Diels–Alder Reactions between *trans*-1-*N*-Acylamino-1,3-dienes and Methyl Acrylate. A Correlation between Diene Photoelectron Ionization Potentials and Reactivity, Stereoselectivity, and Regioselectivity

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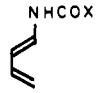
Abstract: A quantitative study of the Diels–Alder reaction of a series of *trans*-*N*-acylamino-1,3-butadienes (**1**) and methyl acrylate is reported. The effect of the dienamide acyl substituent X on the rate, regioselectivity, and stereoselectivity of the cycloaddition reaction was determined. The photoelectron spectra of this series of dienes is also reported and analyzed. The relationship between these ionization potentials and theoretical Diels–Alder reactivities and stereoselectivities is summarized, and these theoretical estimates are compared with the experimental results.

The Diels–Alder reaction is one of the best known and most useful organic reactions.[2] It provides the synthetic chemist with one of his most powerful tools for constructing six-membered rings, and has a singular capability of establishing a large number of stereochemical centers in one synthetic step. Although the reaction has been successfully employed by chemists for decades, it is only within the last few years that a fundamental understanding of the reactivity, stereoselectivity, and regioselectivity phenomena of the Diels–Alder reaction has begun to emerge.[3,4] Frontier molecular orbital theory, in particular when combined with quantitative experimental data about unsaturated systems, has proven notably successful in this regard.[3]

A variety of 1,3-dienes with *N*-acylamino substitution at either the 1 or the 2 position are available as a result of recent investigations in our laboratory.[5] These dienes are useful synthetic intermediates, and their application to solve stereochemical problems in the area of alkaloid total synthesis has been reported.[6] In the parent 1,3-butadiene series, for example, *trans*-1-*N*-acylamino substituted 1,3-butadienes (**1**) (**a**, X =



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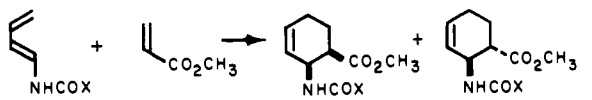
CCl_3; **b**, X = OCH_2CH_3; **c**, X = OC_6H_5; **d**, X = SC_6H_5; **e**, X = $N(CH_2)_4$) are available with a variety of acyl substituents, X.[5] The acyl substituent of **1**, although spatially removed from the diene framework, should directly affect the electronic nature of the diene π system. As a result, these dienes provide a unique opportunity to experimentally examine current ideas about substituent effects in the Diels–Alder reaction in a system in which the substituent is fairly remote and steric effects should thus be at a minimum.

In this paper we wish to report photoelectron spectra of the series of dienes **1**, to show how the ionization potentials are related to theoretical reactivities and selectivities, and to compare these data with quantitative measurements of the reactivity, stereoselectivity, and regioselectivity of the Diels–Alder reaction between dienes **1** and methyl acrylate.

Results and Discussion

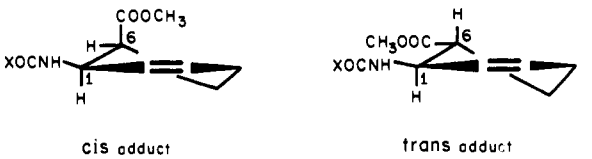
Diels–Alder Reaction. The *trans*-1-*N*-acylamino-1,3-butadienes (**1**) cleanly undergo cycloaddition with methyl acrylate at 110 °C in dioxane to afford, in high yields (64–90%), a mixture of stereoisomeric "ortho" adducts **2** and **3**. In all



1 2 3

a, X = CCl_3
b, X = OCH_2CH_3
c, X = OC_6H_5
d, X = SC_6H_5
e, X = $N(CH_2)_4$

cases the "ortho" regioselectivity was >98%. Careful high pressure liquid chromatographic (HPLC) analysis of the crude reaction mixtures (after filtration through silica gel to remove polymerized diene) failed to detect any products other than **2b** and **3b** formed from diene **1b**, and revealed only traces (<2%) of additional components from cycloaddition of the other dienes. The lowest yield (64%) was obtained with diene **1d**, and this is attributed to the sensitive nature of this material, as was evidenced by the formation of thiophenol as a by-product. The stereoisomeric adducts **2a–d** and **3a–d** were separated by preparative HPLC, and their structural assignments rest on ^1H and ^{13}C NMR data (Table I). The NHCOX substituent is primarily pseudoequatorial in each stereoisomer since the absorption for the C_1 hydrogen is nearly identical for each stereoisomeric pair. This hydrogen, observed as a broad multiplet ($W_{1/2} \sim 20$ Hz) centered at ca. δ 4.6, was not clearly resolved even at 220 MHz.[7] The pseudoequatorial C-6 methine hydrogen of the cis stereoisomer was observed as an



cis adduct trans adduct

unsymmetrical four-line absorption (outer line separation 15–20 Hz) at ca. δ 2.8, and occurred 0.25–0.4 ppm further downfield than the broader, pseudoaxial, C-6 hydrogen absorption of the corresponding trans stereoisomer. This expected[8] downfield shift of the pseudoequatorial C-6 hydrogen of the cis isomer has been observed in other 1,6-disubstituted 2-cyclohexenes.[8b] These structural assignments are confirmed by the ^{13}C NMR spectra. For each isomeric pair the absorptions for C-1 and -6 occur at higher field for the cis adduct. This

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Table I. ^1H and ^{13}C NMR Data for Diels-Alder Adducts **2** and **3**[a]

Compd	^1H NMR[b] C_6H	^1H NMR[b] C_1H	^{13}C NMR[c] C_1	C_2	C_3	C_4	C_5	C_6	$COOCH_3$	NHCOX	Other
2a[d]	2.98 (app q, J = 5)	4.77 ($W_{1/2}$ = 20)	47.3	(130.8	125.7)	(22.4	22.9)	42.3	173.5	52.0	161.4	92.8
3a[d]	2.69 (app q, ols = 22)	4.74 ($W_{1/2}$ = 20)	49.5	(131.2 | 125.4)	(23.6)		44.9	173.5	52.2	161.4	92.6
2b[e]	2.83 (app q, ols = 17)	4.57 ($W_{1/2}$ = 20)	46.6	(129.2 | 127.0)	21.3	23.3	43.4	173.3	51.2	155.7	14.3, 60.5
3b[e]	2.57 (app q, ols = 21)	4.55 (overlaps NH)	49.0	(129.4	127.7)	(23.8	23.6)	46.1	174.1	51.8	154.3	14.6, 60.9
2c[e]	2.90 (app q, ols = 17)	4.57 ($W_{1/2}$ = 18)	47.2	(126.8 | 125.3)	21.7	23.5	43.5	173.8	51.8	154.1	121.6, 129.3 130.1, 151.3
3c[e]	2.50 (m, ols = 28)	4.43 ($W_{1/2}$ = 20)	49.3	(127.0	125.4)	(23.6	23.7)	46.0	174.0	52.0	153.9	121.6, 129.3 130.0, 151.2
2d[f]	2.72 (app q, ols = 17)	4.63 ($W_{1/2}$ = 20)	46.9	(129.7 | 126.5)	22.0	23.1	43.1	173.6	51.9	165.9	129.5, 130.2 135.5

[a] In $CDCl_3$; chemical shifts are given in parts per million from internal Me_4Si (δ). Apparent peak multiplicites: quartet (q), multiplet (m). [b] Apparent couplings (J), peak widths at half-height ($W_{1/2}$), and multiplet outer line separations (ols) are all in hertz. [c] Assignments are based on the multiplicities exhibited in the off-resonance decoupled spectrum, and on the basis of chemical shifts calculated using additivity relationships. [d] ^1H NMR at 220 MHz. [e] ^1H NMR at 90 MHz. [f] ^1H NMR at 60 MHz.

Table II. The Diels-Alder Reaction of *trans-N*-Acylamino-1,3-butadienes and *trans*-2,4-Pentadienoic Acid with Methyl Acrylate[a]

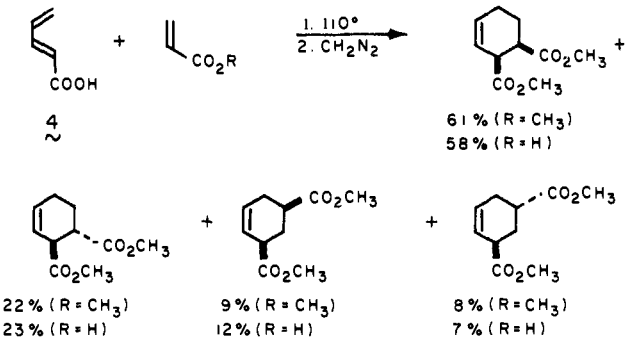
Diene	Regioselectivity, % ortho adducts	Stereoselectivity[b] % endo-**2**	% exo-**3**	Rate constants, $10^5 \times k$, L/mol s s^{-1}
1a (X = CCl_3)	>98	76.9	23.3	6.31 ± 0.19
1b (X = OC-H_2CH_3)	>99	81.0 (at 25 °C, 87.0:13.0)	19.0	13.7 ± 0.5
1c (X = OC_6H_5)	>98	81.1	18.9	16.9 ± 1.0
1d (X = SC_6H_5)	>98	82.3	17.9	*c*
1e (X = N-$(CH_2)_4$)	*c*	78[d]	22[d]	23.7 ± 1.2
4	83	74	26	2.37 ± 0.10

[a] In dioxane at 110 °C. [b] HPLC analysis. The standard deviation from the mean varied from 0.3 to 0.4%. For the formation of ortho adducts. [c] Not determined. See Experimental Section. [d] By ^{13}C NMR analysis, estimated error ±5%. See Experimental Section.

is the expected result since it is well established that an equatorial carbomethoxy substituent deshields the α and β carbons more than an axial one.[9] Our efforts to separate adducts **2e** and **3e** proved unsuccessful; however, the ^1H and ^{13}C NMR spectra of the isomer mixture (see Experimental Section) were informative enough to allow structural assignments.

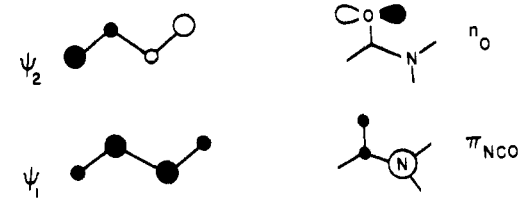
Kinetic stereoselectivities and second-order rate constants for the reaction of acylaminobutadienes **1** and methyl acrylate at 110 °C are summarized in Table II. The reported isomer ratios for dienes **1a–d** are the average of six-fifteen HPLC determinations. They correspond to kinetic stereoselectivities since they were essentially time invariant and different from the thermodynamic isomer compositions. The isomer ratios reported for diene **1e** were obtained from the crude reaction mixture by ^{13}C NMR, and are considerably less accurate than the others in this study.

The high regioselectivity observed in the reaction of acylaminobutadienes **1** and methyl acrylate stands in marked contrast to the isomer ratios (±2%) obtained, under identical conditions, with *trans*-2,4-pentadienoic acid (**4**). In the latter case, careful HPLC analysis indicated that all four possible isomers were produced. Structural assignments were achieved, after hydrogenation, by comparison with authentic samples of the appropriate dicarbomethoxycyclohexanes (see Experimental Section). The considerably lower regioselectivity observed with *trans*-2,4-pentadienoic acid is anticipated (vide supra), but contrasts with earlier reports of the reaction of this diene with acrylic acid.[10]



Photoelectron Spectra. To facilitate the analysis of the spectra of the substituted dienes, and especially to allow conclusive assignments of the diene π-orbital ionization potentials (IPs), the photoelectron spectra of the dienes and of the corresponding substituted amides were measured. The photoelectron spectra of *cis*-**1a**, *trans*-**1b**, **1c** and **1e**, and the corresponding amides are shown in Figures 1 and 2. The *cis*-trichloroacetamide was used, since the corresponding trans compound decomposed at temperatures required for volatilization. Ionization potentials for the phenylthiodiene, **1d**, are reported later, but decomposition upon volatilization prevented the obtention of a high-resolution spectrum. The vertical IPs, taken as band maxima, of all of the compounds studied here are tabulated graphically in Figure 3. This figure also shows the assignments which could be made by comparison with IPs of simpler molecules.

The first and third IPs of butadiene are 9.06 and 12.23 eV, assigned to ionizations from orbitals ψ_2 and ψ_1, respectively.[11,12] The lowest IPs of all the dienes studied here are lower than those of butadiene, indicating that the amido substituents raise the energy of ψ_2, lowering the IP. This is especially apparent upon comparison of the spectra of the model amides with those of the corresponding dienes.



Simple amides, such as formamide, have two low energy ionizations, one due to the carbonyl lone pair, n_O, and the other due to the highest "π" orbital,[13,14] π_{NCO}, which is the antibonding combination of the amine lone-pair orbital and the carbonyl π orbital. In formamide, these orbitals give rise to

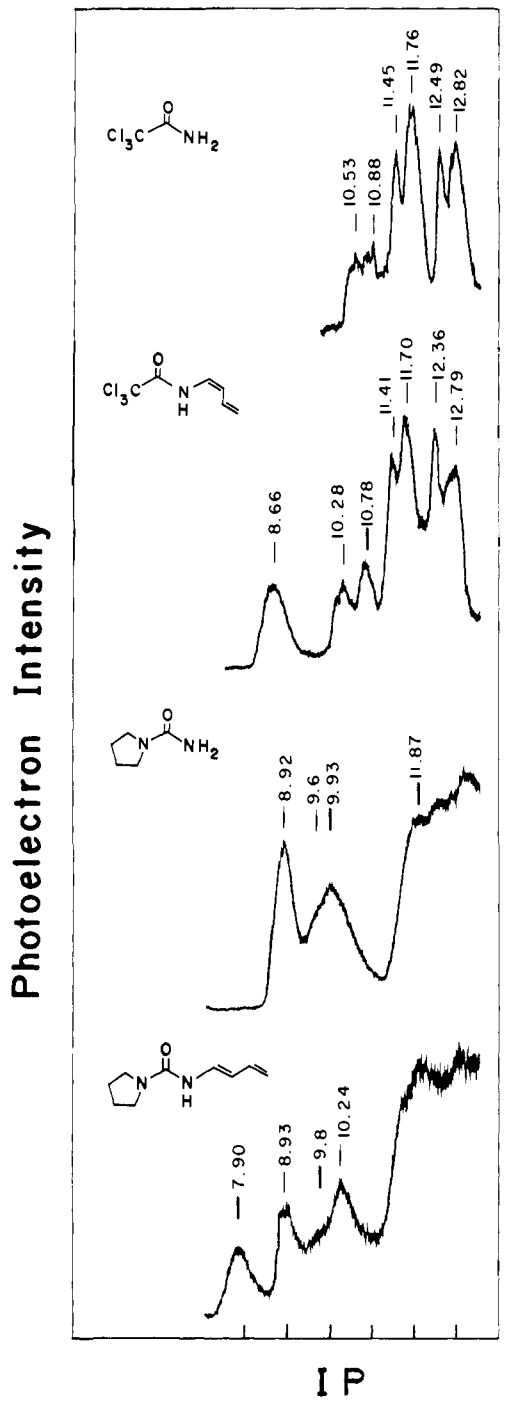


Figure 1. Photoelectron spectra of *cis*-diene trichloroacetamide *cis*-**1a**, dieneurea **1e**, trichloroacetamide, and *N,N*-tetramethyleneurea.

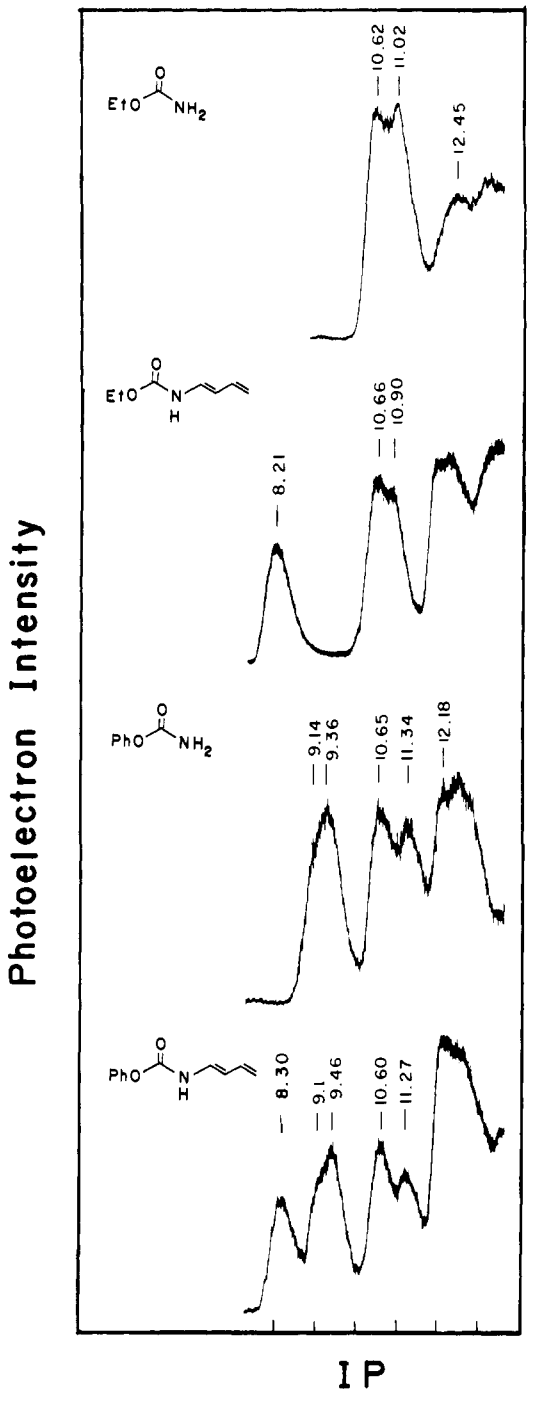


Figure 2. Photoelectron spectra of diene carbamates **1b** and **1c**, ethyl carbamate, and phenyl carbamate.

closely spaced IPs at 10.32 and 10.52 eV, respectively.[15] In all of the amides studied here, these two ionization bands are not well resolved and it is impossible to definitively distinguish between them. The n_0 and π_{NCO} assignments in the amides should, therefore, be considered tentative.

In the trichloroacetamide spectrum, there are two closely spaced IPs at 10.53 and 10.88 eV, which are assigned to the π_{NCO} and n_0 IPs, or vice versa. The trichloromethyl group slightly raises the amide IPs compared with those in formamide. The higher IPs of trichloroacetamide (11.45, 11.76, 12.49, and 12.82 eV) correspond closely to the six chlorine lone-pair ionizations in chloroform, which appear at 11.48, 11.91, 12.01, and 12.85.[16a] The assignments of the chloroform ionizations are in some doubt, but are generally assigned, in various orders, to the a_2, a_1, e′, and e″ orbitals formed by interaction of the six chlorine lone pairs. The C_{3v} symmetry of chloroform is reduced to C_s in trichloroacetamide, but the shapes and positions of the bands change little from those in chloroform. The second and fourth bands in this group appear to contain nearly degenerate ionizations. The patterns correspond to the assignments made by Dixon et al. or Kimura et al. for chloroform.[16b,c]

In *cis*-**1a**, the chlorine lone-pair IPs are nearly unaffected, while the 10.28- and 10.78-eV IPs are 0.25 and 0.10 eV lower than those of trichloroacetamide. Since the 10.28-eV IP is broader than that at 10.78 eV, and since the *N*-butadienyl substituent is expected to influence the π_{NCO} orbital more than the n_0,[15,17] the lower IP is assigned to the π_{NCO} orbital. The lowest IP of *cis*-**1a**, at 8.66 eV, must arise from the butadiene ψ_2 orbital, destabilized by mixing with the lower energy π_{NCO} orbital. The broadness of the first band indicates that this orbital has taken on appreciable nitrogen lone-pair character,

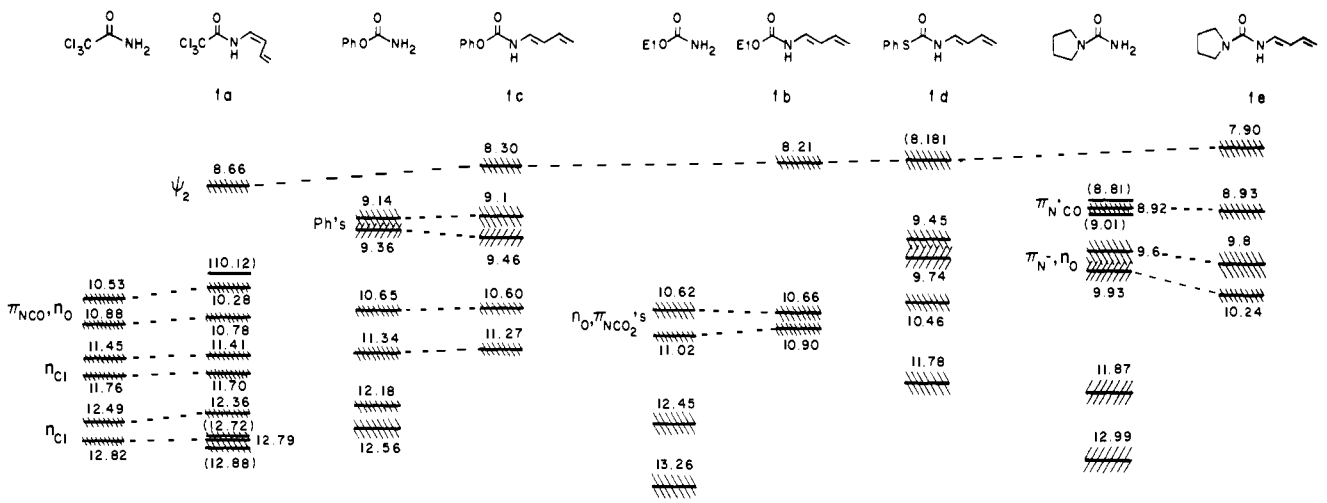
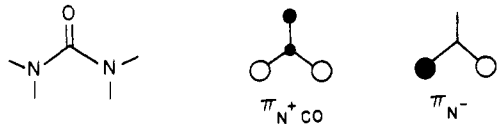


Figure 3. Vertical ionization potentials and assignments.

as has been observed in simpler enamines.[18] The second diene-like π orbital, which appears at 11.5 eV, is obscured by the chlorine lone-pairs IPs, but may be in the 12-12.2-eV region, which has a much shallower minimum than is observed in the trichloroacetamide spectrum.

The trichloroacetamide group acts as a moderately good π donor, but is appreciably weaker than an alkylamino group. Thus, 1-diethylaminobutadiene has IPs of 6.95, 9.38, and 10.83 eV. The first two IPs correspond to ionizations from the antibonding and bonding combinations, respectively, of ψ_2 of butadiene with the nitrogen lone pair.

The photoelectron (pe) spectrum of *N,N*-tetramethyleneurea, shown in Figure 1, is considerably more complex and less resolved than that of the acetamide. Urea has three ionizations which fall in a broad, asymmetrical band in the region 9.7-11 eV (band maximum 10.2 eV),[19] owing to n_0 and two π orbitals, $\pi_N + _{CO}$, and π_N-, represented as shown. These are



the symmetric combination of nitrogen lone pairs combined with the π_{CO} and the antisymmetric combination of nitrogen lone pairs, respectively. In *N,N*-tetramethyleneurea, the nitrogen lone pairs are no longer the same in energy, so that the shapes of these orbitals will be appreciably distorted. For example, pyrrolidine has a lone pair IP of 8.77 eV,[20] while ammonia has an IP of 10.84 eV.[21] Thus, the first band of *N,N*-tetramethyleneurea at 8.92 eV, which has typical amine lone-pair vibrational spacings of ~800 cm^{-1},[21] is expected to be rather heavily concentrated on the dialkylated nitrogen, and the broad band centered at 9.93 eV includes two bands due to n_0 and π_{NCO} ionizations.

In the corresponding diene, **1e,** the basic shape of the urea spectrum is retained with only small shifts, while the diene HOMO IP appears at 7.90 eV, lowered by ~1.2 eV from its value in butadiene. The strong donor ability of the pyrrolidine moiety is transmitted relatively efficiently through the acetamide moiety.

The spectra of the carbamates studied here are shown in Figure 2. Ethyl carbamate should have three ionizations in the 10.5-11-eV region, due to the carbonyl lone pair, n_0, and two π orbitals corresponding very roughly to those of the urea. The higher energy π orbital will be somewhat more heavily concentrated on nitrogen than oxygen (compare the IPs of ammonia, 10.16 eV,[21] and ethanol, 10.65 eV[22]). As observed in the dienes discussed already, the ethyl butadienecarbamate, **1b,** has only a slightly changed region around 10.5-11 eV, and a well-separated butadiene HOMO band at 8.21 eV. Once again, this band is relatively broad, indicating appreciable nitrogen lone-pair character, and it has been shifted by 0.85 eV to lower IP than its position in butadiene. In this diene, there is a large increase in the intensity of the 12-eV region, the position expected for the diene π band.

Phenyl carbamate has, in addition to orbitals similar to those of ethyl carbamate, two high-lying aromatic orbitals similar to those at 8.56 and 9.28 eV in phenol.[23] These orbitals are, of course, those related to the degenerate HOMOs of benzene, which appear at 9.24 eV. In phenyl carbamate, these orbitals give rise to the IPs at 9.14 (sh) and 9.36 eV. The fact that these IPs are only slightly lower, and higher, respectively, than those of benzene indicate that the carbamate group is nearly electroneutral. It lowers the IP of the b_1 orbital of benzene by conjugative electron donation, but raises the IP of the a_2 orbital by inductive electron withdrawal. In the phenyl-*N*-butadiene carbamate, **1c,** small changes in the aryl carbamate IPs are observed, and the butadiene HOMO has an IP of 8.30 eV, slightly higher than that of the ethyl analogue.

Finally, the spectrum of the thiophenoxy diene, **1d,** not reproduced here, was of poor quality because of apparent decomposition upon heating at 90 °C to achieve volatilization. A relatively broad band at 8.18 eV in the spectrum of **1d** is assigned to the butadiene π IP, in a position about the same as that of the carbamates. Additional IPs listed in Figure 3 can be assigned tentatively, but the positions of these IPs are less accurate than those of the other compounds in the study.

Relationships between Ionization Potentials and Reactivities. The relationships between ionization potentials and rates of Diels-Alder reactions have been discussed in detail in recent references.[3,4,24,25] In summary, if the major difference between the energies of two transition states is determined by the difference in mixing of the lowest energy charge-transfer configuration (D^+, A^-) into the ground configuration or, alternatively, of different extents of mixing of the donor HOMO with the acceptor LUMO, then the difference between the activation energy is

$$\Delta\Delta E = \frac{C}{IP_D - EA_A - Q} - \frac{C'}{IP_{D'} - EA_A - Q'}$$

where C is a term containing the matrix elements related to the overlap of the diene HOMO and the dienophile LUMO, the IPs are ionization potentials for two different donor dienes, D and D', and EA_A is the electron affinity of the dienophile, which is kept constant in the reactions studied here. Q is a term

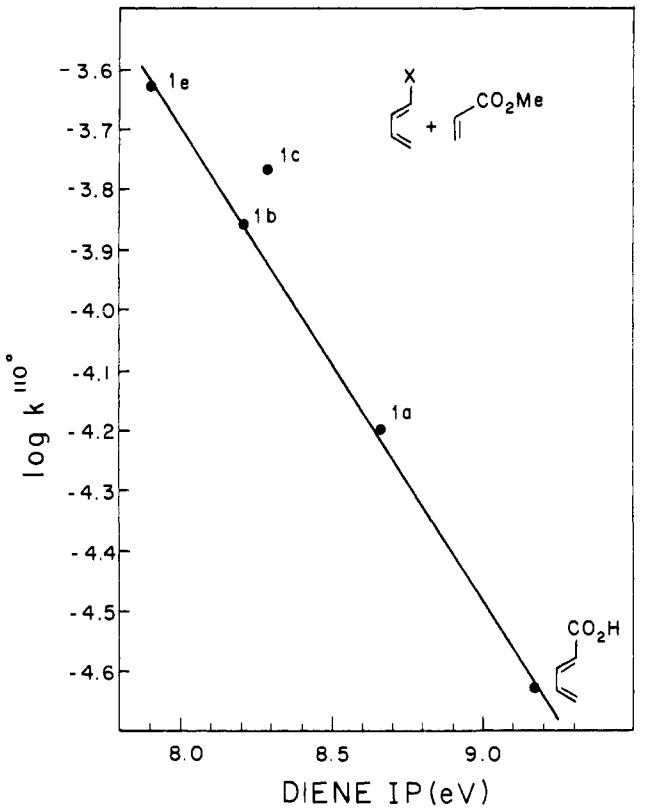


Figure 4. Plot of log k for Diels–Alder reactions of acylaminobutadienes and pentadienoic acid with methyl acrylate vs. the diene first ionization potential.

which includes changes in both IP and EA from their gas phase values to those hypothetical values in solution in the activated complex, as well as the electrostatic attraction of D^+ for A^- in the activated complex.

The numerators, C and C', are not constant, but are related to the IP, as has been shown earlier.[25] That is, in terms of orbitals,

$$C = \left(\sum_i C_D{}^i C_A{}^i \beta_{DA}{}^i\right)^2$$

where $C_D{}^i$ and $C_A{}^i$ are the orbital coefficients of the donor HOMO and acceptor LUMO at sites, i, of interaction in the transition state, and $\beta_{DA}{}^i$ is the resonance integral, which is related to the overlap between orbitals at the sites of interaction. The $C_A{}^i$ values are kept constant here, since a constant acceptor is used, and we have shown earlier that the differences between coefficients of two related π alkenes (or here, dienes) are related to differences in their IPs.[25] This results from the fact that the coefficient changes, which result from mixing of the butadiene HOMO with other butadiene MOs, is inversely related, in second-order perturbation theory,[26] to the difference between the diene HOMO and the donor orbital energies, while the change in HOMO energies is also inversely related to this energy difference.[25] Thus, the assumption that C is a constant can be relaxed to the assumption that C is linearly related to IP_D.

Thus, the equation for $\Delta\Delta E$ can be simplified as shown. If this equation is valid, then a plot of log k, which, of course, is proportional to ΔE_{act}, vs. $1/(IP_D - Q'')$, should be linear. Alternatively since Q'' cannot be measured (although it should have a value of approximately $EA_A - 4$ (± 1) eV),[24] $(\log k)^{-1}$ can be plotted vs. IP. It is more usual, and perhaps more straightforward, to plot IP vs. log k, and linear relationships are frequently observed. We have discussed in some detail the reasons that log k vs. IP plots may be more linear than plots of $(\log k)^{-1}$ vs. IP.[3a,24] It is worthy of note here that over a limited range of log k and IP, both of these plots may appear linear.

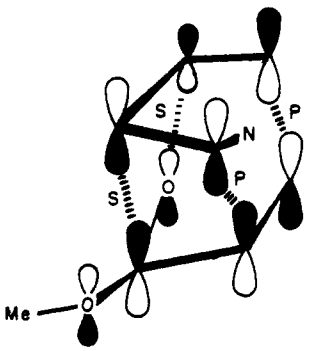


Figure 5. Secondary orbital interactions between the acylaminodienes HOMO and acrylate LUMO that can stabilize the endo Diels–Alder transition state.

Figure 4 shows a plot of the rates of reaction of four of the acylaminobutadienes and pentadienoic acid with methyl acrylate vs. the first IPs of the dienes.[27,28] There is excellent correspondence between the rates of these cycloadditions and the electron donor abilities of these dienes. Only **1b** and **1c** are out of order, and these molecules have both similar IPs and rates of reaction. For compounds with such similar IPs, minor differences in higher IPs, and of extra-frontier orbital interactions, may cause small differences in reactivity.

Although data are not available for the same conditions, the rates of reactions of several simple dienes with methyl acrylate have been measured. 2,3-Dimethyl-1,3-butadiene and cyclopentadiene react with methyl acrylate at 40 °C with rate constants of 1.8×10^{-7} and 5.3×10^{-5} L/mol s, respectively,[31] while *trans*-1-ethoxy-1,3-butadiene reacts with methyl acrylate at 65 °C with a rate constant of 4.8×10^{-6} L/mol s.[32] 2,3-Dimethylbutadiene has a first IP (8.62 eV)[33a] comparable with that of diene trichloroacetamide **1a** (8.66 eV), and these compounds probably react at similar rates at similar temperatures, while cyclopentadiene, with a similar IP (8.58 eV),[33b] is considerably more reactive, because of the constrained cisoid geometry. The first IP of 1-ethoxybutadiene is expected to be ~8.0 eV,[34] comparable to that of dieneurea **1e** (7.9 eV). A rate constant of 8×10^{-5} L/mol s may be estimated[35] for the reaction of 1-ethoxybutadiene with methyl acrylate at 110 °C, which is comparable to those of the acylaminobutadienes studied here.

Stereoselectivity and Regioselectivity. As shown in Table II, the endo stereoselectivity (formation of the cis adduct) of the reactions studied here increases slightly as the reaction rate increases or, approximately, as the IP of the diene decreases.[36] Increased selectivity with increased reactivity is a common feature of cycloadditions, and is readily rationalized using frontier orbital concepts.[3a,37] The endo stereoselectivity in Diels–Alder reactions has been attributed to attractive secondary orbital interactions.[38] These are shown schematically in Figure 5 for the systems of interest. According to the second-order perturbation treatment, considering only the diene donor HOMO and the dienophile acceptor LUMO, the difference between the stabilization energies of the exo and endo transition states is

$$\Delta\Delta E = \Delta E_{endo} - \Delta E_{exo} = \frac{\left(\sum_i^p C_D{}^i C_A{}^i \beta_{DA}{}^i + \sum_i^s C_D{}^i C_A{}^i \beta'_{DA}{}^i\right)^2}{IP_D - EA_A - Q} - \frac{\left(\sum_i^p C_D{}^i C_A{}^i \beta_{DA}{}^i\right)^2}{IP_D - EA_A - Q}$$

where the sum of the coefficient product terms is over primary interactions (p) and secondary interaction (s) for the endo adduct, but only over primary interactions for the exo adduct. Expanding this expression gives

$$\Delta\Delta E = \frac{2\sum_{i}^{p} C_D{}^i C_A{}^i \beta_{DA}{}^i \sum_{i}^{s} C_D{}^i C_A{}^i \beta'_{DA}{}^i + \left(\sum_{i}^{s} C_D{}^i C_A{}^i \beta'_{DA}{}^i\right)^2}{IP_D - EA_A - Q}$$

If, as before, we assume that the various coefficients in the series of dienes are constant, or linearly related to IPs then the following approximation can be made,

$$\Delta\Delta E = \frac{C}{IP_D - Q'}$$

since EA_A is a constant. Thus, as the IP of the diene decreases, the rate of the reaction increases and the endo stereoselectivity increases. However, this effect is relatively small over the series of compounds studied here, and is undoubtedly very sensitive to steric effects. Cyclopentadiene, with a similar IP, reacts somewhat less stereoselectively (70:30 endo/exo, 100 °C) with methyl acrylate.[39] We note that from the practical point of view the ability to conduct conveniently the cycloaddition of a reactive diene at low temperature may be the more important factor in achieving high endo stereoselectivities in practice (cf. Table II).

Finally, we note the high regioselectivities observed in the reaction of dienes **1**. We have shown elsewhere that the polarization of an alkene HOMO is proportional to the IP of the alkene.[25] In the present case, the relatively large destabilization of the butadiene HOMO by the acylamino group will be accompanied by relatively large coefficient changes. In terms of second-order perturbation theory, and considering only the diene HOMO and LUMO, the mechanism of HOMO polarization is shown in Figure 6.[40] The donor orbital causes the HOMO to mix in some of the LUMO in an antibonding fashion. In terms of sequential first-order perturbations, the donor mixes in the diene LUMO in a bonding fashion to give D′. When the diene HOMO mixes with D′ in an antibonding fashion, some of the LUMO "comes along" to increase HOMO coefficients at C-2 and C-4, and diminish those at C-1 and C-3. As the IP of the donor substituent orbital (several orbitals are involved for the substituents discussed in this paper) decreases, the extent of HOMO raising and of enlargement of the coefficient at C-4 (relative to C-1) increases. In the series of dienes studied here, the donor raises and polarizes the HOMO sufficiently, so that >98% of the ortho isomer is formed in every case, the result of greater stabilization of the transition state where C-4 of the diene, the site of largest HOMO coefficient, becomes united with the terminal vinyl carbon of methyl acrylate, the site of largest LUMO coefficient. Dienes substituted by weaker electron-donating groups generally give 90–95% of the ortho isomer at best.[2]

The case of pentadienoic acid is particularly revealing, since this molecule reacts slower than the acylaminobutadienes and is less regio- and stereoselective. The carboxyl group is a net electron withdrawer, since the π^*_{CO} LUMO and the π_{CO} HOMO are both low lying. The π_{CO} orbital will weakly polarize the diene HOMO in the same direction as shown for donor groups in Figure 6, while the π^*_{CO} will have a small influence on the HOMO in the opposite direction. Calculations indicate that the unsubstituted diene terminus will have a slightly higher coefficient than the substituted terminus in the HOMO.[41a] The LUMO will have a much larger coefficient at the unsubstituted terminus than at the substituted. Similar conclusions can be made for methyl acrylate. The result is relatively low regioselectivity for the pentadienoic acid cycloadditions with methyl acrylate, since neither frontier orbital interaction highly favors one regioisomeric transition state. Furthermore, as reactivity decreases, frontier orbital interactions become weaker in the transition state, and both regioselectivities and stereoselectivities decrease accordingly.

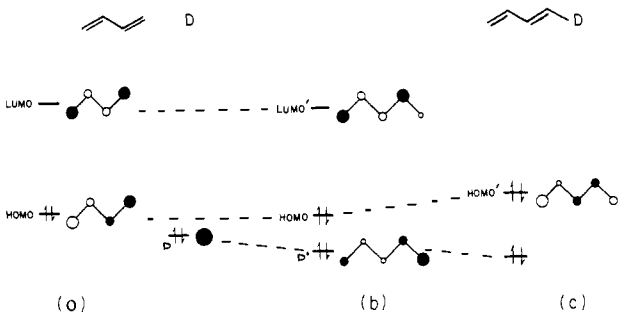


Figure 6. Donor orbital causes the diene HOMO to mix in some of the diene LUMO in an antibonding fashion: (a) isolated frontier orbitals of a diene and a donor, (b) diene LUMO mixed into donor orbital to give D′, (c) HOMO mixed with D′ in an antibonding fashion.

Conclusions

The Diels–Alder reactions of acylaminobutadienes with the mediocre dienophile, methyl acrylate, proceed with remarkable ease, and with high regioselectivity and stereoselectivity. These phenomena can be readily understood by frontier molecular orbital theory, using ionization potentials of the diene obtained from photoelectron spectroscopy. The significant influence of substituents on the diene IPs, and, as a consequence, on reactivity and regioselectivity, even though the substituent effect is "filtered" through the carboxamide group, suggests that the synthetic utility of cycloadditions in general might be further enhanced by the rational design of modified dienes and dienophiles having functionality necessary for subsequent synthetic transformation, but with minor modifications designed to facilitate electronically reactivity and selectivities.

Experimental Section

Dioxane was purified by the method of Hess and Frahm[41b] and distilled from calcium hydride. 4-*tert*-Butylcatechol was purified by sublimation and recrystallization from hexane. Methyl acrylate was distilled and stored at 0 °C with 1% w/v 4-*tert*-butylcatechol. ^{1}H NMR spectra were determined with a Varian EM360 (60 MHz) or Bruker WH-90 (90 MHz) spectrometer. ^{13}C NMR spectra were determined at 22.63 MHz with a Bruker WH-90 spectrometer. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane at 0. Infrared spectra were determined on a Beckman Acculab-2 spectrometer. Mass spectra were determined with a Du Pont 21-492B double-focussing spectrometer at the Caltech Analytical Facility. HPLC was performed with Waters components consisting of a 6000-A pump, U6K injector, and R401 differential refractometer. Photoelectron spectra were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer, using xenon and argon as internal calibration standards. Resolution was at least 35 meV. Experimental precision is reported as the mean ± the standard deviation of the mean.

Diels–Alder Reactions of *trans*-1-*N*-Acylamino-1,3-butadienes and Methyl Acrylate. Ethyl *cis*- and *trans*-6-Carbomethoxy-2-cyclohexen-1-yl Carbamates (2b and 3b). A solution of ethyl *trans*-1,3-butadiene-1-carbamate (**1b**,[5b] 564 mg, 4.0 mmol), methyl acrylate (1.0 g, 12 mmol), 4-*tert*-butylcatechol (20 mg), and 4 mL of anhydrous dioxane was sealed in a glass ampule and heated at 110 °C for 2.5 h. Concentration and filtration of the residue through a 4-in. column of silica gel (4:1 hexane–ethyl acetate) afforded a light yellow liquid. Careful HPLC analysis[42] of a comparable sample showed that the cis and trans stereoisomers **2b** and **3b** were formed in a ratio of 4:1 (90% combined yield, *p*-dinitrobenzene internal standard), and that regioisomers were not detectable (upper limit 1%).[43] This isomer mixture was conveniently separated by preparative HPLC (Porasil A, 12 ft × 3/8 in., 9:1 hexane–ethyl acetate) to give chromatographically homogeneous samples of **2b** (470 mg, 52%) and **3b** (90 mg, 10%). **2b**; a colorless liquid; HPLC[42] (k' = 5); mass

spectrum *m/e* (%) 227.116 ($C_{11}H_{17}NO_4$ requires 227.116) (10), 169 (82), 153 (65), and 141 (100); ν_{max} (film) 3340, 1730, 1310, and 1240 cm^{-1}. **3b**: mp 57–58 °C; HPLC (k' = 7); ν_{max} (Nujol) 3330, 1730, 1690, 1310, and 1257 cm^{-1}.

2,2,2-Trichloro-*N*-(*cis*- and *trans*-6-carbomethoxy-2-cyclohexene-1-yl)acetamides (2a and 3a). In a similar manner, *trans*-1-trichloroacetamido-1,3-butadiene[5b] (**1a**) was allowed to react with methyl acrylate (110 °C, 15 h) to afford, in 75% yield, a 3:1 mixture of the cis and trans stereoisomers **2a** and **3a**, respectively. Analysis by HPLC[42] of a sample of comparable material showed that the addition was highly regiospecific since only traces (upper limit 2%)[43] of other products were detectable. The mixture of isomers was conveniently separated by preparative TLC (silica gel, 5:1 hexane–ether) to afford chromatographically homogeneous samples of **2a** (34%) and **3a** (17%). **2a**: mp 73–74 °C; HPLC[42] (k' = 6); mass spectrum *m/e* (%) 298.989 ($C_{10}H_{12}Cl_3NO_3$ requires 298.988) (21), 264 (78), 213 (15), 154 (22), 138 (89) and 79 (100); ν_{max} (film) 3360, 1720, 1500, and 820 cm^{-1}. **3a**: a colorless liquid; HPLC[42] (k' = 9); ν_{max} (film) 3310, 1710, 1500, and 815 cm^{-1}.

Phenyl *cis*- and *trans*-6-Carbomethoxy-2-cyclohexen-1-yl Carbamates (2c and 3c). In a similar manner, phenyl *trans*-1,3-butadiene-1-carbamate (**1c**)[5b] was allowed to react with methyl acrylate (110 °C, 15 h) to afford, in 85% yield, a 4:1 mixture of the cis and trans stereoisomers **2c** and **3c**, respectively. Analysis by HPLC[42] of a sample of comparable material indicated that the addition was highly regiospecific showing only a trace (upper limit 2%)[43] of an unknown material of slightly higher k' than **2c** and a trace of phenol. Separation of the isomer mixture by preparative HPLC (Porasil A, 4 ft × 3/8 in., 9:1 hexane–ethyl acetate) afforded chromatographically homogeneous samples of **2c** and **3c**. **2c**: mp 86–87 °C; HPLC[42] (k' = 7); mass spectrum *m/e* (%) 275.114 ($C_{15}H_{17}NO_4$ requires 275.116) (3), 183 (6), 139 (12), 94 (100), and 79 (32); ν_{max} (Nujol) 3340, 1735, 1715, 1600, and 1530 cm^{-1}. **3c**: mp 80–81 °C; HPLC[42] (k' = 13); mass spectrum *m/e* 275.113 ($C_{15}H_{17}NO_4$ requires 275.116); ν_{max} (Nujol) 3330, 1725, 1700, 1595, and 1530 cm^{-1}.

Phenyl *cis*- and *trans*-6-Carbomethoxy-2-cyclohexen-1-yl Thiocarbamates (2d and 3d). In a similar manner, phenyl *trans*-1,3-butadiene-1-thiocarbamate (**1d**)[5b] was allowed to react with methyl acrylate (110 °C, 15 h) to afford, in 64% yield, a 4:1 mixture of the cis and trans stereoisomers **2d** and **3d**, respectively. Careful HPLC[42] analysis of a sample of comparable material failed to detect additional adducts (upper limit 2%),[43] but did show that significant amounts (~5%) of thiophenol were formed. Separation of the isomer mixture by preparative HPLC (Porasil A, 4 ft × 3/8 in., 9:1 hexane–ethyl acetate) afforded a chromatographically homogeneous sample of **2d** and a less pure (~90%) sample of **3d**. **2d**: mp 64–66 °C; HPLC[42] (k' = 10); mass spectrum *m/e* (%) 291.092 ($C_{15}H_{17}NO_3S$ requires 291.093) (<1), 182 (24), 151 (37), 139 (38), and 110 (100); ν_{max} (film) 3330, 1740, 1695, 1675, 1520, and 1480 cm^{-1}. **3d**: a pale yellow liquid; HPLC[42] (k' = 15); ν_{max} (film) 3320, 1740, 1690, 1675, 1515, and 1480 cm^{-1}.

***N*-(*cis*- and *trans*-6-Carbomethoxy-2-cyclohexen-1-yl)-1-pyrrolidine Carboxamides (2e and 3e).** In a similar manner, *N*-(*trans*-1,3-butadien-1-yl)-1-pyrrolidinecarboxamide (**1e**)[5b] was allowed to react with methyl acrylate (110 °C, 5 h) to afford, in 73% yield, a 4:1 mixture of the cis and trans stereoisomers **2e** and **3e**, respectively. We were unable to cleanly separate these isomers by preparative HPLC or TLC. Structural assignments were therefore based on the ^1H and ^{13}C NMR spectra of the isomer mixture. The ^1H NMR spectrum ($CDCl_3$, 90 MHz) showed an apparent quartet (outer line separation = 15 Hz) at δ 2.91 for the C-6 hydrogen of **2e**, a broader quartet (outer line separation = ~25 Hz) at 2.54 for the C-6 hydrogen of **3e**, and a multiplet ($W_{1/2}$ = 17 Hz) at 4.77 for the C-1 hydrogen of both isomers. The proton decoupled ^{13}C spectrum ($CDCl_3$) showed characteristic signals (see Table I) at 43.6 and 46.2 ppm for C-6 and C-1, respectively, of the cis isomer **2e**, and a small signal at 48.2 ppm for C-1 of the trans isomer **3e**. The absorption for C-6 of **3e** is not resolved from the signal at δ 45.6 (NCH_2CH_2). Using gated NOE suppression techniques and long pulse delays (12–15 s) the intensities of the absorptions at 48.2 and 43.6 ppm were determined. In a cycloaddition reaction which had proceeded for 8 min (~20% completion) the **2e**:**3e** ratio was 78:22, while a similar reaction conducted for 30 min (~60% completion) yielded a ratio of 76:24. A mass spectrum of the isomer mixture showed a molecular ion at *m/e* (%) 252.150 ($C_{20}H_{13}N_2O_3$ requires 252.147) (24) and fragment ions at 166 (13) and 154 (100).

Table III. Typical Kinetic and Stereoselectivity Data. The Reaction of Diene **1c** and Methyl Acrylate[a]

Time, min	Adduct yield, M		Stereoisomer ratio		Rate constants, $10^5 \times k$, L/mol s
	2c	**3c**	% endo	% exo	
20	0.351	0.085	81.9[b]	18.1[b]	17.4
30	0.492	0.114	81.2	18.8	19.6
40	0.490	0.114	80.5[b]	19.5[b]	14.6
60	0.638	0.165	79.8[b]	20.2[b]	18.3
90	0.687	0.165	81.2[b]	18.8[b]	14.6
120			81.9	18.1	16.9 ± 1.0[c]
240			80.8	19.2	
900			81.4[b]	18.6[b]	
			81.1 ± 0.3[c]	18.9 ± 0.3[c]	

[a] In dioxane at 110 ± 0.2 °C. [b] Average of two determinations. [c] Mean.

General Procedure for the Kinetic and Stereoselectivity Experiments. Freshly chromatographed diene (1.00 mmol), methyl acrylate (0.27 mL, 3.0 mmol, containing 1% w/v 4-*tert*-butylcatechol), and *p*-dinitrobenzene (25.2 mg, 0.150 mmol) were weighed into a 1-mL volumetric flask and diluted to volume with dioxane. Aliquots of this solution were sealed in ca. six 1/2-mL ampules and submerged in a constant temperature bath at 110.0 ± 0.2 °C. Ampules were quenched in ice–water when removed from the bath and stored at 0 °C until analysis. Analysis consisted of removing dioxane and unreacted methyl acrylate on a rotary evaporator at ~40 °C and immediate analysis of the residue by HPLC using a refractive index detector.[42] Chromatogram areas were determined by the Xerox cut–weigh method. For each diene the RI detector response was calibrated by analyzing weighed mixtures (two determinations) of the corresponding cis adduct and *p*-dinitrobenzene. The RI detector response for the trans adduct was assumed to be identical with that of the corresponding cis isomer. To minimize nonlinearity problems of the RI detector, the actual analysis was carried out using conditions similar to that of the calibration. At each time interval the second-order rate constant was calculated from the integrated rate equation[44] with a_0 = 1.00 M, b_0 = 3.00 M, and x = combined yield (by HPLC analysis) of the cis and trans adducts at time t. The rate constant is reported as the mean (± the standard deviation of the mean) of the rate constants calculated at different times. A typical set of data is summarized in Table III. Kinetic points were taken from 40–80% conversion for dienes **1b**, **1c**, and **1e**, from 10–80% conversion for diene **4**, and during the first half-life for diene **1a**. We were unable to obtain good kinetic data for diene **1d**, even during the first half-life.

Diels–Alder Reaction of *trans*-2,4-Pentadienoic Acid with Methyl Acrylate and Acrylic Acid. Methyl Acrylate. A solution of freshly recrystallized *trans*-2,4-pentadienoic acid (**4**, 0.50 g, 5.0 mmol), methyl acrylate (1.35 mL, 15 mmol), 4-*tert*-butylcatechol (~20 mg), and 5 mL of anhydrous dioxane was sealed in a glass ampule and heated at 110 °C for 24 h. Concentration and filtration of the residue through a 4-in. plug of silica gel (diethyl ether) yielded an ethereal solution of the crude adduct mixture, which was esterified by treatment with diazomethane. Excess diazomethane was removed by gentle heating on a stream bath, and the ether was removed in vacuo to afford a mixture of cyclohexene diesters: a light yellow liquid; ν_{max} (film) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.3–5.9 (m, alkenic), 3.51 and 3.53 (s, $COOCH_3$). Careful HPLC analysis[45] indicated the presence of four isomers: k' = 16 (dimethyl *trans*-3-cyclohexene-1,2-dicarboxylate (**5**), 26%); k' = 20 (dimethyl *trans*-4-cyclohexene-1,3-dicarboxylate (**6**), 7.3%); k' = 21 (dimethyl *cis*-4-cyclohexene-1,3-dicarboxylate (**7**), 11%); and k' = 22 (dimethyl *cis*-3-cyclohexene-1,2-dicarboxylate (**8**), 56%). Chromatogram areas were determined by the Xerox cut-weight method with the assumption that the isomers had identical RI response factors. The structural assignments were made by conversion of this isomer mixture (H_2, 1 atm, Pd/C, ethanol) to a mixture of the corresponding dimethyl cyclohexanedicarboxylates. HPLC analysis[45] of the latter mixture revealed four isomers: k' = 18 (dimethyl *trans*-1,3-cyclohexanedicarboxylate, 7.2%); k' = 20 and 21 (a poorly resolved, ~2:1 mixture of dimethyl *cis*- and *trans*-1,2-cyclohexanedicarboxylates, respectively, 82.1% total); and k' = 24 (dimethyl *cis*-1,3-cyclohexanedicarboxylate, 10.6%). These assignments were established by peak enhancements with authentic samples of the dimethyl 1,2-[46] and 1,3-cyclohexanedicarboxylates.[47]

Table IV

Time, h	Isomer composition, %			
	Ortho isomers		Para isomers	
	5	**8**	**6**	**7**
0.5	22.1	61.9	7.5	8.5
1	18.4	63.8	9.2	8.6
1.5	21.7	62.4	8.0	8.0
1.5	22.9	58.1	6.9	12.1
2	20.4	63.6	7.6	8.4
3.25	20.6	60.3	9.5	9.6
4	21.8	60.1	9.0	9.2
7	21.9	60.3	8.3	9.5
8	22.5	59.0	8.3	10.2
9	23.5	59.4	7.8	9.3
24	25.8	55.8	7.3	11.1
	21.6 ± 0.5^a	60.9 ± 0.6^a	8.2 ± 0.3^a	9.3 ± 0.4^a

[a] Mean (0.5-9-h data).

Control experiments established that our workup procedure did not affect the isomer ratios. For example addition of diazomethane directly to the crude reaction mixture followed by direct HPLC analysis afforded results within 2% of those obtained by the procedure described above. This direct procedure was not generally used since the HPLC analysis was complicated by the presence of products derived from the reaction of methyl acrylate and diazomethane.

The isomer compositions observed at various reaction times are summarized in Table IV. The regioisomer ratios were strictly time invariant; however, the ratio of ortho stereoisomers did exhibit a small time dependence. The mean values obtained from 0.5 to 9 h (~5–80% conversion) are taken as good approximations of the true kinetic isomer ratios.

Acrylic Acid. The procedure was identical with that employed with methyl acrylate. The isomer compositions (after methylation) observed at reaction times of 1.5 h (and 15 h) follow: **5**, 23% (35%); **6**, 6.9% (9.2%); **7**, 12.1% (13.3%); **8**, 58% (43%).

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(35) The activation parameters reported for the reaction of this diene with acrylonitrite were used in this estimate.[32]
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