Heterodiene Syntheses. XV.[1] Kinetics of the Reaction between 4-Arylidene-5-pyrazolones and Alkyl Vinyl Ethers: A Frontier-Controlled Cycloaddition

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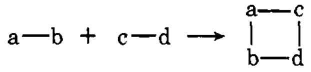
Abstract: The kinetics of the reaction between 4-arylidene-5-pyrazolones and alkyl vinyl ethers have been studied by quantitative spectroscopic analysis. The rate of formation of cis and trans adducts depends on both the arylidene substituents of the pyrazolone and the alkyl group of the ether. When the arylidene substituent is changed, the rate increases with an electron-withdrawing group and a correlation is obtained with $\sigma_p{}^+$ constants. When the alkyl vinyl ether is changed, the rate increases with the order of increase in the electron-releasing effect of the alkyl group, with the exception of *tert*-butyl ether, and a correlation with σ^* constants is obtained. Rationalization in terms of frontier orbitals can be proposed if the cycloaddition is regarded as $\mathrm{LUMO_{pyrazolone}/HOMO_{vinyl\ ether}}$ controlled and if the substituent constants represent the effect of the groups on the energy levels of the frontier orbitals.

The modern approach to cycloadditions derives from application of the perturbation theory. Salem showed[2,3] that the energy gain in the bond formation between the centers of two molecules



involved in cycloaddition can be represented by the sum of three terms: the repulsion between the filled orbitals, the Coulombic interaction between the reagents, and finally the interaction of the highest filled orbital (HOMO) of each molecule with the lowest empty orbital (LUMO) of the other.

If the first and the second terms are neglected, the equation becomes

$$\Delta E = \frac{[(c_{\mathrm{Ho}}{}^{a}c_{\mathrm{Lu}}{}^{c} + c_{\mathrm{Ho}}{}^{b}c_{\mathrm{Lu}}{}^{d})\gamma]^2}{E_{\mathrm{Ho}}{}^{ab} - E_{\mathrm{Lu}}{}^{cd}} + \frac{[(c_{\mathrm{Ho}}{}^{c}c_{\mathrm{Lu}}{}^{a} + c_{\mathrm{Ho}}{}^{d}c_{\mathrm{Lu}}{}^{b})\gamma]^2}{E_{\mathrm{Ho}}{}^{cd} - E_{\mathrm{Lu}}{}^{ab}} \qquad (1)$$

Three types of cycloadditions can be distinguished from the relative position of the frontier orbitals of the reagents[4-6] (Figure 1).

For case B, both terms of eq 1 have to be considered. In case A the main interaction occurs between the HOMO of the diene and the LUMO of the dienophile if the cycloaddition is a Diels-Alder-type reaction, and therefore the first term of eq 1 can be neglected. Case C is $\mathrm{LUMO_{diene}}$/$\mathrm{HOMO_{dienophile}}$ controlled and the second term of eq 1 can be ignored.

The energy associated with the frontier orbitals can be determined by ionization potentials (HOMO) and electron affinities (LUMO); therefore, one can deduce from these parameters of the reagents which type of cycloaddition has to be taken as a model.

The Diels-Alder reactions which can be classified "with normal electron demand"[7] follow case A, i.e., the lower the electron affinity of the dienophile the faster the reaction (tetracyanoethylene > tricyanoethylene > dicyanoethylene > acrylonitrile[7]).

However, if we take the frontier orbital energies of acrolein[8] as a model for α,β-unsaturated carbonyl derivatives, we can easily deduce that the dominant interaction in the reaction with a nucleophilic olefin like a vinyl ether occurs between the HOMO of the dienophile and the LUMO of the heterodiene (Figure 2). These reactions can therefore be represented by case C shown in Figure 1.

The Diels-Alder reactions have been investigated fully from the kinetic point of view[7] and rationalization of the kinetic results in terms of frontier orbital interactions of an A-type cycloaddition was given.[9,10] Only when the diene has a strong acceptor character, e.g., the reaction of phenylcyclones with arylethylenes[11,12] or arylacetylenes,[13] can the reaction be rationalized as a "neutral" Diels-Alder, i.e., a B-type reaction where both electron-releasing and -attracting substituents on the dienophile accelerate the reaction rate.

The reaction with α,β-unsaturated carbonyl compounds acting as dienes[14] has been investigated far less, and the only kinetic data available in the literature concern the reaction between aryl-substituted cinnamaldehydes and octyl vinyl ether.[15] These data generally agree with the assumption that electron-attracting substituents in the diene favor the reaction because they lower the LUMO energy as required for a C-type cycloaddition. The authors' interpretation of the small substituent effect (ρ value of +0.71 for a correlation with σ values) in terms of a dipolar intermediate, taking into account that the polarity of the solvent also has little effect on the rate,[16] is questionable. Furthermore, the authors do not consider the configuration of the adducts which could not be single isomers.

In this paper we wish to discuss the kinetic data of the reaction between 1-phenyl-4-arylidene-5-pyrazolones (**1**) and isopropyl vinyl ether (**2A**), which gives a mixture of *cis*- and *trans*-2-isopropyl-4-aryl-7-phenyl-2,3-dihydropyrano[2,3-*c*]pyrazoles (**3** and **4**) (Scheme I).

Results and Discussion

The kinetic runs were studied in benzene at 70° and followed to 60–80% completion by quantitative spectroscopic analysis of the disappearing pyrazolone **1** in the uv-visible region (see Experimental Section for details).

The reactions were shown to be second order, first order with respect to each reagent; a 200-fold molar excess of vinyl ether gave pseudo-first-order conditions.

The product composition is kinetically controlled since the molar ratio [cis adduct]:[trans adduct], $(c_3{:}c_4) = \alpha$, is constant throughout the reaction.

Samples were taken from the kinetic experiments and the adducts separated on TLC plates to determine c_3 and c_4 and hence k_{cis} and k_{trans}. Elution of the separated spots with equal amounts of ethanol followed by quantitative spectroscopic analysis gave the absorbance values. The rela-

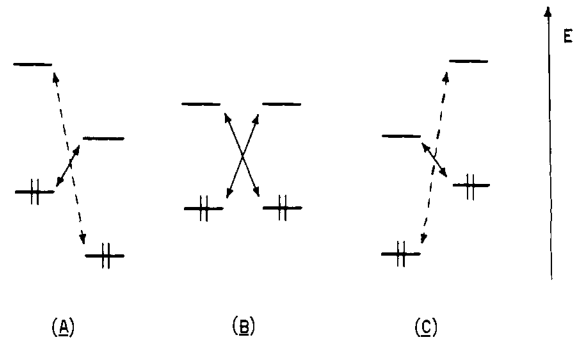


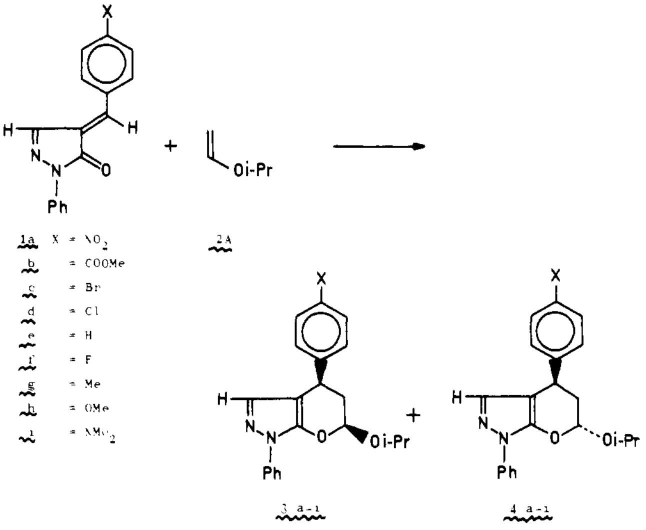
Figure 1. Frontier orbitals in direct (A), neutral (B), and inverse (C) cycloadditions.

Table I. Rate Constants (l. mol^{-1} s^{-1}) for the Reaction of Arylidenepyrazolones and Isopropyl Vinyl Ether in Benzene at 70°

Pyrazolone	Substituent	$10^4 k_{tot}$[a]	α[b]	10^4-k_{cis}[c]	10^4-k_{trans}[d]
1a	NO_2	50.5 ± 1.2	2.97	37.8	12.7
1b	COOMe	25.8 ± 1.1	2.82	19.0	6.76
1c	Br	14.0 ± 1.5	2.38	9.86	4.14
1d	Cl	13.3 ± 0.5	2.24	9.19	4.11
1e	H	10.9 ± 0.35	2.38	7.67	3.23
1f	F	8.58 ± 0.08	2.68	6.25	2.33
1g	Me	5.75 ± 0.15	2.32	4.02	1.73
1h	OMe	2.13 ± 0.09	2.39	1.50	0.63
1i	NMe_2	0.409 ± 0.005	2.72	0.299	0.110

[a] Overall rate constants. [b] Molar ratio $[c_{cis}]:[c_{trans}]$ equivalent to $k_{cis}:k_{trans}$. [c] Rate constants for the formation of the cis adduct 3. [d] Rate constants for the formation of the trans adduct 4.

Scheme I



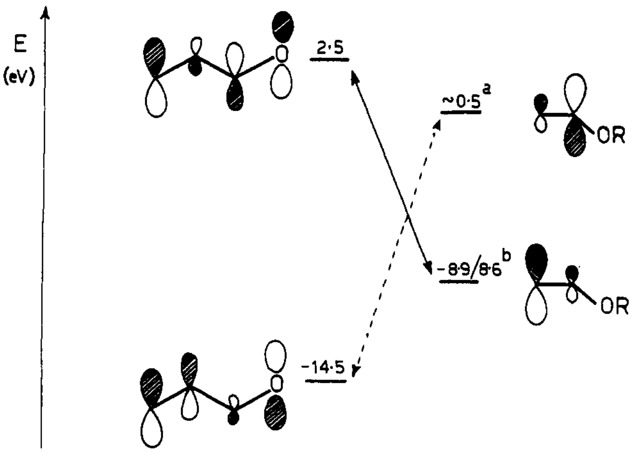


Figure 2. Estimated π frontier orbital energies for the reaction between acrolein and unsaturated ethers. [a] Taken from K. N. Houk, J. Sims, R. E. Duke Jr., R. W. Strozier, and J. K. George, *J. Am. Chem. Soc.*, **95**, 7287 (1973). [b] Taken from ref 26.

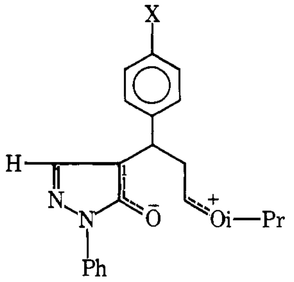
tive molar ratio α was obtained from the molar extinction coefficients calculated from the pure adducts 3 and 4.

From the overall rate coefficients (k_{tot}) and molar ratios α, k_{cis} and k_{trans} coefficients were determined by the formulas $k_{cis} = k_{tot}(\alpha/1 + \alpha)$ and $k_{trans} = k_{tot}(1/1 + \alpha)$. The results are shown in Table I.

The constant presence of the cis isomer as the major one is rationalized in terms of stabilizing nonbonding interactions in the transition state (t.s.) which can be determined quantitatively from the mean α value in a difference in the activation free energy ($\Delta\Delta G^{\ddagger}$) between 3 and 4 of 0.6 kcal/mol. The *E* configuration of the starting pyrazolones 1[17] requires an endo configuration of the t.s. for a cis adduct and the $LUMO_{pyrazolone}/HOMO_{vinyl\ ether}$ MO's give rise to a stabilizing secondary nonbonding interaction between the vinyl ether oxygen and the carbon of the carbonyl pyrazolone,[18] which explains the preference.

The results which can be obtained by plotting log k_{cis} and log k_{trans} vs. σ^+ constants[19] are far more interesting (Figure 3). The correlation coefficients indicate a good linear correlation for both k_{cis} and k_{trans} (ρ = 0.844 and 0.834, respectively; correlation coefficient r = 0.9992 and 0.9983 respectively).

This substituent effect cannot be explained by a traditional intermediate like **5** as the required resonance cannot operate to stabilize the charges, and furthermore the α value is not constant.[20]



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In the light of the above reported considerations and from MO level proximities, asymmetry of the reagents, and previous data,[14] a reasonable reaction model can be proposed (see Scheme II).

The t.s. are unsymmetrical[21] with the C-C bond closing faster than the C-O bond, but a common dipolar intermediate (**5**) giving the adducts via a two-step mechanism seems far more improbable than a concerted pathway.

The substituent effect found can be rationalized if Sustmann's approximation of eq 2 vs. eq 1[6] is accepted. If the coefficients in the numerator do not vary for a homogeneous series of reagents, ΔE is a function of the orbital separations only.

$$\Delta E = A\gamma^2 \left[\frac{1}{E_{Ho}{}^{ab} - E_{Lu}{}^{cd}} + \frac{1}{E_{Ho}{}^{cd} - E_{Lu}{}^{ab}} \right] \qquad (2)$$

The pattern of this function is represented by two branches of hyperbolas, corresponding to the two terms; if both operate, superimposition of the two curves gives a U-shaped function.[6]

Sustmann himself showed that the kinetic data of A-type Diels-Alder reactions agrees with eq 2 if the first term is neglected because log k plotted vs. $HOMO_{diene}$/

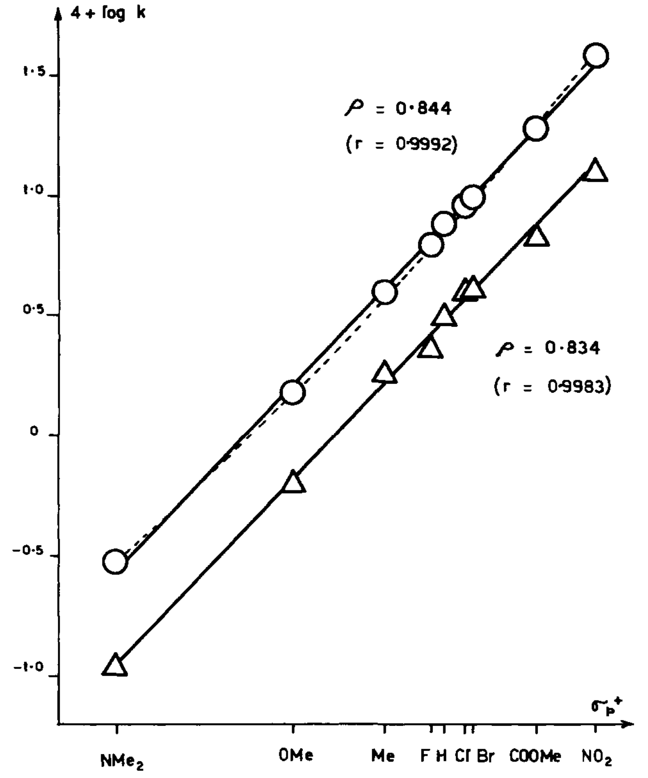
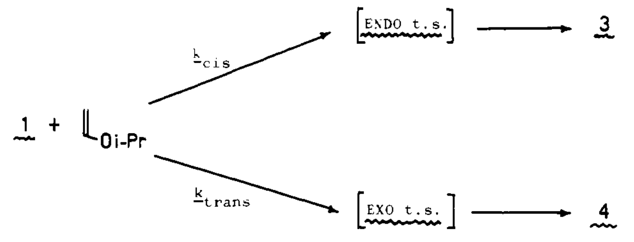


Figure 3. Correlation of log k_{cis} (O) and log k_{trans} (Δ) and σ_p^+ for the reaction of 1-phenyl-4-arylidene-5-pyrazolones and isopropyl vinyl ether in benzene at 70°.

Scheme II



LUMO$_{dienophile}$ energy separation fits quite convincingly on a hyperbola branch.[9]

Konovalov[11-13] found that the kinetic data of B-type diene syntheses fits a parabolic curve, the superimposition of two hyperbola branches, since both terms of eq 2 need to be considered.

Our results also fit the same eq 2 if the second term is neglected, due to the predominance of the HOMO$_{vinyl\ ether}$/LUMO$_{pyrazolone}$ interaction. But HOMO$_{vinyl\ ether}$ is a constant (isopropyl vinyl ether) and, in the series **1a–i**, LUMO energies must be a function of the substituents at the aryl group only. If the substituent X acts on the orbital energies with both inductive and mesomeric effects, it seems reasonable to represent the energy variation by the σ^+ constants, which can be taken as a quantitative measure of the effect of the electron-donating groups to increase the energy and the electron-withdrawing groups to decrease the energy of MO's.[22]

A similar log k/σ^+ dependence can be found in the previously mentioned reaction between 1-(p-substituted phenyl)-1,3-butadiene and maleic anhydride.[10] A linear correlation was observed between the energies of the HOMO of the diene, from CNINDO calculations, and the logarithm of the relative rates (r with INDO values = 0.989). But an excellent correlation (r = 0.999) can also be found between σ^+ and the HOMO energies, and consequently σ^+ and log k also correlate (r = 0.983).

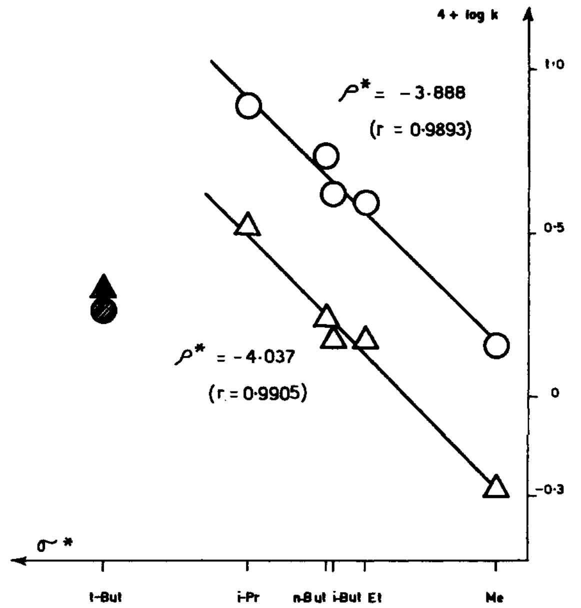
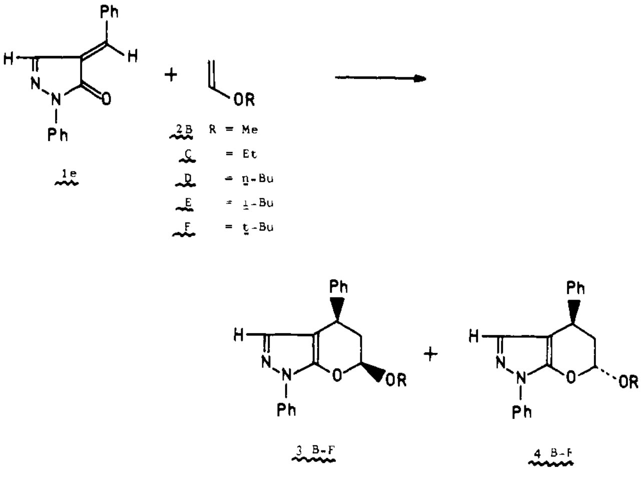


Figure 4. Correlation of log k_{cis} (O) and log k_{trans} (Δ) vs. σ_p* for the reaction of 1-phenyl-4-benzal-5-pyrazolone and alkyl vinyl ethers in benzene at 70°.

Table II. Rate Constants (l. mol^{-1} s^{-1}) for the Reaction of Alkyl Vinyl Ethers with 1-Phenyl-4-benzal-5-pyrazolone in Benzene at 70°

Vinyl ether	Alkyl group	10^4k_{tot}	α	10^4k_{cis}	10^4k_{trans}
2B	Me	1.96 ± 0.08	2.72	1.43	0.53
2C	Et	5.40 ± 0.07	2.62	3.91	1.49
2D	n-Bu	7.09 ± 0.04	3.13	5.38	1.71
2E	i-Bu	5.64 ± 0.17	2.80	4.16	1.48
2F	t-Bu	3.95 ± 0.09	0.86	1.82	2.13
2A	i-Pr	10.9 ± 0.35	2.38	7.67	3.23

Scheme III



A comparable effect should occur in heterodiene cycloadditions if the vinyl ether is changed and the substrate is constant. Therefore we have determined the kinetics of reaction between 1-phenyl-4-benzal-5-pyrazolone (**1e**) and various alkyl vinyl ethers (**2B–F**) (Scheme III).

The kinetics data (k_{tot}, α, k_{cis}, and k_{trans}) are reported in Table II where the values previously found for the reaction of **1e** with isopropyl vinyl ether are also reported.

If we exclude *tert*-butyl vinyl ether, which also has an unusual α value, the rate increases in the order of increase in the electron-releasing effect of the alkyl group of the vinyl ether. In Figure 4 we have plotted log k against Taft's

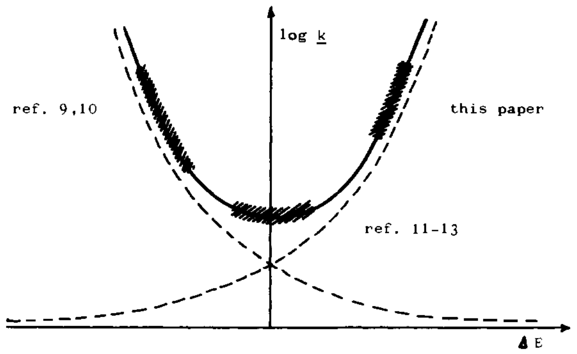


Figure 5. Graphical representation of ΔE/log k dependence with the experienced regions shown by solid part. Diagram is schematic.

σ^* values[23] which show the polar character of the substituents. The alternative correlation with σ_I parameters depends on the relationship of these parameters to σ^*.[24]

The ρ^* values for k_{cis} and k_{trans} are very similar, −3.888 (r = 0.989) and −4.037 (r = 0.991), respectively. In the light of previous results, these data can be interpreted as due to the variation in the energy levels involved in the cycloadditions. In this case the LUMO energy is a constant (1-phenyl-4-benzal-5-pyrazolone) and only the HOMO energies of vinyl ethers are required. In accordance with Koopmans' theorem,[25] the ionization potentials should give the required values. The data available concern values determined by charge-transfer complexes.[26] The order of increase agrees with the kinetic data but a quantitative correlation was unsatisfactory. Nevertheless, it seems reasonable to explain the variation in the energy levels of alkyl vinyl ethers in terms of a polar effect; probably reinvestigation with more modern techniques will show the IP energies of vinyl ethers to be a function of σ_I and σ^* as for nearly all other series of organic compounds.[27]

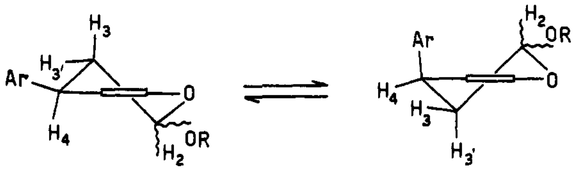
A recent study of the cationic polymerization of alkyl vinyl ethers[28] gave a good correlation between the rate constants and σ^* parameters which can be rationalized analogously; unfortunately the *tert*-butyl derivative was not investigated. Its deviation (Table II) can probably be inter-

Table III. Preparation, Characters, and Uv Spectra of Adducts 3 and 4

Compd	Type of separation[a]	Mp, °C (solvent)[b]	Physical state	Analyses	Uv spectra[c]	
					λ_{max}, nm	ϵ
3a	A	126 (EtOH)	Soft white needles	($C_{21}H_{21}N_3O_4$) C, H, N	251	20 100
4a	A	142 (cyhex)	Colorless small needles	($C_{21}H_{21}N_3O_4$) C, H, N	252	20 900
3b	B	89–90 (dIPE)	Small white crystals	($C_{23}H_{24}N_2O_4$) C, H, N	244	28 850
4b	B + A		Oil	($C_{23}H_{24}N_2O_4$) C, H, N	243	25 100
3c	C	113–114 (cyhex)	Soft white needles	($C_{21}H_{21}N_2O_2Br$) C, H, N, Br	235	21 550
4c	C + A	138–139 (pet. eth.)	Small white prisms	($C_{21}H_{21}N_2O_2Br$) C, H, N, Br	234	22 000
3d	C	109–110 (cyhex)	Soft white needles	($C_{21}H_{21}N_2O_2Cl$) C, H, N, Cl	241	18 750
4d	C + A	132–133 (pet. eth.)	Colorless small prisms	($C_{21}H_{21}N_2O_2Cl$) C, H, N, Cl	241	18 600
3e		88–89[37]			245	16 200
4e		115[37]			244.5	16 600
3f	C	106–107 (cyhex)	Soft white needles	($C_{21}H_{21}N_2O_2F$) C, H, N	245	16 600
3f	C + A	126–127 (pet. eth.)	Large white prisms	($C_{21}H_{21}N_2O_2F$) C, H, N	245	16 100
3g	D	115–116 (dIPE)	Soft white needles	($C_{22}H_{24}N_2O_2$) C, H, N	245	17 400
4g	D + A	113–114 (pet. eth.)	Colorless platelets	($C_{22}H_{24}N_2O_2$) C, H, N	244	16 700
3h	A	98 (cyhex)	Small white crystals	($C_{22}H_{24}N_2O_3$) C, H, N	244	18 000
4h	A	80 (dIPE/pet. eth.)	Colorless needles	($C_{22}H_{24}N_2O_3$) C, H, N	243	17 550
3i	E	106–107 (cyhex)	Cream colored small crystals	($C_{23}H_{27}N_3O_2$) C, H, N	258.5	31 250
4i	E	70–71 (pet. eth.)	Beige small crystals	($C_{23}H_{27}N_3O_2$) C, H, N	257.5	27 050
3B		115–116[37]			245	14 750
4B		125–126[37]			244.5	14 650
3C		87–88[37]			245.5	16 800
4C		104–105[37]			244.5	16 100
3D	A	73 (cyhex/pet. eth.)	White needles	($C_{22}H_{24}N_2O_2$) C, H, N	245	16 950
4D	A	58–59 (cyhex/pet. eth.)	Soft white needles	($C_{22}H_{24}N_2O_2$) C, H, N	244	15 850
3E	D	109–110 (dIPE)	Small white needles	($C_{22}H_{24}N_2O_2$) C, H, N	245.5	16 650
4E	D + A	Bp 185° (0.1 mm)	Oil	($C_{22}H_{24}N_2O_2$) C, H, N	244	15 000
3F		119–120[37]			245.5	14 800
4F		122–123[37]			244.5	16 300

[a] A: chromatographic separation with cyhex/AcOEt 9:1 as eluent; B: fractional crystallization from dIPE/pet. eth.; C: fractional crystallization from cyhex; D: fractional crystallization from dIPE; E: chromatographic separation on Silica gel Merck 0,05–0.2 mm diameter with cyhex/AcOEt 4:1 as eluent. [b] Cyhex refers to cyclohexane; dIPE, diisopropyl ether; pet. eth., petroleum ether (40–60°). [c] In EtOH on Perkin-Elmer 137 uv–visible spectrophotometer.

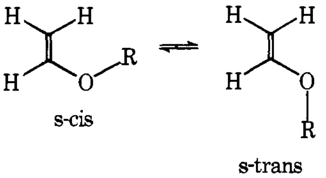
Table IV. NMR Spectra[a] of Adducts 3 and 4



Compd	Chemical shift				Coupling constants				
	H_2	H_3	$H_{3'}$	H_4	J_{23}	$J_{23'}$	J_{34}	$J_{3'4}$	$-J_{33'}$
3a	5.61	2.09	2.33	4.25	6.50	1.93	7.47	6.56	14.00
3b	5.54	2.13	2.35	4,20	7.39	1.74	8.52	6.47	13.67
3c	5.49	2.01	2,26	4.06	7.85	1,91	8.76	6.37	13.79
3d	5.49	2.06	2.29	4.08	7.74	1.78	8.54	6.23	13.85
3e[b]	5.50	2.09	2.30	4.10	8.53	1.50	9.47	6.60	13.91
3f	5.44	2.06	2.28	4,02	8.13	1.56	8,89	6.57	13.56
3g	5.50	2.12	2.35	4.09	8.60	1.70	9.70	6.55	13.76
3h	5.45	2.04	2.24	4.02	8.72	1.54	10.26	6.23	13.77
3i	5.48	2.06	2.25	4.04	9.28	1.40	10.37	6.13	13.73
4a	5.61	1.90	2.24	4.31	2.39	2.36	11.30	5.36	13.62
4b	5.58	1.91	2.21	3.76	2.38	2,45	11.10	5.82	13.58
4c	5.58	1.87	2.20	4.17	2.59	2,43	11.19	5.29	13.38
4d	5.59	1.87	2.19	4.17	2.56	2.46	11.17	5.35	13.65
4e[b]	5.65	1.85	2.14	4.17	2,08	2.76	10.99	5.51	13.44
4f	5.59	1.89	2.20	4.17	2.32	2.36	11.26	5.32	13.35
4g	5.56	1.90	2.18	4,15	2,44	2.66	10.97	5.66	13.54
4h	5.57	1,87	2.17	4,12	2.58	2.61	11,02	5.48	13.82
4i	5.54	1.87	2.16	4,06	2.44	2.73	10.74	5.32	13.59
3B[b]	5.24	2.06	2.30	4.05	8.16	1.88	9.23	6.34	13.92
3C[b]	5.41	2.10	2.35	4.10	8.15	1.98	9.30	6.31	13.64
3D	5.46	2.15	2.38	4.10	8.21	1.72	9.31	6.29	13.62
3E	5.44	2.12	2.34	4.10	8.20	1.70	9.35	6.35	13.80
3F[b]	5.64	2.08	2.18	4.10	8.77	1.70	9.75	6.27	13.85
4B[b]	5.35	1.92	2.26	4.15	2.51	2,51	11.23	5.51	13.78
4C[b]	5.50	1.92	2.25	4.17	2,61	2,65	11.17	5.62	13.99
4D	5.57	1.93	2,26	4,15	2.43	2.62	11.11	5.56	13.68
4E	5.55	1.93	2.27	4.15	2.45	2,67	11.12	5.55	13.70
4F[b]	5.74	1.90	2.11	4.19	2.30	2.89	10.61	5.20	13.17

[a] Performed on a Perkin-Elmer R-12A spectrometer; chemical shifts are expressed in ppm (δ scale) from Me_4Si as internal standard. All spectra were analyzed as ABMX systems using the LAOÇOON 3 computer program. [b] Data taken from ref 37.

preted in terms of the different conformation of the reacting vinyl ether.



Both methyl and ethyl vinyl ethers (**2B,C**) predominantly adopt the s-cis conformation.[29,30] For steric reasons this more favorable conformation[31,32] cannot be adopted by the *tert*-butyl derivative **2F**.[33,34] Therefore a gap between *tert*-butyl and other alkyl vinyl ethers is not surprising, even though similar behavior was not found in the acid-catalyzed hydrolysis of alkyl vinyl ethers.[35] However, the overall reactivity of this class is far from settled.

Conclusion

From the above reported results, kinetic data interpretation shows that Diels-Alder reactions really fall in all three types of cycloadditions reported in Figure 1, and Figure 5 gives a graphical representation of eq 2 with the regions experimentally investigated.

The fact that sometimes a hyperbolic section and sometimes a line is found depends on the small sector investigated (~0.3 eV in the variation of vinyl ethers[26]) which does not give a clear definition of the shape of the graphical representation. Only the B-type cycloaddition, for its particular location in the graph, shows the typical U shape.

Figure 3 shows also a possible hyperbolic correlation of the k_{cis} data, but this seems much less important than the evidence of the presence of the second branch curve, which has not previously been investigated.

These results are further support of what a powerful instrument the perturbation approach to cycloadditions is, even for simpler models.

Experimental Section[36]

Materials. Methyl vinyl ether (Fluka), ethyl vinyl ether (Erba), isopropyl vinyl ether (BASF), *n*-butyl vinyl ether (EGA), isobutyl vinyl ether (EGA), and *tert*-butyl vinyl ether (K and K Lab.) were used after purification by two distillations. 1-Phenyl-4-arylidene-5-pyrazolones (**1a–i**) were prepared in accordance with the literature method.[17]

***cis*-[2,4] and *trans*-[2,4]2-Alkoxy-4-aryl-7-phenyl-2,3-dihydropyrano[2,3-c]pyrazoles (3 and 4).** A mixture of the required pyrazolone **1** (0.001 mol) and vinyl ether (0.03 mol) was heated in a sealed tube at 70° until the color of the starting pyrazolone disappeared. The light amber solution was evaporated and the oily residue crystallized from the appropriate solvent. Generally a single isomer, the major one, crystallized from the solution. The mother liquors were evaporated to dryness and chromatographed, unless otherwise stated, over silica gel (Merk H). The same treatment was performed directly on the reaction mixture if the fractional crystallization was not successful. In both cases the minor isomer **4** was eluted first, followed by the eventual crop of the major one **3**. The crude adducts were crystallized and their structures determined by elemental analysis and NMR. The type of separation and physical characters of all the adducts obtained by the above method are reported in Table III. The NMR parameters of the mobile dihydropyran fragment of **3** and **4** are reported in Table IV. In general these values do not differ greatly from the previously described examples[37] and easily allow assignment of the configuration of the adducts. Some unusual variations of the *J* values in the

Table V. Wavelength Used for the Kinetic Runs

Pyrazolone	Substituent	λ, nm
1a	NO_2	329
1b	COOMe	328
1c	Br	337
1d	Cl	330
1e	H	328
1f	F	326
1g	Me	340
1h	OMe	362
1i	NMe_2	436[a]

[a] Tungsten lamp used.

cis series can be due to a different position in the conformational equilibrium and will be discussed in detail elsewhere.

Kinetics, Kinetic Method. The benzene solvent used for the kinetic runs was redistilled reagent grade. The uv-visible spectra of the pyrazolones were determined, and suitable wavelengths were selected to follow the reaction in a region of minimum slope and maximum extinction coefficient of the pyrazolones and "zero" absorbance of the adducts. A Beckman DU-2 spectrophotometer was used. Solutions were measured in 1.00-cm OS Hellma cells of 3-ml capacity. The wavelengths chosen are reported in Table V.

Determination of the Overall Rate Constants (k_{tot}). A sample of pyrazolone **1** (in the range 0.0004–0.0009 M) was accurately weighed into a 50-ml volumetric flask and dissolved in benzene; an accurately weighed sample of alkyl vinyl ether (in the range 0.15–0.35 M) was added into a thin sealed glass tube. The reagents were shaken to mix and benzene was added up to 50 ml. Immediately 0.30-ml portions of the homogeneous solution were removed with a microsyringe and placed in sealed tubes. Freezing was required for **1a–f** and 12–20 samples were prepared for each run. At time zero the samples were placed into a water ultrathermostat at 70° and a 0.30-ml portion of the starting solution was diluted to 7.00 ml with benzene and the absorbance determined. About 10–12 samples were measured after dilution to 7.00 ml with benzene at appropriate time intervals (1 min for **1a** to 90 or 120 min for **1i**). The reactions were followed to 60–80% completion and a sample was kept for several days at 70° to ensure that the absorbance of the adducts was negligible at the λ used. TLC showed that only the adducts previously isolated were present in the colorless reaction mixture. The kinetic data reported in Tables I and II are the average of three to five kinetic runs using different initial concentrations of pyrazolone and vinyl ether for each run. Rate constants were calculated graphically, experimental results being fitted to the appropriate pseudo-first-order rate equation by a least-squares fit regression program.

Determination of the Molar Ratios [3]:[4] = α. The residual five to six samples from the kinetic determinations were used to determine the molar ratio of cis vs. trans adducts. A small portion of solution (about 0.1 ml) was placed on TLC aluminum sheets of silica gel F_{254} Merck and eluted with the same mixture used for the chromatographic separation of the pure adducts (Table III). The separated spots were cut out and put into 1.00-cm quartz cells (3.0 ml capacity), each fitted with a ground-glass stopper. Spectral grade ethanol (2.80 ml) was added to both samples and, after a few minutes of shaking, the uv spectra were registered on a Perkin-Elmer 137 uv spectrophotometer. From the absorbances obtained and the ε values at λ_{max} of the pure adducts (Table III), the ratio α was determined. These values, reported in Tables I and II, are the average of at least six determinations. The extreme values were excluded and the maximum deviation was 0.5 ± 2.5%.

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