreased the rate. Hammett correlations of this substituent effect were obtained with σn values in three solvents: methylene chloride, dimethyl sulfoxide, and tetrahydrofuran. A determination of the relative frontier orbital energies of these exocyclic dienes indicated that the effect of the substituent on the rate of the Diels–Alder reaction was primarily through a homoconjugative interaction. This interaction altered the LUMO energies of the diene causing a novel substituent effect on the reaction rate.

The effect of spiroconjugation and homoconjugation on the chemical reactivity and the electronic spectrum of spirarenes is currently of considerable interest.[1-4] It has been found that two seemingly independent π systems with a specific stereochemical relationship interact through a spatial mode such that the energies of the respective HOMO's and LUMO's are influenced. It is well known[5-10] that the HOMO and LUMO energies of the reactants in the Diels–Alder reaction can be used to predict both the reactivity and regioselectivity of this reaction. Recently Semmelhack, *et al.*,[11] have attempted to explain diene reactivity in the Diels–Alder reaction through spiroconjugative effects. In this paper, we have investigated the effect of homoconjugation on the diene reactivity of 1-(substituted phenyl)-3,4-dimethylenepyrrolidines in the Diels–Alder reaction.

Kinetic Study

The 1-(substituted phenyl)-3,4-dimethylenepyrrolidines (**1**) were allowed to react with acrolein (**2**) to give the corresponding Diels–Alder adducts (**3**) in quantitative yield (determined by nmr). The concentrations of the reactants at any given time during the reaction of the exocyclic dienes with acrolein were determined by means of nmr spectroscopy. The reaction which is shown below is uncomplicated by side reactions. The rate of reaction was usually followed by observing the change in chemical shift of the aldehyde proton in going from acrolein to the Diels–Alder product.[12] This change in chemical shift was 4–8 Hz depending on the solvent used and afforded distinct integrations of the area of each peak. In the cases where the change in chemical shift was not large enough to give a complete separation of the reactant and product aldehyde proton peaks, the reaction was followed by the disappearance of the vinyl peaks (δ 5.55) of the diene and the aldehyde proton peaks were used as the internal standard.



It was found that a plot of log ([acrolein]$_t$/[diene]$_t$) *vs.* time for all dienes used yielded a straight line. This linear relationship indicates that the reaction is second order overall, first order with respect to acrolein and the diene. The rate constant of the reaction was determined from the slope of the straight line as follows.

$$\text{rate constant } (k) = \frac{2.303 \times \text{slope} \times 60 \text{ sec/min}}{[\text{acrolein}]_{t=0} - [\text{diene}]_{t=0}}$$

Hydroquinone was used as an inhibitor of the polymerization of the reactants in the reaction. The concentration of hydroquinone used was usually 0.01–0.02 *M*. It was found that the concentration of hydroquinone had no effect on the observed rate constant of this reaction.

The possibility that charge-transfer interaction between the aryl group of the diene and acrolein could have an effect on the observed rate constant was investigated. The reaction of 1-(*p*-methoxyphenyl)-3,4-dimethylenepyrrolidine with acrolein was carried out with varying concentra-

Table I
Effect of Concentration Changes on the Rate Constant of the Reaction of 1-(*p*-Methoxyphenyl)-3,4-dimethylenepyrrolidine with Acrolein in Methylene Chloride at 33°

$[\text{Acrolein}]_{t=0}/[\text{diene}]_{t=0}$	Concn, M Acrolein	Concn, M Diene	Rate constant,[a,b] M^{-1} min^{-1}	Std dev
2.0:1.0	0.905	0.453	2.14	0.13
3.6:1.0	1.78	0.500	2.09	0.08
5.1:1.0	2.59	0.506	2.13	0.11
7.6:1.0	4.30	0.564	2.17	0.09

[a] Average of three kinetic runs. [b] The rate constants were determined from kinetic runs that were followed to 70–80% completion. Also, the changes in concentration had no effect on the observed rate constants when the kinetic runs were followed to 20–40% completion.

Table II
Rate Constants for the Reaction of 1-(Substituted phenyl)-3,4-dimethylenepyrrolidines with Acrolein in Methylene Chloride at 33°

Substituent	Registry no.	Rate constant, M^{-1} min^{-1}, 10^2k	Concn, M[a] Diene	Concn, M[a] Acrolein	10^2 SD	Rel rate
p-COOEt	50872-60-1	3.50	0.471	1.84		1.67
p-Cl	32515-69-8	3.27	0.500	1.86	0.069	1.57
p-CH_3	50872-61-2	2.83	0.497	1.78	0.022	1.35
m-OCH_3	50872-63-4	2.78	0.495	1.82	0.054	1.33
H	50521-41-0	2.45	0.513	1.87	0.075	1.17
m-CH_3	50872-62-3	2.20	0.489	1.81	0.065	1.05
p-$N(CH_3)_2$	50872-58-7	2.16	0.487	1.81	0.047	1.03
p-OCH_3	50872-59-8	2.09	0.500	1.78	0.080	1.00

[a] Average of three kinetic runs for all dienes except 1-(*p*-carboethoxyphenyl)-3,4-dimethylenepyrrolidine for which one kinetic run was made.

tions of acrolein. Using an argument similar to Andrews and Keefer,[13] the rate constant should decrease in magnitude with increasing acrolein concentration if charge-transfer formation is taking place. It was found that the observed rate constants were essentially unchanged by increasing the initial dienophile to diene concentration to eightfold (Table I). Thus, it appears that no significant charge-transfer formation between acrolein and the aryl substituent took place.

These Diels–Alder reactions were carried out on a preparative scale under conditions similar to the kinetic study for three dienes (1-phenyl-3,4-dimethylenepyrrolidine, 1-(*p*-methoxyphenyl)-3,4-dimethylenepyrrolidine, and 1-(*p*-methylphenyl)-3,4-dimethylenepyrrolidine), and the adducts were isolated in near-quantitative yields (90–95%).[14] The nmr spectra of the isolated adducts were in agreement with the nmr spectra obtained from the kinetic study. The adducts were stable in a deuteriochloroform solution for several days at room temperature.

Hammett Relationship

Kinetic studies of the substituent effect on the rate of reaction of 1-(substituted phenyl)-3,4-dimethylenepyrrolidines with acrolein were carried out. In this diene system, the substituent is removed from direct conjugation with the diene portion of the molecule by a methylene group. All previous studies of the effect of substituents on the rate of the Diels–Alder reaction have employed substituents in direct conjugation with the diene.[15,16] In these prior studies, the observed effect of substituents of the diene on a normal electron demand Diels–Alder reaction was that electron-donating groups increase the rate of reaction and electron-withdrawing groups decrease the rate.

The substituent effect observed in this study, however, showed that electron-withdrawing groups increased the rate of reaction and electron-donating groups decreased the rate of reaction (Figure 1).[17] This substituent effect was observed in three solvent systems, methylene chloride, dimethyl sulfoxide, and tetrahydrofuran (Tables II and III). Hammett relationships were obtained for the reaction in these three solvents using van Bekkum's σ n values[18] (Figure 2). These Hammett relationships had similar ρ values and gave good correlation coefficients (Table IV). The magnitudes (0.294–0.440) of these ρ values compared favorably with the ρ value of −0.685 found for the reaction of 1-(substituted phenyl)-1,3-butadienes with maleic anhydride in dioxane.[16] These small ρ values preclude the possibility of a zwitterion intermediate[15] and support a transition state with small ionic character.

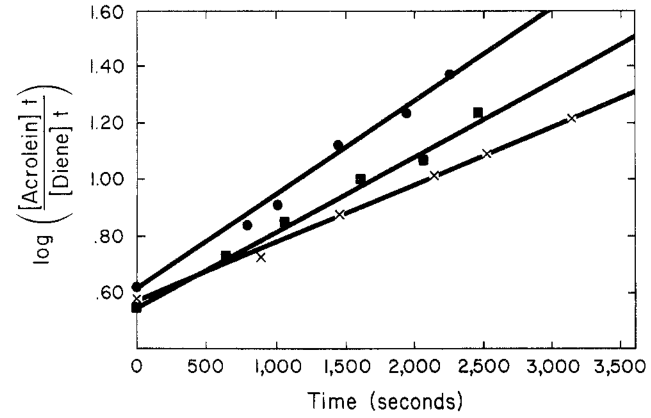


Figure 1. Diels–Alder reaction of 1-(substituted phenyl)-3,4-dimethylenepyrrolidines with acrolein in methylene chloride: (●) *p*-Cl; (X) *p*-$N(CH_3)_2$; (■) *m*-OCH_3.

Homoconjugative Effects on Diene Frontier Orbitals

It has been shown[5–10] that the chemical reactivity can often be predicted from the frontier orbital energies of the diene and dienophile in the Diels–Alder reaction. Consequently, this approach was used to investigate this novel

Table III
Rate Constants for the Diels–Alder Reaction of 1-(Substituted phenyl)-3,4-dimethylenepyrrolidines with Acrolein in Tetrahydrofuran at 35°

Substituent	Registry no.	Solvent	Rate constant,[a] M^{-1} min^{-1}, $10^2 k$	Concn, M		10^2 SD	Rel rate
				Diene	Acrolein		
p-Cl		THF	1.25	0.338	1.24	0.02	1.33[b]
H		THF	1.06	0.333	1.28	0.03	1.13[b]
p-OCH$_3$		THF	0.941	0.378	1.13	0.04	1.00[b]
p-N$^+$(CH$_3$)$_3$	53352-46-8	DMSO	9.08	0.136	0.435	0.13	2.02[c]
H		DMSO	6.03	0.1795	0.551	0.11	1.34[c]
p-OCH$_3$		DMSO	4.50	0.0591	0.133	0.13	1.00[c]

[a] Average of three kinetic runs. [b] Relative rates in THF. [c] Relative rates in DMSO.

substituent effect on the diene reactivity in the Diels–Alder reaction between 1-(substituted phenyl)-3,4-dimethylenepyrrolidines and acrolein.

Since the experimental HOMO and LUMO energies are not available for the dienes in this study, INDO calculations were used to obtain relative frontier orbital energies.[19] The INDO calculations[20,21] predict an occupied frontier orbital arrangement in which the highest occupied molecular orbital (HOMO-1) of the 1-(substituted phenyl)-3,4-dimethylenepyrrolidines has mostly aniline character and the highest occupied molecular orbital with mostly diene character (HOMO-2) is of lower energy than HOMO-1 (Table V). They also predict an unoccupied frontier orbital arrangement in which the lowest unoccupied molecular orbital (LUMO-2) has mostly diene character and the lowest unoccupied molecular orbital with mostly aniline character (LUMO-1) is of higher energy than LUMO-2 (Table V).[22]

The INDO calculations yielded a trend in the frontier orbital energies of the dienes in which the orbital energies situated mostly on the aniline portion of the molecule (HOMO-1) were lowered by electron-withdrawing substituents and raised by electron-donating substituents. The effect of the aniline substituents on the HOMO-2 and LUMO-2 energies of the diene was not large enough to be seen with the INDO calculations (Table V). This is not surprising when one considers the distance between the substituent and the diene portion of the molecule.

In determining the diene reactivity, however, the energies of HOMO-2 and LUMO-2 are more important than the energies of HOMO-1 and LUMO-1 since they represent the orbitals of the diene portion of the molecule that are directly involved in the Diels–Alder reaction. Consequently, the relative trends in the frontier orbital energies of the diene portion of the molecule were determined by a perturbation molecular orbital treatment of the 1-(substituted phenyl)-3,4-dimethylenepyrrolidines. In this treatment[23] the relative energies of the frontier molecular orbitals of the 1-phenyl-3,4-dimethylenepyrrolidine were determined from an orbital interaction diagram of the frontier orbitals of aniline and cisoid 1,3-butadiene. A similar approach has been used by Simmons and Fukunaga[1] and Hoffmann, *et al.*,[2] to predict the electronic spectra and chemical reactivity of spirarenes. The orbital interaction diagram of the frontier orbitals for aniline and cisoid 1,3-butadiene was constructed from the molecular orbitals determined by INDO calculations and experimental HOMO and LUMO energies.

Table IV
Hammett Relationship of the Diels–Alder Reaction of 1-(Substituted phenyl)-3,4-dimethylenepyrrolidines with Acrolein

Solvent	ρ value	Intercept	Corr coeff	No. of points
Methylene chloride	0.440	−0.00068	0.983	7
Dimethyl sulfoxide	0.294	−0.050	0.951	3
Tetrahydrofuran	0.344	−0.0081	0.993	3

It is apparent from the orbital interaction diagram for aniline and 1,3-butadiene (Figure 3) that the interaction between the HOMO of aniline and the LUMO of the diene is the strongest. Since electron-withdrawing groups lower the HOMO energy of aniline, they will cause a weakening of the HOMO aniline–LUMO diene interaction and the resulting LUMO-2 of the 1-(substituted phenyl)-3,4-dimethylenepyrrolidines will be of lower energy than the LUMO-2 of 1-phenyl-3,4-dimethylenepyrrolidine. By similar analysis, electron-donating substituents on aniline will increase the energy of the LUMO-2 of the 1-(substituted phenyl)-3,4-dimethylenepyrrolidines relative to the unsubstituted case. The effect of the aniline group on the HOMO energy of the diene was neglected because of the large energy separation between the HOMO-2 of the diene and the LUMO-1 of the aniline.

Table V
Orbital Energies (au) of 1-(Substituted phenyl)-3,4-dimethylenepyrrolidines from INDO Calculations

Substituent	Registry no.	HOMO-2[a]	HOMO-1[b]	LUMO-1[c]	LUMO-2[d]
p-COOH	53352-47-9	−0.452	−0.373	0.124	0.113
m-OCH$_3$		−0.446	−0.358	0.173	0.126
H		−0.445	−0.355	0.171	0.126
m-CH$_3$		−0.444	−0.355	0.162	0.126
p-OCH$_3$		−0.446	−0.347	0.169	0.125
p-NHCH$_3$	53352-48-0	−0.443	−0.320	0.170	0.127

[a] Highest occupied molecular orbital with mostly diene character. [b] Highest occupied molecular orbital with mostly aniline character. [c] Lowest occupied molecular orbital with mostly aniline character. [d] Lowest occupied molecular orbital with mostly diene character.

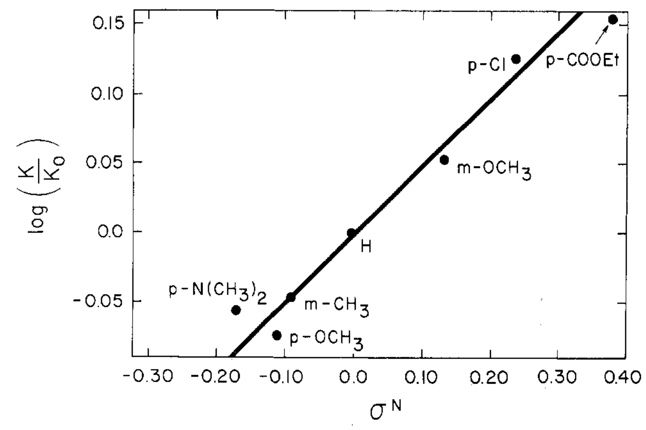


Figure 2. Hammett relationship for the Diels–Alder reaction of 1-(substituted phenyl)-3,4-dimethylenepyrrolidines and acrolein in methylene chloride.

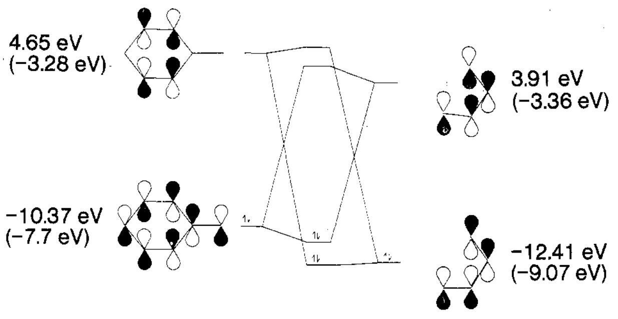


Figure 3. Orbital interaction diagram for INDO molecular orbitals of aniline and cisoid 1,3-butadiene (experimentally determined orbital energies are given in parentheses).

Frontier orbital theory predicts that the rate of the Diels–Alder reaction should increase as the energy difference between the frontier orbitals of the diene and dienophile decreases. Since electron-withdrawing substituents on the aniline cause a decrease in the energy of the aniline HOMO, these groups through homoconjugation of aniline and the diene portions of the molecule decrease the energy of the LUMO-2 relative to the 1-phenyl-3,4-dimethylenepyrrolidine case. Consequently, this decrease in LUMO-2 of the diene causes a stronger orbital interaction to take place between the HOMO of acrolein and the LUMO-2 of the diene, thus increasing the rate of Diels–Alder reaction. By similar analysis, electron donating on the aniline would decrease the rate of reaction relative to 1-phenyl-3,4-dimethylenepyrrolidine. This theoretical prediction is in direct agreement with the experimentally observed substituent effect.

Conclusion

In all prior frontier orbital studies of substituent effects on the diene reactivity of a normal electron demand Diels–Alder reaction, the effect of the substituents has been investigated through the HOMO energies (electron-donating groups increasing the rate and electron-withdrawing groups decreasing the rate). Sustmann[24] has indicated that the interaction between LUMO dienophile and HOMO diene is the dominant frontier orbital interaction and that the interaction between LUMO diene and HOMO dienophile can be neglected in determining the diene reactivity in such a Diels–Alder reaction. In this study, the unique substituent effect on the diene reactivity is caused by altering the LUMO energies of the diene through homoconjugation in contrast to Sustmann's suggestions.[24] Consequently, substituents which affect the energy of LUMO diene can have an important effect on the rate of a normal electron demand Diels–Alder reaction.

Experimental Section

Materials and Apparatus. A water bath was maintained at ±0.01° by means of a Haake E-51 temperature controller. All kinetic measurements were made on a Varian A-60 spectrometer. The accuracy of the nmr integrations was ±2.0% for the Varian A-60 and ±5.0% for the Perkin-Elmer R-24. Certified ACS dimethyl sulfoxide and tetrahydrofuran obtained from Fisher Scientific Co. were used without further purification. The methylene chloride (bp 40° (760 mm)) and acrolein (bp 52.5° (760 mm)) were distilled directly before use. All 1-(substituted phenyl)-3,4-dimethylenepyrrolidines were prepared according to the procedure reported.[14] These dienes were recrystallized in ether–petroleum ether and sublimed immediately before use. A 1-ml glass luer tip tuberculin syringe made by Becton-Dickinson was used for the measurement of solvent volumes. The accuracy of this syringe was determined to be ±0.01 ml with H_2O. Weighings were carried out on an analytical balance with an accuracy of ±0.0001 g.

Kinetic Procedure. Two different experimental procedures were used depending on the solubility of the diene.

Procedure I. An appropriate amount of the diene was weighed in a nmr tube. This nmr tube was placed, along with an air-tight vessel containing a quantitative amount of acrolein in the reaction solvent, into the constant temperature water bath and allowed to equilibrate. The bath was maintained at the nmr probe temperature. The nmr probe temperature was monitored by the use of a methanol solution. The variation found in the probe temperature was less than ±0.3°. An appropriate amount of the preheated reaction solvent (measured with a 1.0-ml syringe) was then added to the nmr tube and a timer was started. Solvation time was between 30 and 60 sec and was taken into account by subtracting one-half of the magnitude of the solvation time from the actual time the reaction was started. However, neglecting this, solvation time had no effect on the observed rate constant. During the solvation of the diene, the nmr tube was kept in the water bath, after which time it was placed directly into the nmr probe. The rate of this Diels–Alder reaction was determined by the integration of the appropriate nmr signals. Four or five integrations were taken at each time and the average value used. Usually six or seven determinations were made during each kinetic run and the reaction was followed to 70–80% completion. The volume of the reaction solution was determined by calibration of the nmr tubes. The length of the nmr tubes was calibrated with known volumes of solvent. This method was found to have an accuracy of ±1%.

Procedure II. This procedure was used for dienes whose solvation time was large enough to affect the rate constant. In this case the appropriate amount of acrolein was placed in an air-tight 10-ml volumetric flask and the appropriate amount of the diene dissolved in the reaction solution in a second air-tight 10-ml volumetric flask. The two separate solutions were brought to the reaction temperature and then mixed together. Three nmr tubes were filled with the reaction mixture and the reaction was followed by integration of the appropriate nmr peaks.

Method of Calculations. It is well known[27] that the area of an nmr absorption is proportional to the nuclei contributing to it. Thus, the area of the aldehyde peak of acrolein is proportional to the amount of acrolein present and the area of the aldehyde peak of the Diels–Alder adduct is proportional to the amount of adduct present. Using this rationale the amounts (moles) of reactants and adduct present in the reaction mixture at any given time were determined as follows.

Case I. The rate of reaction was determined by the change in chemical shift of the aldehyde proton. Let the moles of acrolein at any given time (t) be M_A. Let the initial moles of acrolein $(t = 0)$ be M_{A0}. Let the area of aldehyde proton absorption of acrolein be A_A. Let the area of aldehyde proton absorption of Diels–Alder adduct be A_P. Then:

$$\frac{M_A}{M_{A0}} = \frac{A_A}{A_P + A_A}$$

$$M_A = M_{A0}\,\frac{A_A}{A_P + A_A} \qquad (1)$$

From the stoichiometry of the chemical reaction it can be seen that for every mole of acrolein reacted a corresponding mole of the diene must react. Let M_{D} equal the moles of diene at any given time (t). Let the initial moles of diene ($t = 0$) be $M_{\mathrm{D}0}$. Therefore:

$$M_{\mathrm{D}} = M_{\mathrm{D}0} - (M_{\mathrm{A}0} - M_{\mathrm{A}}) \tag{2}$$

Case II. The rate of reaction was determined by the disappearance of the vinyl proton absorption (δ 5.55) of the diene. Let A_{DV} be the area of vinyl proton absorption of the diene (2 H). Let A_{AP} be the area of aldehyde proton absorptions of acrolein and Diels–Alder product (1 H). Then:

$$\frac{M_{\mathrm{D}}}{M_{\mathrm{D}0}} = \frac{A_{\mathrm{DV}}}{2A_{\mathrm{AP}}}\frac{M_{\mathrm{A}0}}{M_{\mathrm{D}0}}$$

$$M_{\mathrm{D}} = M_{\mathrm{D}0}\left(\frac{A_{\mathrm{DV}}}{2A_{\mathrm{AP}}}\frac{M_{\mathrm{A}0}}{M_{\mathrm{D}0}}\right) \tag{3}$$

$$M_{\mathrm{D}} = \frac{A_{\mathrm{DV}}}{2A_{\mathrm{AP}}}M_{\mathrm{A}0}$$

Therefore:

$$M_{\mathrm{A}} = M_{\mathrm{A}0}(M_{\mathrm{D}0} - M_{\mathrm{D}}) \tag{4}$$

Since the Diels–Alder reaction was carried out under constant volume conditions, the molar concentration ratios of the second-order rate equation are equal to their mole ratios (eq 5–9). Thus,

$$\log\frac{[M_{\mathrm{D}0}]_{t=0}[M_{\mathrm{A}}]_t}{[M_{\mathrm{A}0}]_{t=0}[M_{\mathrm{D}}]_t} = \frac{([M_{\mathrm{A}0}]_{t=0} - [M_{\mathrm{D}0}]_{t=0})^{kt}}{2.303} \tag{5}$$

$$\frac{[M_{\mathrm{D}0}]_{t=0}}{[M_{\mathrm{A}0}]_{t=0}} = \frac{M_{\mathrm{D}0}}{M_{\mathrm{A}0}} \tag{6}$$

$$\frac{[M_{\mathrm{A}}]_t}{[M_{\mathrm{D}}]_t} = \frac{M_{\mathrm{A}}}{M_{\mathrm{D}}} \tag{7}$$

$$\log\frac{M_{\mathrm{D}0}M_{\mathrm{A}}}{M_{\mathrm{A}0}M_0} = \frac{([M_{\mathrm{A}0}]_{t=0} - [M_{\mathrm{D}0}]_{t=0})^{kt}}{2.303} \tag{8}$$

$$\log\frac{M_{\mathrm{A}}}{M_{\mathrm{D}}} = \frac{([M_{\mathrm{A}0}]_{t=0} - [M_{\mathrm{D}0}]_{t=0})^{kt}}{2.303} + \log\frac{M_{\mathrm{A}0}}{M_{\mathrm{D}0}} \tag{9}$$

integration of the appropriate nmr signals during the course of this Diels–Alder reaction allows one to determine the corresponding rate constant. The rate constant was determined from the rate equation (9) by plotting log $M_{\mathrm{A}}/M_{\mathrm{D}}$ *vs.* time. The slope of this line which is equal to

$$\frac{([M_{\mathrm{A}0}]_{t=0} - [M_{\mathrm{D}0}]_{t=0})^{k}}{2.303}$$

was determined by a least-squares regression analysis.[28]

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Registry No.—Acrolein, 107-02-8.

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