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The Polar [$_{\pi}4 + _{\pi}2$] Cycloaddition Reaction. Enamines as Dipolarophiles in 1,3-Dipolar Additions[1]

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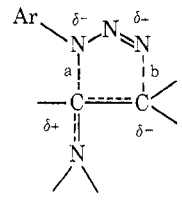
Hammett ρ values of −1.0, +2.1, and −0.66, respectively, were obtained for the addition of (1) phenyl azide to a series of meta- and para-substituted acetophenone piperidine enamines, (2) a series of meta- and para-substituted phenyl azides to phenylacetaldehyde piperidine enamine, and (3) *m*-nitrophenyl azide to a series of meta- and para-substituted phenylacetaldehyde piperidine enamines. Measured activation parameters and the insensitivity of reaction rate to ion-solvating power of the solvent implicate a concerted cycloaddition process. Hammett parameters and the regiochemistry of the enamine–azide reaction are consistent with a polar transition state in the electron reorganization process, in contrast to the more usually encountered isopolar transition states of 1,3-dipolar additions. Molecular orbital calculations on ground-state enamine and the observed dependence of reaction rate on the nature of the amino substituent lend support to the mechanism suggested.

One of the striking features of the 1,3-dipolar addition of organic azides to enamines is the high degree of regiospecificity observed over a broad range of azide and enamine substrates.[3,4] Without exception, that terminal nitrogen atom of the 1,3 dipole bearing the substituent is directed to the carbon atom of the dipolarophile bearing the amino group. The preferred orientation of addition could not be reversed, even partially, by manipulation of steric effects. Thus, the addition of phenyl azide to the piperidine enamine of acetophenone gives 1,5-diphenyl-5-(1-piperidino)-4,5-dihydro-1,2,3-triazole, the product of kinetic control, exclusively.[4] Control of the direction of addition appeared to be the result of electronic stabilization and therefore it was suggested that the reaction proceeds via a polar transition state (**1** or **2**) in the rate-determining step. An important role was attributed to electron-releasing nitrogen in delocalizing positive charge. Orientation phenomena provided no distinction between the stepwise and concerted cycloaddition.



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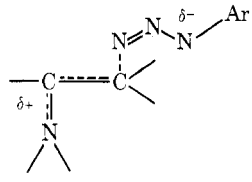

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To further illuminate the nature of the transition state activation parameters, solvent dependence, Hammett correlations, and the stereochemistry[5] of cycloaddition have been examined. A number of pertinent kinetic studies have been published[6-8] and these will be contrasted with results reported herein.

Two reactions were chosen for initial kinetic study (Table I). In each case a first-order relationship was derived for both enamine and azide. Activation parameters for these reactions are summarized in Table I.

Table I
Activation Parameters. Addition of Phenyl Azide[a] to Piperidine Enamines in Chloroform

Enamine	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$	Registry no.
Acetophenone	16 ± 1.2	15 ± 1.2	−34 ± 4.0	14990-66-0
Phenylacetaldehyde	14 ± 1.2	13 ± 1.2	−35 ± 4.0	332-15-0

[a] Registry no., 622-37-7.

Table II
Solvent Dependence. Addition of Phenyl Azide to Acetophenone Piperidine Enamine at 44.8°

Solvent	*Z* value, kcal/mol[a]	$k_2 \times 10^4$, l. mol^{-1} min^{-1}
Chloroform	63.2	9.1 ± 0.26
Acetonitrile	71.3	12.0 ± 0.5
Ethanol	79.6	7.0 ± 0.38

[a] Reference 10.

The large negative entropies of activation are indicative of highly ordered transition states[9] and provide presumptive, but not compelling, evidence favoring the concerted mechanism. The insensitivity of rate to solvent polarity (Table II) is also consistent with the concerted process, but, it should be noted, does not require a cyclic transition totally devoid of charge separation. No correlation between the solvent polarity parameter *Z* and rate is evident;[10] rather the most rapid reaction, by a modest margin, occurs in acetonitrile.[11] Huisgen[8] has reported a similar pattern of

Table III
Rate Constants for Cycloaddition in Chloroform at 44.8°

Substituent	Rate constant, $k_2 \times 10^3$ l.·mol^{-1} min^{-1}		
	Reaction 1[a,e]	Reaction 2[b,f]	Reaction 3[c,g]
p-OCH_3	1.9 ± 0.04[d]	3.8 ± 0.13	
p-CH_3	1.1 ± 0.09	4.5 ± 0.07	280 ± 5
m-CH_3	0.95 ± 0.004		
H	0.91 ± 0.026	10.0 ± 0.3	210 ± 8
m-OCH_3	0.89 ± 0.014		190 ± 3
p-Cl	0.52 ± 0.018	29.0 ± 0.6	150 ± 3
p-Br	0.50 ± 0.001	42.0 ± 0.7	150 ± 6
m-NO_2	0.17 ± 0.012	210.0 ± 8	
p-NO_2		980.0 ± 9	

[a] Addition of PhN_3 to the piperidine enamine of meta- and para-substituted acetophenones. [b] Addition of meta- and para-substituted phenyl azides to phenylacetaldehyde piperidine enamine. [c] Addition of *m*-nitrophenyl azide to the piperidine enamine of meta- and para-substituted phenylacetaldehydes. [d] Average deviation. [e] Registry no. of the piperidine enamine of substituted acetophenones are, respectively, 53927-01-8, 53927-02-9, 53927-03-0, 53927-04-1, 53927-05-2, 53927-06-3, 53927-07-4. [f] Registry no. of the substituted phenyl azides are, respectively, 2101-87-3, 2101-86-2, 3296-05-7, 2101-88-4, 1516-59-2, 1516-60-5. [g] Registry no. of the piperidine enamine of substituted phenylacetaldehydes are, respectively, 53927-08-5, 53927-09-6, 53927-10-9, 53927-11-0.

bon bearing the amino substituent, and the known superior +R quality of the pyrrolidine group relative to piperidine.[15]

In the acetophenone enamine series (reaction 1), steric inhibition of resonance may account for the reduced role of phenyl, as molecular models[16] indicate that phenyl and amino group cannot simultaneously achieve the coplanarity required for delocalization of positive charge because of severe steric crowding.

Equally good Hammett σ and σ^- correlations were derived for the addition of a series of meta- and para-substituted phenyl azides to phenylacetaldehyde piperidine enamine;[17] σ^0 values gave a somewhat less satisfactory fit. The extended form of the Hammett equation,[18] $Q_X = \alpha\sigma_I + \beta\sigma_R + h$, gave an ϵ value approaching unity (para substituents only; reaction 2, Table V) indicating a balance of inductive and resonance effects better expressed by normal Hammett σ values than σ^- values.[19] Kinetic data for the addition of para-substituted phenyl azides to cyclohexanone pyrrolidine enamine[8] (reaction 4), norbornene[6,8] (reaction 5), and cyclopentene[8] were also processed by us using the extended form of the Hammett equation (Table V) and show a gradual decline in ϵ in the order given,[19] consistent with a reduction in charge separation in the transition state.

The sign and magnitude of ρ for reaction 2 (Table IV) is suggestive of negative charge at nitrogen bearing phenyl in the transition state. This result complements that derived from reaction 1, and together they provide convincing evidence for substantial charge separation at bond a, as depicted in expression 1.

Table IV
Hammett Relationship. Correlations with Various Substituent Constants[a]

Reaction studied[b]	Hammett ρ value (correlation coefficient)			
	σ	σ^0	σ^+	σ^-
Reaction 1	−1.0 (0.98)	−0.97 (0.96)	−0.71 (0.94)	
Reaction 2	+2.1 (0.98)	+2.2 (0.96)		+1.7 (0.98)
Reaction 3	−0.66 (0.99)	−0.63 (0.99)	−0.59 (0.95)	

[a] Substituent constants taken from C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, 2, 323 (1964). [b] Reactions described in Table III.

solvent insensitivity in the cycloaddition of phenyl azide to cyclopentanone piperidine enamine. A more profound rate dependence on solvent polarity is expected in cycloadditions proceeding by way of zwitterionic intermediates,[12] e.g., **2**. Finally, the conservation of the configuration of the enamine during electron reorganization lends strong support to the concertedness of cycloaddition.[5]

The Hammett relationship was chosen to assess the magnitude and distribution of charge among the centers undergoing electron reorganization. In the addition of phenyl azide to a series of meta- and para-substituted acetophenone piperidine enamines, the rate constants (Table III, reaction 1) correlate best with the original Hammett σ values[13] (Table IV).

The sign of ρ in reaction 1 is consistent with the development of positive charge in the transition state at the carbon atom bearing the substituent probe. However, the magnitude of ρ may not reflect the full extent of electron deficiency because of the presence of a second and powerful electron donor, the amino group, at that site. Evidence in support of the latter point is found in a study of the dependence of the rate of cycloaddition on the nature of the amino group (Table VI). Although piperidine and pyrrolidine are nearly equal in basicity, the acetophenone enamine of the latter amine is 34 times more reactive toward phenyl azide. In sharp contrast the piperidine enamine reacts only 4.5 times faster than the morpholine enamine in spite of the 1000-fold difference in amine basicity.[14] This behavior is explicable in terms of electron deficiency at car-

Table V
Correlation of Rate Data with the Extended Hammett Equation

Reaction	No. of data points[a]	h[b]	α[b]	β[b]	ϵ (α/β)
1[c]	5	−0.092 (80.0)	−0.99 (98.0)	−1.2 (98.0)	1.2
2[c]	6	−2.0 (99.9)	2.4 (99.0)	2.2 (99.0)	0.91
3[c]	4	−0.68 (99.9)	−0.69 (99.0)	−0.75 (99.0)	1.1
4[d,e]	4	3.9 (99.0)	2.8 (99.0)	2.3 (98.0)	0.83
5[f,e]	4	2.4 (99.0)	1.0 (95.0)	0.77 (95.0)	0.77
5[f,g]	5	0.041 (50.0)	0.98 (99.0)	0.70 (95.0)	0.71
6[h,e]	4	0.38 (80.0)	1.0 (80.0)	0.67 (50.0)	0.67

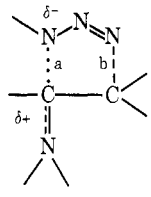
[a] Only rate constants for para-substituted derivatives used. [b] Confidence levels for the significance of h, α, and β appear in parentheses. [c] Reaction described in Table III. [d] Addition of para-substituted phenyl azides to cyclohexanone pyrrolidine enamine. [e] Data from ref 8. [f] Addition of para-substituted phenyl azides to norbornene. [g] Data from ref 6. [h] Addition of para-substituted phenyl azides to cyclopentene.

In Hammett studies related to reaction 2, Huisgen[8] obtained $\rho = +2.54$ in the addition of substituted phenyl azides to cyclohexanone pyrrolidine enamine, but ρ drops in magnitude to ~+0.9 with norbornene[6,8] and cyclopen-

tene.[8] The latter observation suggests less charge separation in the transition states of olefin cycloadditions.

The substituent probe was next attached to the β carbon atom of the dipolarophile to examine charge separation at bond b in the transition state **1**. An excellent fit was obtained with both σ and σ^0 values in the addition of *m*-nitrophenyl azide to a series of substituted phenylacetaldehyde piperidine enamines. The ϵ value (reaction 3, Table V) of 1.1 suggests that σ values provide a better measure of substituent effects.

The negative sign of ρ is inconsistent with the generation of negative charge at the β carbon atom as shown in transition state **1**. Rather, it is best accommodated by well-advanced bond formation at bond b, and therefore, little or no charge separation at bond b (**3**). The rate-enhancing



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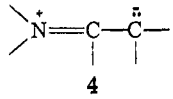
qualities of electron donors on the substituent probe at the β carbon atom are then explicable in terms of the modest stabilization of positive charge at the α carbon atom. Transmission of the electronic effect occurs through the nearly saturated β-carbon atom and this accounts for the reduced magnitude of ρ.[20]

Alternatively, the sign of ρ in reaction 3 could implicate a substituent effect more profoundly influencing the ground-state dipolarophile than transition state. If the ground-state enamine is characterized by charge separation as expressed by the polar resonance form **4**, an electron-attract-



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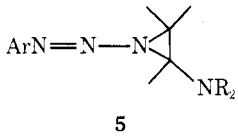
ing substituent could stabilize the enamine and retard the rate of cycloaddition. Such a ground-state controlled model of cycloaddition is not, however, consistent with the sign of ρ in reaction 1.[21] Further, the MO calculations described below suggest little contribution of resonance form **4** to the enamine ground state.

Mechanistically, the cycloaddition of aryl azides to electron-rich enamines[22] proceeds in a concerted fashion with the simultaneous, but uneven, formation of two new σ bonds.[23] Electron reorganization leads to an ordered transition state in which bond formation at b is considerably further advanced than at bond a. The resultant charge separation at bond a accounts for the observed regiospecificity even in sterically encumbered transition states.

Finally, a mechanism based on initial triazene formation (**5**), followed by rearrangement to triazoline,[24] was also re-



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jected in light of the observed conservation of enamine configuration in the cycloadduct.[5] The results of the analogous conversion of *N*-acylaziridines to oxazolines[25] would suggest inversion of configuration in the rearrangement of triazene **5**.

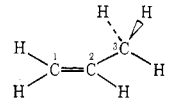
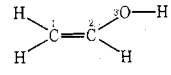
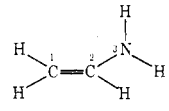
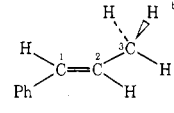
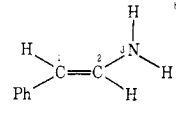
Semiempirical CNDO molecular orbital calculations[26] on a series of 1-substituted alkenes shed light on the nature of

Table VI
Dependence of Rate on Amine. Addition of Phenyl Azide to Acetophenone Enamines[a]

Amine	Basicity of amine (K)	$k_2 \times 10^3$, l. mol^{-1} min^{-1}	Registry no.
Piperidine	1.6×10^{-3}	0.91	
Morpholine	2.4×10^{-6}	0.20	7196-01-2
Pyrrolidine	1.3×10^{-3}	31.	3433-56-5

[a] In chloroform at 44.8°.

Table VII
CNDO Molecular Parameters[a]

Compd	π electron density, q			π bond order, p	
	q_1	q_2	q_3	p_{12}	p_{23}
	1.0570	0.9809		0.9855	
	1.0888	0.9745	1.9367	0.9670	0.2539
	1.0957	0.9708	1.9336	0.9644	0.2623
	1.0577	0.9556		0.9532	
	1.1266	0.9335	1.9236	0.9246	0.2829

[a] Convergence requirements set at $E = 0.0001$, TCONV = 0.001. [b] Phenyl group in plane of carbon–carbon double bond.

ground-state enamine. Although a number of physical phenomena establish π electron delocalization in enamines,[27,28] the evidence adds little to our knowledge of the extent of charge separation in the ground state relative to an alkene as the standard of comparison. π electron density (q) and π bond order (p) were chosen as a measure of the importance of the polar resonance form **4** (Table VII).

The p_{12} values of the five compounds listed are close to unity, with propene displaying the greater degree of π bond localization as expected. Values for the first three entries follow the generally accepted order of increasing resonance effect (+R effect).[29] The π bond orders, p_{23}, reflect the same trend. These data suggest strong localization of π electrons for all compounds listed, and thus little charge separation in the ground state. This conclusion finds support in the calculated q values at C-1, which differ little for the just three compounds.

Although limited in scope, the MO calculations do appear to lend support to the proposed mechanism of cycloaddition and the assertion that substituent effects influence the transition state more profoundly than the initial state.

In reactions in which carbon develops positive charge in the transition state, both OR and NR_2 substituents at the reaction site generally accelerate the rate relative to an alkyl group, e.g., solvolysis reactions. Such is not the case in azide cycloadditions.[30] The striking discrepancy in rates of addition of aryl azides to enamines and enol ethers is likely

Table VIII
Comparative 1,3-Dipole Reactivity

Entry	Dipolarophile	1,3 Dipoles: relative rates of cycloaddition					
		PhC≡NNPh[a]		PhN_3		PhC≡NO[b]	
1	$PhCH{=}CH_2$	11.8	3.5×	1.66[c]	50,000×	3.71	22×
2	PhCH=CH(Pyr)[g]	40.9		83,000.[d]		81.3	
3	$CH_2{=}CHC_5H_{11}$-*n*	1.00		1.00[c]		1.00	
4	$CH_2{=}CHCO_2Et$	350.		41.0[c]		25.8	
5	$Me_2NCH{=}CHCO_2Et$	1.97					
6	(Pyr)CH=$CHCO_2Et$[f]			600.[e]		5.85	

[a] Relative second-order rate constants in benzene: A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashey, and E. Spindler, *Chem. Ber.*, **100**, 2192 (1967). [b] Relative second-order rate constants in ether: ref 35. [c] Relative second-order rate constants: ref 8. [d] $k_2 = 5.7 \times 10^{-5}$ l. mol^{-1} sec^{-1} ($CHCl_3$, 30°) for addition of PhN_3 to phenylacetaldehyde piperidine enamine (Table IX). This value multiplied by pyrrolidine/piperidine rate factor of 35 (Table VI) for relative rate calculation. [e] Estimated by dividing $k_2 = 8 \times 10^{-6}$ l. mol^{-1} sec^{-1} for addition of *m*-nitrophenyl azide to 3-methyl-3-pyrrolidinoacrylic ethyl ester (Experimental Section) by 20 (rate ratio *m*-nitrophenyl azide/phenyl azide, Table III) and multiplying by 36 (rate ratio $CH_2{=}CHCO_2Et/CH_3CH{=}CHCO_2Et$, ref 8). [f] Registry no., 53927-12-1. [g] Pyr = 1-pyrrolidyl.

due to differences in the transition states.[31] It would appear that in the cycloaddition of the enol ether, electron reorganization proceeds with less charge separation, and, therefore, the transition state more closely resembles those involving alkenes where regioselectivity is more sensitive to steric influences.

The chemical phenomena described in this paper implicate a charge-separated transition state in the 1,3-dipolar addition of aryl azides to enamines. In fact, the magnitude of charge separation as revealed by the Hammett correlations appears unmatched in concerted 1,3-dipolar additions. This suggested that the azide–enamine cycloaddition stands apart, not only with regard to 1,3-dipolar additions of azides, but among 1,3-dipolar additions in general. A number of other observations, taken together, lend support to that view.

First, there is the insensitivity of the regiochemistry of cycloaddition to steric effects,[4] which has already been mentioned. Second, compared to other 1,3 dipoles with a "double bond and octet stabilization",[9] the rate of azide cycloaddition is dramatically enhanced by substitution of an electron-releasing amino group at the dipolarophile π electron system (entries 1 and 2, Table VIII). In contrast, the magnitude of rate enhancement brought about by the electron-attracting carboethoxy group is more comparable for all three 1,3 dipoles (entries 3 and 4, Table VIII). Finally, the rate data in Table VIII reveal another example of the selective and powerful rate-enhancing qualities of the amino group in azide 1,3-dipolar additions. For all three 1,3 dipoles, a powerful electron-releasing or a powerful electron-attracting substituent at the dipolarophile π electron system increases the rate. However, in the case of diphenylnitrilimine and benzonitriloxide, substitution of an amino group in a dipolarophile already bearing a carboethoxy group retards the rate of cycloaddition (entries 4–6, Table VIII). In contrast, substitution of an amino group in the β position of ethyl acrylate enhances the rate of phenyl azide addition by a factor of 15 (entries 4 and 6, Table VIII).

Where then does the azide–enamine cycloaddition fit mechanistically into the larger scheme of 1,3-dipolar additions? The reaction, while concerted in nature and consonant with the principle of conservation of orbital symmetry, apparently diverges mechanistically from the more usually encountered isopolar-like transition states.[32] It appears that the azide–enamine reaction is representative of a limiting mechanistic model of concerted 1,3-dipolar addition: the polar transition state model.

A powerful new approach to the rationalization and prediction of substituent effects on the rate and regiochemistry of 1,3-dipolar addition has been advanced by Houk[33] and by Sustmann,[34] and more recently applied advantageously by Huisgen[35] in a study of dipolarophile reactivity toward benzonitriloxide. The model proposed by Houk and Sustmann, which has as its basis perturbation MO theory, promises a more coherent insight into the nature of the reaction; however, the method neither requires consideration of, nor treats the question of charge separation in the transition state.

Experimental Section

Kinetic Method—Data in Table III. Infrared Absorbance Measurements. A Beckman Model IR 12 infrared spectrophotometer was used to determine the absorbance of the azides in all kinetic runs. The base line (I_0) was defined by a line extending from the established base lines on each side of the azide absorption in the 2100-cm^{-1} region. The maximum deflection of each azide was taken as I. The average of three scans provided the actual value of I used. The Bouguer–Beer plots (log I_0/I vs. concentration) were linear in all cases over the concentration ranges studied.

Determination of the Aromatic Azide Concentration. The absorbance, A_s, of a freshly prepared standard azide solution of known molar concentration, M_s, and the absorbance of the unknown sample, A, were determined. Substitution into eq 1 allows the calculation of the unknown molar concentration, M. The term a_ib is the slope of the Bouguer–Beer plot for the azide.

$$\frac{A - A_s}{a_ib} = M - M_s \quad (1)$$

Error Analysis. The major source of error in this method is the reproducibility of I, which varies slightly from scan to scan. The *maximum* error introduced in any single scan was estimated to be ±1.5%. Since the value of azide concentration used is the average of three scans, the magnitude of the error is reduced. The concentration of known phenyl azide solutions containing various concentrations of enamine and aminotriazoline were analyzed for phenyl azide via this method and the concentrations were determined within ±1%.

Determination of Rate. Freshly purified enamine was weighed into a volumetric flask, dissolved in the solvent, stoppered, and placed in a constant-temperature bath (±0.2°). A known amount of pure azide was placed in a small vial and placed in the constant-temperature bath along with a vial of solvent and the reaction vessel. After thermal equilibrium was established, the azide was rapidly and quantitatively transferred into the volumetric flask, diluted to volume by the addition of solvent, mixed, and transferred to the foil-encased reaction vessel. The solution was blanketed with a nitrogen atmosphere and the flask was sealed with a silicone rubber septum. Periodically 0.1 ml of the solution was removed via microliter syringe, quenched in cold solvent in a 1-ml volumetric flask, and diluted to volume. The absorbance was immediately determined on this solution. Reactions were followed to between 20

Table IX
Rate Constants Derived for Calculation of Activation Parameters (Table I)

	Rate constant, $k_2 \times 10^3$ l. mol^{-1} min^{-1}		
Dipolarophile[a]	30.0°	38.9°	44.8°
PhC(Pip)=CH_2[b,d]	0.26 ± 0.01	0.58 ± 0.02	0.91 ± 0.03
PhCH=CH(Pip)[c]	3.4 ± 0.1	6.9 ± 0.1	10.0 ± 0.3

[a] PhN_3 is the dipole. [b] Initial concentration in moles/liter; azide, 1.20; enamine, 2.40. [c] Initial concentration in moles/liter; azide, 1.00; enamine, 2.00. [d] Pip = *N*-piperidyl.

Table X
Initial Concentrations of Reactants in Kinetic Runs (Table III)

Reaction[a]	Azide[b]	Enamine[b]
1.	1.20	2.40
2. *p*-OCH_3, CH_3, H, Br, Cl	0.86	1.72
p-NO_2, *m*-NO_2	0.10	0.20
3.	0.10	0.20

[a] Reactions described in Table III. [b] Concentration in moles/liter.

and 40% of completion. In several cases clean second-order kinetics were followed for at least 70% of reaction. The rate constants reported are the average of multiple runs in all cases. The average deviation from the mean is also recorded.

Kinetic Method—Pyrrolidine Enamine of Ethyl Acetoacetate. To a solution of 0.175 g (0.00096 mol) of 3-methyl-3-pyrrolidinoacrylic ethyl ester in a 1-ml volumetric flask was added 0.330 g (0.0020 mol) of *m*-nitrophenyl azide. Deuteriochloroform was added to bring the volume of the solution to 1 ml. About 0.4 ml of the solution was transferred to an NMR sample tube which was sealed with a stopper. Periodically the NMR spectrum of the solution was recorded and from the integration of the region of δ 4.85–3.75, the concentration of the enamine and the adduct was determined. The rate constant in Table VIII is the average of two independent runs.

Solvents. Analytical reagent grade chloroform (Mallinckrodt Chemical Works) was used without purification in all the kinetic work with the exception of the study of solvent effects. Reagent-grade acetonitrile (Matheson Coleman and Bell) was distilled from P_2O_5 prior to use. Absolute ethanol was distilled from magnesium. The samples run in acetonitrile were quenched and diluted in acetonitrile and the samples run in absolute ethanol were quenched and diluted with chloroform.

Material Balance. 1,5-Diphenyl-5-(1-piperidino)-4,5-dihydro-1,2,3-triazole. A solution of 0.528 g (0.0044 mol) of phenyl azide and 0.834 g (0.0045 mol) of the piperidine enamine of acetophenone in chloroform (5 ml) was sealed in a flask with a nitrogen atmosphere and placed in the dark for 2 days. The solvent was removed *in vacuo* and distillation of the residue at a bath temperature of 36° (0.12 mm) afforded 0.326 g (62%) of phenyl azide as determined by GLC (20% DC550/Anakrom ABS, 170°, 15 psi). The nonvolatile material was dissolved in pentane and decolorized. Crystallization afforded 0.349 g (26%) of the crude aminotriazoline, mp 96–103° (lit.[4] mp 109–110.5°).

Duplication of the above procedure accounted for 85% of the starting material as the aminotriazoline or the unreacted phenyl azide.

Preparation of Enamines (Table XI). Enamines of ketones were prepared by the method of Stork.[15] The procedure of Mannich[36] was employed for the preparation of enamines of aldehydes. The substituted phenylacetaldehydes were prepared by rearrangement of the corresponding styrene oxide.[37] The following enamines are reported in the literature: the piperidine enamine of phenylacetaldehyde,[36] *p*-chlorophenylacetaldehyde,[38] acetophenone,[4] the pyrrolidine enamine of acetophenone,[39] the morpholne enamine of acetophenone,[40] and the pyrrolidine enamine of ethyl acetoacetate.[41]

Preparation of Azides. Phenyl azide was prepared by the method of Linsay and Allen.[42] The following substituted phenyl azides were prepared by the method of Smith and Boyer:[43] *m*-nitrophenyl azide,[44] *p*-nitrophenyl azide,[44] *p*-chlorophenyl azide,[45] *p*-bromophenyl azide,[45] *p*-methylphenyl azide,[45] *p*-methoxyphenyl azide.[46]

Table XI
New Enamines

Piperidine enamine	Physical properties[a]
Substituted Phenylacetaldehydes	
m-Methoxy	bp 136–138° (0.1 mm), n^{25}D 1.6110
p-Bromo	mp 87.5–88.5°
p-Methyl	mp 42–43°
Substituted Acetophenones	
p-Bromo	bp 99–102° (0.1 mm), n^{25}D 1.5845
m-Methoxy	bp 104–106° (0.1 mm), n^{25}D 1.5563
m-Methyl	bp 69–72° (0.1 mm), n^{25}D 1.5505
p-Methoxy	bp 92.5–94.5° (0.1 mm), n^{25}D 1.5592
m-Nitro	mp 76–77°
p-Chloro	bp 80–83° (0.06 mm), n^{25}D 1.5661
p-Methyl	bp 78° (0.1 mm), n^{25}D 1.5510

[a] Satisfactory analytical data for C, H, N (±0.35%) were provided for these compounds: Ed.

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Registry No.—3-Methyl-3-pyrrolidinoacrylic acid ethyl ester, 2723-42-4.

References and Notes

(1) (a) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N.Y., Sept 7–12, 1969. (b) Taken in part from the Ph.D. Thesis of M.K.M., Arizona State University, 1967. (c) Supported in part by a generous grant from Parke, Davis and Co.
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Cycloaddition. XVII. The Twelve Products of Photosensitized Addition of 1-Chloropropene to Cyclopentadiene

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cis- and *trans*-1-chloropropene have been added to cyclopentadiene both thermally at 200° and with β-acetonaphthone as a photosensitizer. As in other similar cases, the thermal reaction is a stereospecific Diels–Alder process. The photosensitized cycloaddition leads to mixtures of the same four 1,4 and eight 1,2 cycloadducts from both geometrical isomers of 1-chloropropene. Structures were established by a set of syntheses, identities, and correlations involving the thermal and photosensitized cycloadducts of 1,1-dichloropropene to cyclopentadiene, their dechlorination with tributyltin hydride, catalytic hydrogenation of the bicyclo[3.2.0]heptenes to the bicycloheptanes, and close comparison of NMR spectra.

In connection with our studies of cycloaddition reactions proceeding through biradical intermediates, we have studied the thermal and photosensitized cycloaddition of both *cis*- and *trans*-1-chloropropene to cyclopentadiene. This paper describes the isolation and identification of the products of those reactions.

Results

Isolation of Pure *cis*- and *trans*-1-Chloropropene. Commericial technical grade "1-chloropropene" (Columbia Organic Chemicals Co., Inc., Columbia, S.C.) as received was a mixture of about 10% 2-chloropropene, bp 23–24°, 25% *cis*-1-chloropropene, bp 31–32°, and 65% *trans*-1-chloropropene, bp 35–36°.[2]

Several workers have separated the above compounds by distillation and VPC, and established the structures of the cis and trans materials by NMR,[3] ir correlation,[4a] and dipole moment.[4b]

Isolation of pure *cis*- (98+%) and *trans*-1-chloropropene (98+%) was accomplished by distillation using a spinning band column. Because of the great difficulty of the separation, however, a mixture consisting of 15% cis and 85% trans was used for generating photoadduct mixtures for preparative VPC.

Isolation and Identification of the 1,4 Adducts. The 1,4 adducts of cyclopentadiene and *cis*- and *trans*-1-chloropropene were produced by thermal reaction of a mixture of the 1-chloropropene isomers (15:85, respectively) with cyclopentadiene at 200° in a sealed tube. VPC analysis of the product on a β,β'-oxydipropionitrile (β,β'-ODPN) column indicated the presence of four peaks of retention times greater than those of dicyclopentadiene. From pure *trans*-1-chloropropene (99+%) and cyclopentadiene, olefin was recovered unisomerized and the product mixture consisted of dicyclopentadiene and two fractions (ratio 67.5:32.5) of retention time corresponding to the first and third peaks in the chromatogram from the mixed olefin isomers and cyclopentadiene. Therefore the first and third peaks correspond to the thermal *trans*-1-chloropropene–cyclopentadiene adducts and the second and fourth peak correspond to the *cis*-1-chloropropene–cyclopentadiene adducts. Each component in the cis, trans thermal reaction was collected preparatively on β,β'-ODPN.

The assignment of the structures is based chiefly on the NMR spectra and some chemical evidence to follow. The assumptions relied upon were (a) 1,4 Diels–Alder addition with retention of configuration in common with dichloroethylene[4a] and alkylethylenes;[5] (b) that endo substituents (proton[6] or methyl[5]) are shifted upfield (shielded) relative to exo substituents; (c) that C_7 protons couple in a W pattern with endo protons.[6a,7]

The NMR peaks of the Diels–Alder addition compounds are listed in Table I with their structural assignments.

Chemical evidence that further confirms the identity of