

## 1,3-Dipolar Character of Six-membered Aromatic Rings. Part 38.<sup>1</sup> FMO Treatment of Peri-, Site, Regio-, and Stereo-selectivity, and Relative Reaction Rates of Cycloaddition Reactions

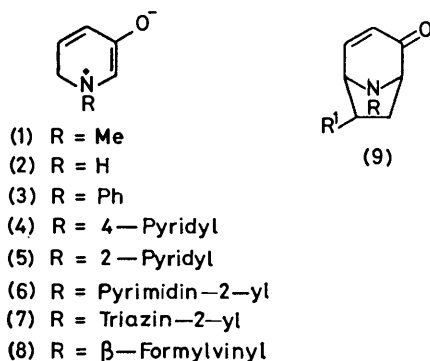
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The kinetic rates and peri-, site, regio-, and stereo-selectivity of the reactions of variously 1-substituted 3-oxido-pyridiniums have been correlated by FMO theory. Regioselectivity is well explained by the standard perturbation treatment, but for correlation of the relative rates it is necessary to use the simpler equation of Sustmann. For the most part, stereoselectivity is well explained by a simple monopole repulsion treatment. Peri- and site selectivity are also discussed and are well correlated for reactions of dienes but not for fulvenes.

PREVIOUS papers of this series demonstrated that approximate CNDO/2 calculations on 1-methyl-3-oxido-pyridinium (1)<sup>2</sup> rationalised the site, peri-, regio-, and stereo-selectivity of olefinic dipolarophile cycloadditions of type (1, 2, 3, 5, 6, 7)  $\rightarrow$  (9) (cf. ref. 3). We now report more precise calculations and compare them with these selectivities and with kinetic rates (already reported in ref. 4).

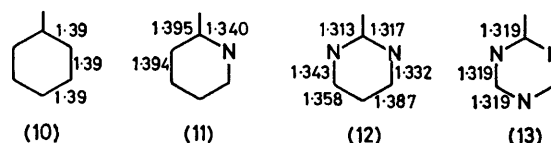
**Molecular Geometries.**—We have used the same bond lengths and angles for the pyridinium ring of the betaines as previously justified.<sup>2</sup> The bond lengths and angles for the betaine *N*-substituents and dipolarophiles utilised are given in formulae (10)—(13) [geometry (11) was also used for 4-pyridyl]. For the 5-nitro-2-pyridyl, 4,6-dimethylpyrimidin-2-yl, and for the 4,6-dimethoxy-(and 4,6-diphenyl)-triazin-2-yl substituents, we have used in the calculations the corresponding unsubstituted heteroaryl substituents (11)—(13) respectively.



This approximation is needed because of considerations of calculation time: the neglect of methyl substituents should have little effect; neglecting the 5-nitro-group is expected to give a less reactive molecule whereas neglecting two methoxy-groups should give a more reactive molecule (the effects of phenyl substitution are less easily predicted).<sup>†</sup>

<sup>†</sup> Throughout this paper, and particularly in the Tables, wherever the 2-pyridyl, pyrimidin-2-yl, and triazin-2-yl substituents are referred to, the experimental data actually come from the corresponding 5-nitro-2-pyridyl, 4,6-dimethylpyrimidin-2-yl, and 4,6-dimethoxytriazin-2-yl compounds. Similarly for  $\beta$ -formylvinyl, the experimental data refer to *p*-chlorobenzoylvinyl.

As will become clear, the orbital energies in the 1-aryl-3-oxido-pyridiniums are considerably affected by the dihedral angle between the pyridine ring and the *N*-aryl



For (10), cf. I. L. Karle, *J. Chem. Phys.*, 1952, **20**, 65; J. N. Murrell, V. M. S. Gil, and F. B. Van Duijneveldt, *Rec. Trav. chim.*, 1965, **84**, 1399; for (11), B. Bak, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectroscopy*, 1958, **2**, 361; for (12), P. J. Wheatley, *Acta Cryst.*, 1960, **13**, 80; for (13), ref. 7, and P. J. Wheatley, *Acta Cryst.*, 1955, **8**, 224.

ring. For the *N*-phenyl and 4-pyridyl substituents we have taken 30° for this angle: *i.e.* near the values for biphenyls.<sup>5</sup> For the *N*-(pyrimidin-2-yl) and *N*-(triazin-2-yl) substituents, we have taken 0°: X-ray studies of 3,6-diphenyl-*s*-tetrazine,<sup>6</sup> and 2,4,6-tris-(*p*-chlorophenyl)-

TABLE I

Sources of geometry for dipolarophiles

Dipolarophile	Ref.	Dipolarophile	Ref.
Acrylonitrile	<i>a</i>	Cyclohexene	<i>h</i>
<i>n</i> -Butyl vinyl ether	<i>b</i>	Indene	<i>i</i>
Methyl acrylate	<i>c</i>	Cyclopentadiene	<i>j</i>
Propene	<i>d</i>	1,1-Dimethylfulvene	<i>k</i>
<i>s-trans</i> -Butadiene	<i>e</i>	Allyl alcohol	<i>l</i>
<i>s-cis</i> -Butadiene	<i>f</i>	Vinyl acetate	<i>b, c</i>
Difluoroketen	<i>g</i>		

<sup>a</sup> M. Rouault and C. St.-Arnaud, *Canad. J. Phys.*, 1957, **35**, 504. <sup>b</sup> S. Samdal and H. M. Seip, *J. Mol. Structure*, 1975, **28**, 193 (data obtained for methyl vinyl ether). <sup>c</sup> G. Williams, N. L. Owen, and J. Sheridan, *Trans. Faraday Soc.*, 1971, **67**, 922. <sup>d</sup> D. R. Lide, jun., and D. E. Mann, *J. Chem. Phys.*, 1957, **27**, 868. <sup>e</sup> A. Almennigen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, 1958, **12**, 1221. <sup>f</sup> L. A. Burke, G. Leroy, and M. Sana, *Theor. Chim. Acta*, 1975, **40**, 313. <sup>g</sup> J. Sheridan in 'Advances in Molecular Spectroscopy,' ed. A. Mangini, Pergamon, London, 1962, Vol. 1, p. 139; V. W. Laurie and D. T. Pence, *J. Chem. Phys.*, 1963, **38**, 2693 (data obtained by combining CH<sub>2</sub>:C=O and CH<sub>2</sub>:CF<sub>2</sub>). <sup>h</sup> T. Ogata and K. Kozima, *Bull. Chem. Soc. Japan*, 1969, **42**, 1263. <sup>i</sup> J. F. Southern, *Diss. Abstr. Int. B*, 1973, **33**, 3586. <sup>j</sup> L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, 1965, **43**, 2765. <sup>k</sup> L. Praud, P. Millie, and G. Berthier, *Theor. Chim. Acta*, 1968, **11**, 169. <sup>l</sup> R. Gunde and A. Azman, *J. Mol. Structure*, 1975, **27**, 212.

*s*-triazine<sup>7</sup> suggest this. The angle for the *N*-(2-pyridyl) substituent is less easy to decide: it must

reasonably lie between 0 and 30°; we have taken 20° but alteration in the range 17–25° does not significantly change the calculated results (reliable experimental data are not available, thus an early paper<sup>8</sup> suggested 10–17° for 2,2-bipyridyl, and another<sup>9</sup> coplanarity for 3-phenylpyridazine).

Details of the geometry taken for the dipolarophiles are collected in Table 1.

TABLE 2  
Frontier orbital energies (eV) (CNDO/2)  
for a series of betaines [cf. (14)]

R	$\theta$ (°)	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$
Me (1)		-8.892	1.396
H (2)		-9.031	1.303
Ph (3)	0.0	-8.696	1.205
	23.5	-8.691	1.301
	30.0	-8.688	1.355
	37.0	-8.688	1.426
4-Pyridyl (4)	30.0	-8.824	0.931
2-Pyridyl (5)	0.0	-8.745	0.931
	6.5	-8.745	0.939
	20.0	-8.743	0.999
	30.0	-8.740	1.078
	35.0	-8.740	1.124
	40.0	-8.740	1.176
Pyrimidin-2-yl (6)	0.0	-8.699	0.950
Triazin-2-yl (7)	0.0	-8.789	0.708
$\beta$ -Formylvinyl (8)	0.0 <sup>a</sup>	-9.001	0.346
	180.0	-8.968	0.297

<sup>a</sup> As in structure (15).

**HOMO and LUMO Energies for Betaines.**—These energies calculated by the CNDO/2 method are given in Table 2. For the triazinyl and pyrimidinyl substituents we report calculations for a dihedral angle of 0° only, but for phenyl and 2-pyridyl as substituents we illustrate in

importance of 'HOMO-LUMO' contributions and it is generally agreed that for comparisons within a series

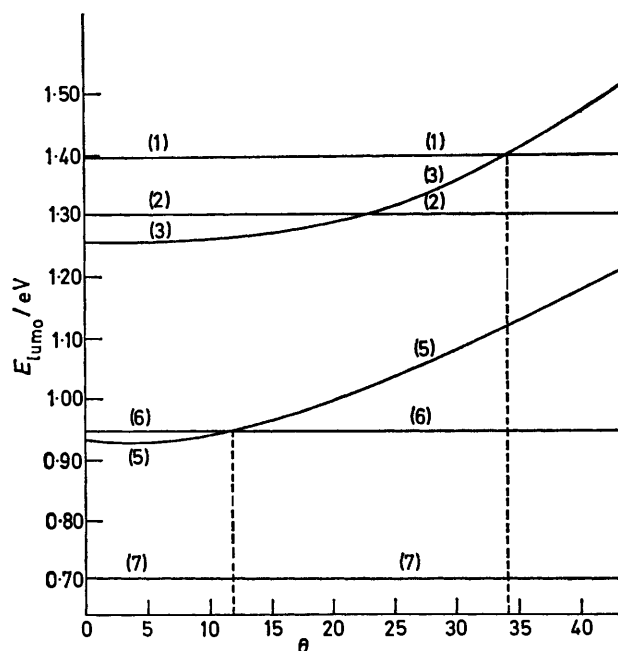


FIGURE 1 LUMO energies (eV) for betaines as a function of dihedral angle (CNDO/2 calculations)

possessing similar transition states, it is the covalent term which varies the most. This has frequently allowed the use of an equation involving such terms alone to interpret successfully experimental results.<sup>10</sup>

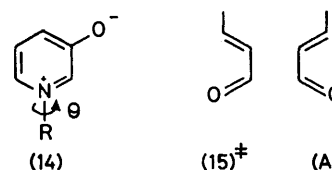
TABLE 3  
Coefficients (CNDO/2) for betaines

R	$\theta$ (°)	C-2		C-4		C-6		O	
		HO	LU	HO	LU	HO	LU	HO	LU
Me (1)		0.5441	0.4746	0.3282	-0.5001	-0.3678	0.4098	-0.6731	-0.0085
H (2)		0.5480	0.4902	0.3271	-0.5167	-0.3704	0.4063	-0.6704	-0.0116
Ph (3)	30	0.5427	0.4244	0.3313	-0.4425	-0.3765	0.3734	-0.6671	-0.0141
4-Pyridyl (4)	30	0.5403	0.4119	0.3306	-0.4222	-0.3688	0.3842	-0.6729	-0.0157
2-Pyridyl (5)	20	0.5375	0.4192	0.3336	-0.4231	-0.3723	0.3872	-0.6727	-0.0212
Pyrimidin-2-yl (6)	0	0.5421	0.4256	0.3295	-0.4348	-0.3673	0.3995	-0.6738	-0.0175
Triazin-2-yl (7)	0	0.5439	0.4115	0.3281	-0.4202	-0.3659	0.3940	-0.6739	-0.0169
$\beta$ -Formylvinyl (8)	0	0.5504	0.3528	0.3243	-0.3716	-0.3673	0.3510	-0.6694	-0.0071

Table 2 and Figure 1 the dependence of the LUMO orbital energies on the dihedral angle taken [whereas the  $E(\text{HOMO})$  remains almost constant]. From Figure 1, and the experimental finding that the *N*-phenyl-betaine (3) is more reactive than the *N*-methyl-betaine (1), it follows that the dihedral angle for (3) must be less than 35°. Similarly, as the *N*-(pyrimidin-2-yl)-betaine (6) is more reactive than the *N*-(2-pyridyl)-analogue (5) (and the experimental comparison involves the 5-nitro-2-pyridyl substituent which is certainly further activated) the dihedral angle for (5) must be above 13°. The values justified previously are in accord with these restrictions. Table 3 records values of orbital coefficients at the positions of interest.

**Theoretical Model.**—The general method of perturbation applied to interacting systems has indicated the

In Hückel calculations in which electron-electron interactions are not included specifically, the evaluation



Cf. E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, 1966, **45**, 104. Calculations for the orientation (A) give very similar results and are not separately included.

of the HOMO-LUMO interaction terms is relatively simple;<sup>11</sup> their evaluation is more complex for SCF methods of the CNDO type. However following Sustmann,<sup>12</sup> the semiempirical nature of the CNDO

method can justify limiting the contribution of covalent interactions to that given in equation (1) which is limited to interaction between atoms which are becoming directly bonded to each other. We use equation (1) in the present paper: the more negative the values of  $\Delta E_{\text{int}}$  the greater the expected stabilisation of the transition state.

In addition, Sustmann<sup>12</sup> found that in certain data sets the experimental findings were rationalised by

$$\Delta E_{\text{int}}^2 = \frac{[(C_{\text{HO}^1}C_{\text{LU}^1} + C_{\text{HO}^2}C_{\text{LU}^2})\beta_{rs}]^2}{E_{\text{HO}^A} - E_{\text{LU}^B}} + \frac{[(C_{\text{HO}^1}C_{\text{LU}^1} + C_{\text{HO}^2}C_{\text{LU}^2})\beta_{rs}]^2}{E_{\text{HO}^B} - E_{\text{LU}^A}} \quad (1)$$

$$\Delta E_{\text{int}}^2 = K^2 \left[ \frac{1}{E_{\text{HO}^A} - E_{\text{LU}^B}} + \frac{1}{E_{\text{HO}^B} - E_{\text{LU}^A}} \right] \quad (2)$$

equation (2), which derives from equation (1) if the numerators remain constant. Trong Anh<sup>13</sup> has justified

neglected in comparison with the second term, thus simplifying equation (3) to the equation (4) utilised in the

$$\Delta E_{\text{AB}}^1 = \sum_k^A \sum_l^B [q_k q_l \gamma_{kl} + (e^2/r_{kl} - \gamma_{kl})Z_k Z_l] \quad (3)$$

$$\Delta E_{\text{steric}}^1 = \sum_k^A \sum_l^B (e^2/r_{kl} - \gamma_{kl})Z_k Z_l \quad (4)^*$$

present paper. Here, the higher the positive value of  $\Delta E_{\text{steric}}$  the less favourable is the transition state.

**Dimerisation.**—Application of equation (1) indicates (Table 4) that regioisomers of type 2,2'-4,6' (16) should be formed more easily than those of type 4,2'-2,6' (17). This is in complete agreement with the experimental findings for the 2-pyridyl (5) and the triazin-2-yl betaines (7)<sup>17</sup> for which only dimers of type (16a) are formed.<sup>2</sup> The pyrimidin-2-yl-betaine (6)<sup>2</sup> forms the dimer of type (16a) by kinetic control although equi-

TABLE 4

Transition-state energies [energies in a.u.; 1 a.u. =  $4.3598 \times 10^{-18}$  J; however energies calculated by formulae (1), (2), and (4) are not directly comparable] for thermal dimerisation of 1-substituted 3-oxidopyridiniums

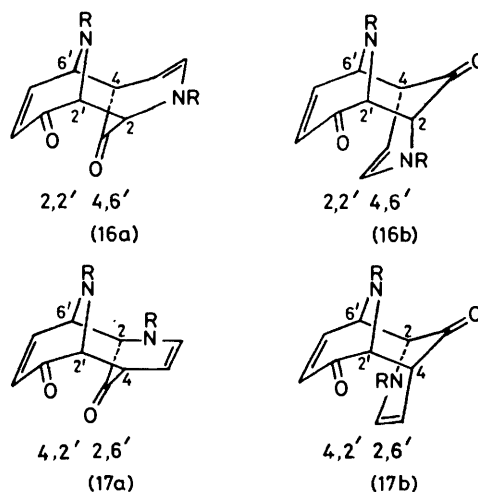
Eqn.	Isomer		Me (1)	Ph (3) ( $\theta = 30^\circ$ )	4-Pyridyl (4) ( $\theta = 30^\circ$ )	2-Pyridyl (5) ( $\theta = 20^\circ$ )	Pyrimidin- 2-yl (6) ( $\theta = 0^\circ$ )	Triazin- 2-yl (7) ( $\theta = 0^\circ$ )	$\beta$ -Formyl- vinyl (8) ( $\theta = 0^\circ$ )
	orientation	structure							
(1)	2,2'-4,6'	(16)	-0.0528	-0.0438	-0.0423	-0.0436	-0.0457	-0.0437	-0.0340
	2,6'-4,2'	(17)	-0.0518	-0.0430	-0.0418	-0.0430	-0.0453	-0.0435	-0.0343
(2)	2,2'-4,6'	(16)	-5.29	-5.42	-5.58	-5.61	-5.64	-5.73	-5.82
	2,6'-4,2'	(17)							
(4)	2,2'-4,6'	{(16a)	5.21	8.58	8.51	8.42	8.47	8.42	6.85
		{(16b)	5.57	8.14	8.09	7.94	7.90	7.88	6.77
	2,6'-4,2'	{(17a)	5.21	10.21	10.04	10.17	8.63	8.57	6.59
		{(17b)	5.44	7.85	7.79	7.87	7.59	7.57	6.51
Exp. %		(none)	(none)	(none)	100% (16a) 2,2'-4,6' <sup>a</sup>	100% (16a) 2,2'-4,6' <sup>a,b</sup>	100% (16a) 2,2'-4,6' <sup>c</sup>	100% (16a) 2,2'-4,6' <sup>d</sup>	

<sup>a</sup> Ref. 2. <sup>b</sup> The equilibrium value is 67% 2,6'-4,2' (17a) and 33% 2,2'-4,6' (16a). <sup>c</sup> Ref. 17. <sup>d</sup> A. R. Katritzky, N. Dennis, G. W. Fischer, S. Rahimi-Rastgoo, and G. J. Sabongi, unpublished results.

this model by the hypothesis that the distance between the reactants in a series of transition states is itself proportional to the product of the coefficients of the frontier orbitals. As the integrals  $\beta_{rs}$  are proportional to the overlap, *i.e.* inversely proportional to the distance, then terms of type  $(C_{\text{HO}}C_{\text{LU}}\beta_{rs})$  become invariant. We have also used equation (2) in the present paper: as with equation (1) the more negative the value of  $\Delta E_{\text{int}}$  the greater the expected stabilisation of the transition state.

If the second-order perturbational treatment is limited to the principal frontier orbital interactions [equations (1) and (2)], it is obviously impossible to differentiate between the formation of *exo*- and *endo*-stereochemical isomers. The inclusion of the so-called secondary interactions as suggested by Woodward and Hoffman is not always sufficient to explain the observed orientation.<sup>14</sup> Sustmann<sup>15</sup> has shown that the orientation of addition of cyclopropene to cyclopentadiene could be correlated by using first-order interaction terms corrected by including repulsion terms of the type proposed by Dewar<sup>16</sup> and adopted in the MINDO/2 treatment. The expression for such interaction terms of the first order is given by equation (3); however, for species not bearing high charges, the first term can be

bration *via* dedimerisation gives considerable amounts of (17a) by thermodynamic control.



However equation (1) cannot explain the relative ease of dimerisation in this series: we find experimentally

\*  $r_{kl}$  is the distance between centre  $s_k$  and  $l$ ;  $\gamma_{kl}$  is the exchange integral, calculated empirically following the method of K. Ohno, *Theor. Chim. Acta*, 1964, 2, 219;  $Z_k$  is the charge on atom  $k$ .

zero tendency for the *N*-methyl (1), *N*-phenyl (3), and 4-pyridyl (4) compounds with dimerisation rate increasing for (5) ~ (8) < (6) < (7). Equation (1) would

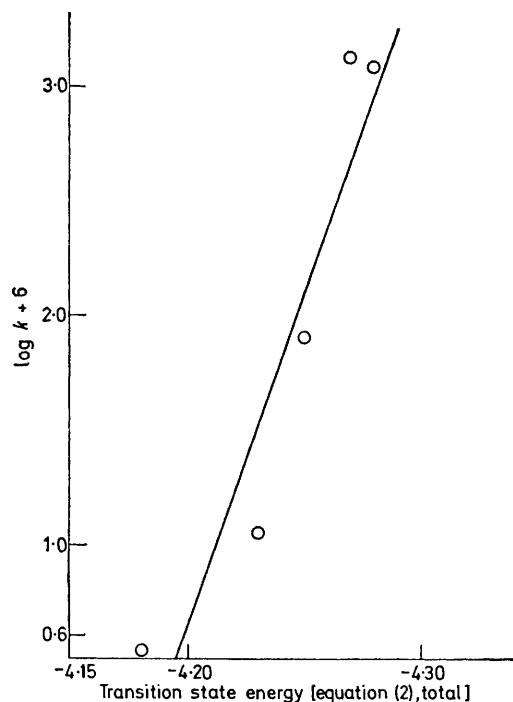


FIGURE 2 Plot of  $\log k + 6$  against transition state energy, as calculated by equation (2), for addition of methyl acrylate to a series of 1-substituted 3-oxidopyridiniums

suggest rates of (1)  $\gg$  (6) > (3) ~ (7) ~ (5), a completely different order. Equation (2) gives the order

formation indeed varies in the way previously discussed; *i.e.*, that the distance between the reactive species in the transition state for dimer formation is related to the orbital coefficients on the atoms becoming linked.

We have utilised equation (4) in an attempt to rationalise the stereochemistry of the addition. However, in each case the steric term should favour *endo*-addition in place of the *exo*-process exclusively found. We believe that steric hindrance between remote parts of the molecules intervenes to disfavour *endo*-attack; this hypothesis is supported by the examination of models.

*Reactions of Methyl Acrylate with a Series of Betaines.*—The data are set out in Table 5. Again equation (1) indicates that regioisomers of type (18) should be preferred in all cases—in complete agreement with experiment. Again the relative rates which are found to increase for (1)  $\ll$  (3)  $\ll$  (6) *cannot* be explained by treatment using equation (1) [which predicts (1) > (6) ~ (3)] but are fully explained by treatment using equation (2) which indicates (1)  $\ll$  (3)  $\ll$  (5) < (6) < (7). The  $\log k$  values (Table 5) show a fair linear relation with the total  $E_{\text{int}}$  calculated by equation (2) (Figure 2). The data for 2-pyridyl are too high for the monotonic relation expected; we ascribe this to the use of the 5-nitro-2-pyridyl substituent in the kinetic work; the points for phenyl, pyrimidin-2-yl, and 4-pyridyl are precisely linear.

Analysis into the individual HOMO (betaine)–LUMO (dipolarophile) ( $H_B L_D$ ) and LUMO (betaine)–HOMO (dipolarophile) ( $L_B H_D$ ) contributions to the total energy term (see Table 5) shows that [using the treatment of equation (2)] the increased reactivity of the phenyl compound over the methyl and hydrogen analogue

TABLE 5

Transition-state energies (a.u.) for addition of methyl acrylate to a series of 1-substituted 3-oxidopyridiniums

Eqn.	Me (1)	H (2)	Ph (3) ( $\theta = 30^\circ$ )	4-Pyridyl (4) ( $\theta = 30^\circ$ )	2-Pyridyl (5) ( $\theta = 20^\circ$ )	Pyrimidin- 2-yl (6) ( $\theta = 0^\circ$ )	Triazin- 2-yl (7) ( $\theta = 0^\circ$ )	$\beta$ -Formyl- vinyl (8) ( $\theta = 0^\circ$ )
(1)								
(18)	$H_B L_D$ -0.0332	-0.0333	-0.0342	-0.0332	-0.0335	-0.0336	-0.0334	-0.0335
	$L_B H_D$ -0.0098	-0.0101	-0.0079	-0.0080	-0.0080	-0.0087	-0.0084	-0.0065
	Total -0.0430	-0.0434	-0.0422	-0.0413	-0.0418	-0.0423	-0.0418	-0.0400
(19)	$H_B L_D$ -0.0285	-0.0287	-0.0298	-0.0287	-0.0291	-0.0290	-0.0287	-0.0287
	$L_B H_D$ -0.0094	-0.0097	-0.0077	-0.0079	-0.0081	-0.0085	-0.0083	-0.0065
	Total -0.0379	-0.0384	-0.0375	-0.0366	-0.0372	-0.0375	-0.0370	-0.0352
(2)								
(18, 19)	$H_B L_D$ -2.40	-2.37	-2.45	-2.42	-2.44	-2.45	-2.43	-2.38
	$L_B H_D$ -1.78	-1.79	-1.78	-1.83	-1.83	-1.83	-1.86	-1.91
	Total -4.18	-4.16	-4.23	-4.25	-4.27	-4.28	-4.29	-4.29
(4)	(18b) <i>exo</i> 3.66	2.88	6.16	6.50	6.07	5.43	5.42	4.43
	(18a) <i>endo</i> 5.64	3.51	4.54	4.81	4.72	4.47	4.47	4.16
	(19b) <i>exo</i> 5.30	2.91	5.22	5.30	5.14	5.29	5.27	4.73
	(19a) <i>endo</i> 4.08	3.72	4.69	4.68	4.60	4.64	4.64	4.37
Exp. %	(18b) 50 <sup>a</sup>	50 <sup>b</sup>	37 <sup>c</sup>	0 <sup>d</sup>	75 <sup>e</sup>	42 <sup>f</sup>	60 <sup>g</sup>	60 <sup>h</sup>
	(18a) 50	50	63	100	25	58	40	40
Exp. $\log k + 6$	0.56 <sup>i</sup>		1.07 <sup>i</sup>	1.90 <sup>j</sup>	3.12 <sup>j</sup>	3.08 <sup>i</sup>		

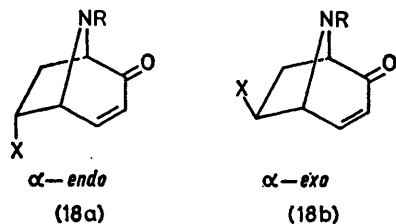
<sup>a</sup> A. R. Katritzky and Y. Takeuchi, *J. Chem. Soc. (C)*, 1971, 874. <sup>b</sup> J. Banerji, N. Dennis, J. Frank, A. R. Katritzky, and T. Matsuo, *J.C.S. Perkin I*, 1976, 2334. <sup>c</sup> (i) N. Dennis, A. R. Katritzky, T. Matsuo, S. K. Parton, and Y. Takeuchi, *J.C.S. Perkin I*, 1974, 746; (ii) N. Dennis, A. R. Katritzky, S. K. Parton, Y. Nomura, Y. Takahashi, and Y. Takeuchi, *J.C.S. Perkin I*, 1976, 2289.

<sup>d</sup> A. R. Katritzky, J. Banerji, A. Boonyarakvanich, A. Cutler, N. Dennis, S. Q. A. Rizvi, G. J. Sabongi, and H. Wilde, preceding paper. <sup>e</sup> Ref. 3. <sup>f</sup> Ref. 20. <sup>g</sup> Ref. 17. <sup>h</sup> Table 4 footnote *d*. <sup>i</sup> Rate constants at 54 °C calculated from variable temperature kinetic data in ref. 4. <sup>j</sup> Measured at 54 °C, unpublished results with B. El-Osta, G. Musumarra, and C. Ögretir.

(1) < (3) < (4) < (5) < (6) < (7) in complete agreement with experiment (Table 4). This result indicates that the structure of the transition state for dimer

depends on increase in  $H_B L_D$ . However the reactivity sequence (3)  $\ll$  (5) < (6) < (7) is dominated by increasing  $L_B H_D$  contributions whilst  $H_B L_D$  remains

almost constant. This is of course as expected: the energy of  $H_B$  increases with increasing conjugation, but



increasing numbers of heteroatoms decrease the  $L_B$  value leaving  $H_B$  little affected.

( $\text{EtOCH}_2\text{CH}_2$ ) again Table 6 data predict preferred regioisomers (18) for all betaines in complete agreement with experiment. Again the relative rates, which from qualitative preparative work we know to increase in the same manner as those for methyl acrylate, cannot be explained by equation (1), but are rationalised by treatment using equation (2). The incomplete quantitative rate data once again indicate too high a value for 2-pyridyl: the discrepancy is greater than previously discussed for the acrylate addition, in good agreement with the supposition that it is the 5-nitro-group which should enhance the addition with the electron-rich olefin more than for the electron-deficient acrylate.

TABLE 6

Transition state energies (a.u.) for addition of ethyl vinyl ether to a series of 1-substituted 3-oxidopyridiniums

Eqn.	Structure	Ph (3) ( $\theta = 30^\circ$ )	4-Pyridyl (4) ( $\theta = 30^\circ$ )	2-Pyridyl (5) ( $\theta = 20^\circ$ )	Pyrimidin- 2-yl (6) ( $\theta = 0^\circ$ )	Triazin- 2-yl (7) ( $\theta = 0^\circ$ )	$\beta$ -Formyl- vinyl (8) ( $\theta = 0^\circ$ )
(1)	(18)	-0.0482	-0.0472	-0.0479	-0.0486	-0.0479	-0.0447
	(19)	-0.0462	-0.0457	-0.0463	-0.0470	-0.0464	-0.0435
(2)		-3.95	-3.99	-4.00	-4.01	-4.03	-4.06
(4)	(18b) <i>exo</i>	5.42	6.69	5.46	4.81	4.79	3.94
	(18a) <i>endo</i>	3.69	3.76	3.64	3.63	3.62	3.33
	(19b) <i>exo</i>	3.87	3.95	3.78	3.89	3.88	3.56
	(19a) <i>endo</i>	4.78	4.89	4.34	4.75	4.74	4.48
Exp. %		<i>a</i>	100% (18a) <sup>b</sup>	100% (18a) <sup>c</sup>	100% (18a) <sup>d</sup>	100% (18a) <sup>e</sup>	100% (18a) <sup>f</sup>
Exp.	$\log k + 5$		0.16 <sup>f</sup>	1.55 <sup>f</sup>	1.10 <sup>f</sup>		

<sup>a</sup> No reaction. <sup>b</sup> A. R. Katritzky, A. Boonyarakvanich, N. Dennis, and G. J. Sabongi, unpublished results. <sup>c</sup> Ref. 3. <sup>d</sup> Ref. 20. <sup>e</sup> Table 5, footnote *h*. <sup>f</sup> Table 5, footnote *j*. <sup>g</sup> A. R. Katritzky, M. Abdullah, S. Bayyuk, A. M. A. Bolouri, N. Dennis, and G. J. Sabongi, in preparation.

Treatment by equation (4) indicates that for the methyl (1) and hydrogen compounds (2) *exo*-products should be favoured but that the aryl substituents should

Finally, in every case *endo* is predicted and in every case *endo* is found.

*Reaction of Styrene with a Series of Betaines.*—The

TABLE 7

Transition-state energies (a.u.) for addition of styrene to a series of 1-substituted 3-oxidopyridiniums

Eqn.	Structure	Energy separation	Ph (3) ( $\theta = 30^\circ$ )	4-Pyridyl (4) ( $\theta = 30^\circ$ )	2-Pyridyl (5) ( $\theta = 20^\circ$ )	Pyrimidin- 2-yl (6) ( $\theta = 0^\circ$ )	Triazin- 2-yl (7) ( $\theta = 0^\circ$ )	$\beta$ -Formyl- vinyl (8) ( $\theta = 0^\circ$ )
(1)	(18)	$H_B L_D$	-0.0183	-0.0178	-0.0179	-0.0180	-0.0179	-0.0179
		$L_B H_D$	-0.0115	-0.0116	-0.0119	-0.0124	-0.0120	-0.0094
		Total	-0.0298	-0.0294	-0.0298	-0.0304	-0.0299	-0.0273
(2)	(19)	$H_B L_D$	-0.0161	-0.0155	-0.0158	-0.0157	-0.0156	-0.0155
		$L_B H_D$	-0.0109	-0.0113	-0.0115	-0.0121	-0.0118	-0.0094
		Total	-0.0270	-0.0268	-0.0273	-0.0278	-0.0274	-0.0249
(4)	(18, 19)	$H_B L_D$	-2.34	-2.32	-2.34	-2.34	-2.32	-2.28
		$L_B H_D$	-1.98	-2.04	-2.03	-2.04	-2.08	-2.14
		Total	-4.32	-4.36	-4.37	-4.38	-4.40	-4.42
(4)	(18b)	<i>exo</i>	6.76	7.91	6.74	5.97	5.94	4.77
		<i>endo</i>	4.97	5.23	5.17	4.89	4.88	4.52
		(19b) <i>exo</i>	5.71	5.75	5.56	5.81	5.79	5.25
		(19a) <i>endo</i>	5.25	5.37	5.02	5.21	5.20	4.92
Exp. %			100% (18a) <sup>a</sup>	100% (18a) <sup>b</sup>	92% (18a) <sup>c</sup> 8% (18b)	100% (18a) <sup>e</sup>	100% (18a) <sup>d</sup>	100% (18a) <sup>f</sup>
Exp.	$\log k + 5$			0.30 <sup>f</sup>	1.65 <sup>f</sup>	1.33 <sup>f</sup>		

<sup>a</sup> Table 5 footnote *c* (ii). <sup>b</sup> Table 6 footnote *b*. <sup>c</sup> Ref. 3. <sup>d</sup> Ref. 17. <sup>e</sup> Table 5 footnote *h*. <sup>f</sup> Table 5 footnote *j*.

afford more *endo*-addition. Experimentally from the crude and approximate data presently available there is some support for this: whereas the H and the Me substituents both yield about equal amounts of *endo*- and *exo*-conformers, some of the aryl substituents (phenyl and 4-pyridyl) give a predominance of *endo*.

*Reactions of Ethyl Vinyl Ether with a Series of Betaines.*

—For the representative electron-rich dipolarophile

position described in Table 7 for the conjugated dipolarophile styrene is very similar to that just described for ethyl vinyl ether: regioisomers (18) are predicted by equation (1), relative rates explained by equation (2), except for the influence of the 5-nitro-group in 2-pyridyl, and *endo*-isomers correctly predicted by equation (4).

*Reactions of 1-(Pyrimidin-2-yl)-3-oxidopyridinium with a Series of Olefinic Dipolarophiles.*—These data are

collected in Table 8. We now find that equation (1) indicates correctly that regioisomers of type (18) should be preferred for all the monosubstituted ethylenes  $\text{CH}_2=\text{CHR}$  with  $\text{R} = \text{OEt}$ ,  $\text{CN}$ ,  $\text{CO}_2\text{Me}$ ,  $\text{Ph}$ , and 4-pyridyl.

Experimentally,  $\text{CH}_2=\text{CHOEt}$  gives mainly one *endo*-compound [cf. (18a)] whereas the other olefins give comparable amounts of the two stereoisomers [cf. (18a) and (18b)]. The steric terms obtained by the treatment

For vinyl acetate a second MO of type  $\pi$  near to the LUMO characterised by coefficients of considerably greater amplitude on carbon atoms C-1 and C-2:

$$\epsilon_{\text{LUMO}} = 0.1618 \text{ a.u. C-1 } 0.2927 \text{ C-2 } -0.2958$$

$$\epsilon_{\text{SUMO}} = 0.2022 \text{ a.u. C-1 } 0.6598 \text{ C-2 } -0.5978$$

The treatment in Table 9 indicates that the interaction  $\text{H}_\text{B}\text{L}_\text{D}$  is far less than  $\text{H}_\text{B}\text{S}_\text{D}$ . The total interaction is therefore calculated using  $\text{S}_\text{D}$  in place of  $\text{L}_\text{D}$ .\*

TABLE 8

Transition state interaction energies (a.u.) for addition of 1-(pyrimidin-2-yl)-3-oxidopyridinium to a series of monosubstituted olefinic dipolarophiles  $\text{CH}_2:\text{CH}\cdot\text{X}$

Eqn.	Structure	$\text{CH}_2\text{OH}$	Cyclohexene	$\text{OBu}^a$	$\text{OEt}$	$\text{Ph}$	$\text{CN}$	4-Pyridyl	$\text{CO}_2\text{Me}$	
(1)	(18)	$\text{H}_\text{B}\text{L}_\text{D}$	-0.0403	-0.0357	-0.0341	-0.0335	-0.0180	-0.0405	-0.0175	-0.0336
		$\text{L}_\text{B}\text{H}_\text{D}$	-0.0156	-0.0220	-0.0143	-0.0151	-0.0124	-0.0216	-0.0128	-0.0087
		Total	-0.0559	-0.0577	-0.0484	-0.0486	-0.0304	-0.0621	-0.0303	-0.0423
(19)	(19)	$\text{H}_\text{B}\text{L}_\text{D}$	-0.0397	-0.0330	-0.0330	-0.0325	-0.0157	-0.0377	-0.0150	-0.0289
		$\text{L}_\text{B}\text{H}_\text{D}$	-0.0153	-0.0138	-0.0138	-0.0145	-0.0121	-0.0213	-0.0125	-0.0085
		Total	-0.0550	-0.0468	-0.0468	-0.0470	-0.0278	-0.0590	-0.0275	-0.0374
(2)	(18, 19)	$\text{H}_\text{B}\text{L}_\text{D}$	-2.02	-2.06	-2.01	-2.01	-2.34	-2.29	-2.42	-2.45
		$\text{L}_\text{B}\text{H}_\text{D}$	-1.85	-1.66	-2.00	-2.00	-2.04	-1.80	-1.97	-1.83
		Total	-3.88	-4.02	-4.02	-4.01	-4.38	-4.09	-4.39	-4.28
(4)	(18b)	<i>exo</i>	3.86	5.44	5.59	4.81	5.97	3.51	5.94	5.43
	(18a)	<i>endo</i>	3.62	6.59	3.98	3.63	4.89	3.25	4.87	4.47
	(19b)	<i>exo</i>	3.82		4.34	3.89	5.81	3.46	5.79	5.29
	(19a)	<i>endo</i>	3.78		5.45	4.75	5.21	3.38	5.19	4.64
Exp. %		100%	100%		100%	100%	84%	<i>a</i>	58%	
		(18a) <sup>a</sup>	(18a) <sup>a</sup>		(18a) <sup>a</sup>	(18a) <sup>b</sup>	(18a) <sup>a</sup>	16%	(18b)	42%
Exp. $\log k + 7$		0.87 <sup>c</sup>	1.97 <sup>c</sup>	2.75 <sup>d</sup>		2.96 <sup>d</sup>	3.10 <sup>d</sup>	3.20 <sup>d</sup>	3.651 <sup>d</sup>	

<sup>a</sup> Ref. 20. <sup>b</sup> Ref. 3. <sup>c</sup> Extrapolated from variable temperature measurements to 42 °C; unpublished results with B. El-Osta, G. Musumarra, and C. Ögretir. <sup>d</sup> Ref. 4, measured at 42 °C.

using equation (4) favour the *endo*-product for all the additions to give regioisomer (18), the difference is the greatest for ethyl vinyl ether and least for acrylonitrile.

Again the treatment using equation (1) does not reproduce the experimental kinetic results which indicate increasing rates of reaction for the vinyl compounds in the order:  $\text{OBu}^a < \text{Ph} < \text{CN} < 4\text{-pyridyl} < \text{CO}_2\text{Me}$ . However equation (2) does explain the relative rates, provided that styrene and 4-vinylpyridine (which were taken as planar for the calculations) are considered separately from the others.

Table 8 also gives a comparison of the results by the treatment using equation (2) for this wide variety of olefinic dipolarophiles with the kinetic second-order rate constants for reaction at 42 °C.<sup>4</sup> Figure 3 shows that there is a general trend to increasing rates as  $\Delta E$  increases, but that there is no precise relationship between  $\log k$  and  $\Delta E$ .

Such a correlation provides evidence for the model including only the frontier interactions [equation (2)]: no correlation is found with the treatment of equation (1) which involves also the coefficients at the various interaction atoms.

It is further evident from Table 8 that the HOMO (betaine)-LUMO (dipole) interaction is dominating the variation in reactivity. For the planar  $\text{CH}_2=\text{CHX}$  series, a linear correlation (correlation coefficient 0.954) is obtained for a plot of  $\log k$  against  $\text{H}_\text{B}\text{L}_\text{D}$ , but no significant correlation is found between  $\log k$  and  $\text{H}_\text{D}\text{L}_\text{B}$ .

*Site Selectivity of Monoenes.*—Cycloaddition of 3-oxidopyridinium and dienes can obviously occur at

TABLE 9

Transition state energies (a.u.) for addition of *s-trans*- and *s-cis*-vinyl acetate to 1-(pyrimidin-2-yl)-3-oxidopyridinium<sup>a</sup>

Eqn.	Energy separation	<i>s-trans</i>		<i>s-cis</i>	
		2,2'-6,1' (18)	2,1'-6,2' (19)	2,2'-6,1' (18)	2,1'-6,2' (19)
(1)	$\text{H}_\text{B}\text{L}_\text{D}$	-0.0084	-0.0083	-0.0068	-0.0066
	$\text{L}_\text{B}\text{H}_\text{D}$	-0.0164	-0.0160	-0.0179	-0.0174
	Total	-0.0248	-0.0243	-0.0246	-0.0241
(2)	$\text{H}_\text{B}\text{S}_\text{D}$	-0.0342	-0.0355	-0.0355	-0.0366
	$\text{L}_\text{B}\text{H}_\text{D}$	-0.0164	-0.0160	-0.0179	-0.0174
	Total	-0.0506	-0.0515	-0.0534	-0.0540
(4)	$\text{H}_\text{B}\text{L}_\text{D}$	-2.08		-2.07	
	$\text{L}_\text{B}\text{H}_\text{D}$	-1.91		-1.90	
	Total	-3.99		-3.97	
(4)	$\text{H}_\text{B}\text{S}_\text{D}$	-1.92		-1.90	
	$\text{L}_\text{B}\text{H}_\text{D}$	-1.91		-1.90	
	Total	-3.82		-3.80	
Exp. %	<i>exo</i>	4.49	4.46	5.58	5.48
	<i>endo</i>	4.16	4.40	4.57	4.72
		100% (18a) <sup>b</sup>			

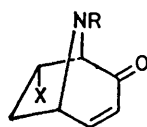
<sup>a</sup> Primed numbers refer to vinyl acetate. C-1' is attached to the oxygen atom. <sup>b</sup> Ref. 20.

several sites. However such site selectivity is also possible for monoenes: besides addition at 2,6 (and the

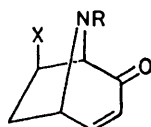
\* It must be noted that the use of solely the  $\text{S}_\text{D}$  in place of  $\text{L}_\text{D}$  would indicate formation of the  $\beta$ -regioisomer: however the differences in  $E_{\text{int}}$  for the  $\alpha$ - and  $\beta$ -isomers is small. Experimentally we found only the  $\alpha$ -isomer.

forbidden addition at 2,4) reaction is allowed at the O,2[ $\rightarrow$ (20)] or O,4 positions [ $\rightarrow$ (21)]. Experi-

most  $2\pi$ -addends) addition at O,2 or O,4 does not lead to a stable product. For difluoroketen, the same

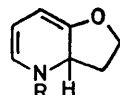


(19a)

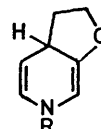


(19b)

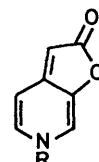
mentally such addition modes have been involved in the reactions of  $\alpha$ -halogenoketens with the betaines [when spontaneous elimination of hydrogen halide yields



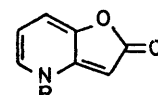
(20)



(21)



(22)



(23)

pattern emerges, but now orientation of addition of type (24 $\alpha$ ) or (25 $\alpha$ ) can lead to stable products by elimin-

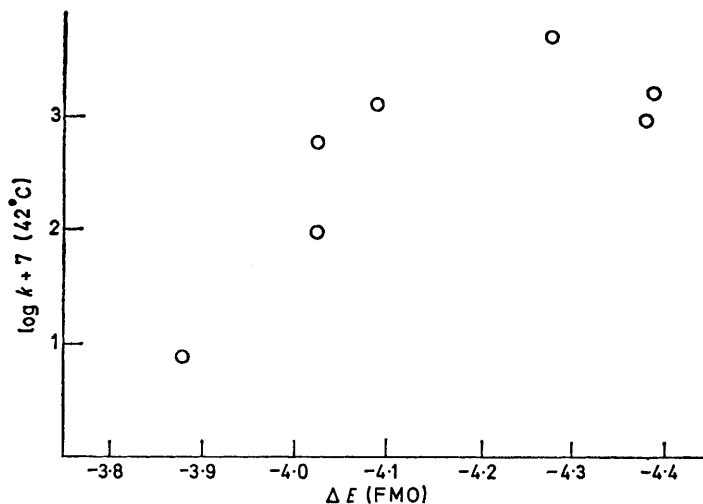


FIGURE 3 Correlation of FMO energies [equation (2)] with rate constants for additions to 1-(4,6-dimethylpyrimidin-2-yl)-3-oxidopyridinium: I, corr. coeff. 0.997; II, corr. coeff. 0.942

products of type (22)<sup>18</sup> and (23)<sup>19</sup>. We have calculated (Table 10) energy terms for various orientations of addition.

ation of HF. Experimentally dichloroketen does add across the O,4 positions<sup>18</sup> while aryl(chloro)ketens react at both the O,2 and O,4 positions.<sup>19</sup>

TABLE 10

Site selectivity for the cycloaddition of acrylonitrile, difluoroketen, and keten to 1-methyl-3-oxidopyridinium

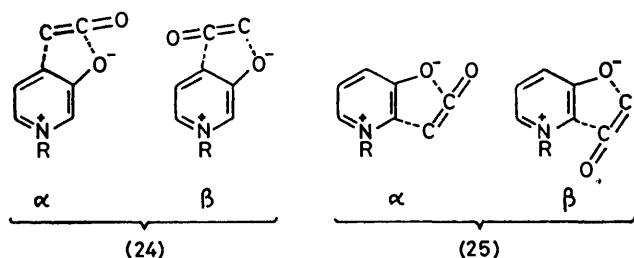
		2' 1' CH <sub>2</sub> =CH-CN			2' 1' CF <sub>2</sub> =C=O			2' 1' CH <sub>2</sub> =C=O			
		2,6 (18) or (19)	O,2 <sup>a</sup> (25)	O,4 <sup>b</sup> (24)	2,6 (18) or (19)	O,2 <sup>a</sup> (25)	O,4 <sup>b</sup> (24)	2,6 <sup>c</sup> (18) or (19)	O,2 <sup>d</sup> (25)	O,4 <sup>e</sup> (24)	
(1)	$\alpha$ {	H <sub>B</sub> L <sub>D</sub>	-0.0401	-0.0689	-0.0447	-0.0396	-0.0750	-0.0523	-0.0389	-0.0651	-0.0413
	L <sub>B</sub> H <sub>D</sub>	-0.0242	-0.0084	-0.0095	-0.0234	-0.0092	-0.0103	-0.0209	-0.0020	-0.0025	
	Total	-0.0643	-0.0773	-0.0542	-0.0630	-0.0842	-0.0626	-0.0598	-0.0671	-0.0438	
(2)	$\beta$ {	H <sub>B</sub> L <sub>D</sub>	-0.0373	-0.0718	-0.0509	-0.0415	-0.0730	-0.0482	-0.0350	-0.0692	-0.0499
	L <sub>B</sub> H <sub>D</sub>	-0.0236	-0.0057	-0.0066	-0.0222	-0.0046	-0.0054	-0.0237	-0.0136	-0.0149	
	Total	-0.0609	-0.0775	-0.0575	-0.0637	-0.0776	-0.0536	-0.0587	-0.0828	-0.0648	
(3)	Total		-2.26			-1.99			-1.82		
	L <sub>B</sub> H <sub>D</sub>		-1.75			-1.99			-1.94		
	Total		-4.00			-3.98			-3.76		
(4)	$\alpha$ {	<i>exo</i>	2.65	2.68	2.37	3.23	2.92	2.81	2.21	2.07	1.96
	<i>endo</i>	2.76	3.07	2.08							
	$\beta$ {	<i>exo</i>	2.66	2.64	2.81	3.18	2.79	2.69	2.23	1.87	1.83
	<i>endo</i>	2.88	2.93	2.17							

<sup>a</sup> Isomers  $\alpha = O,1'-2,2'$ ,  $\beta = O,2'-2,1'$ . <sup>b</sup> Isomers  $\alpha = O,1'-4,2'$ ,  $\beta = O,2'-4,1'$ . <sup>c</sup> Isomers  $\alpha = 2,2'-6,1'$ ,  $\beta = 2,1'-6,2'$ . <sup>d</sup> Isomers  $\alpha = 2,1'-O,2'$ ,  $\beta = 2,2'-O,1'$ . <sup>e</sup> Isomers  $\alpha = 4,1'-O,2'$ ,  $\beta = 4,2'-O,1'$ .

For acrylonitrile, the FO term favours addition across the O,2 positions, while the steric term favours the O,4 orientation. We believe that the observed 2,6-addition arises from the fact that for acrylonitrile (and indeed

*Site Selectivity of Dienes.*—Dienes undergo permitted cycloaddition at either the 2,6 (acting as conjugated monoenes) or 2,4 positions (acting as dienes). Calculations for *trans*-penta-1,3-diene are given in Table II.

Of the twelve possible products, eight from addition at 2,6 [*endo*- and *exo*-forms of (18), (19), (26), and (27)]



and four from addition at 2,4 [*endo*- and *exo*-forms of (28) and (29)] we find experimentally only the three *endo*-forms (18a), (28a), and (29a).

For addition at the 2,4-positions rather similar steric terms and *more* favourable covalent terms are found. Addition is predicted to be *exo*; although the *endo* product is found experimentally, this is believed to be a result of ring inversion after the addition (see later).

For buta-1,3-diene the calculated data are given in Table 12. Here the steric term favours 2,4-addition, and the only product isolated from the reaction mixture<sup>20</sup> was indeed the *endo*-2,4-adduct. Again the *endo*-orientation is considered to arise from ring inversion of an initially formed *exo*-adduct.<sup>3</sup>

Table 13 treats comparable data for cyclopentadiene. The two products isolated experimentally are precisely those expected to be favoured for the 2,4 and for the 2,6 addition modes. Moreover, we can explain the

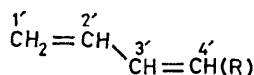
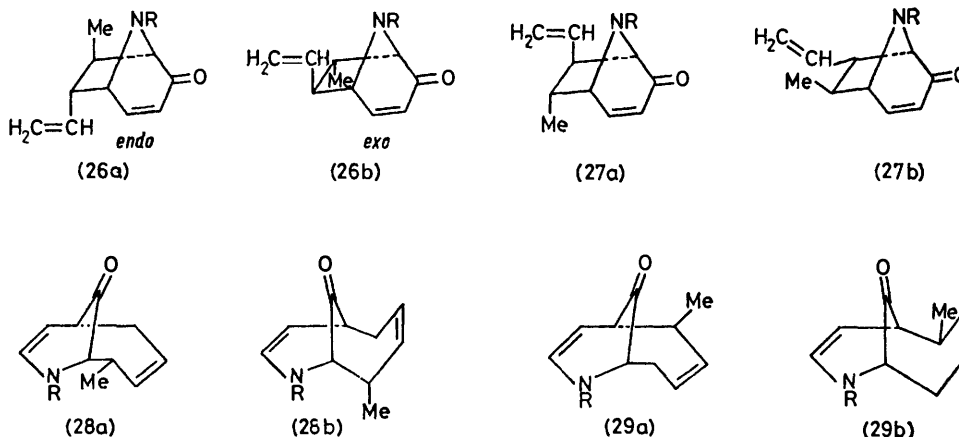
TABLE 11  
Transition-state interaction energies (a.u.) for the addition of *trans*-penta-1,3-diene (31) to 1-(pyrimidin-2-yl)-3-oxopyridinium

Eqn.	Reaction at 2,6-positions of betaine				Reaction at 2,4-position with <i>s-cis</i> -diene	
	<i>s-trans</i> -terminal olefin		<i>s-trans</i> -central olefin		(28)	(29)
	(18)	(19)	(26)	(27)		
(1)	-0.0374	-0.0344	-0.0461	-0.0436	-0.0515	-0.0523
(4)	3.81	4.03	4.49	4.66	4.61	3.87
	4.18	4.12	4.67	4.54	4.24	3.80
Exp. %	33% (18a) <sup>a</sup>				67% [(28a) + (29a)] <sup>a</sup>	

<sup>a</sup>Ref. 3.

For addition at the 2,6-positions the steric factors considerably favour forms (18) and (19) over (26) and

comparable amounts which are formed: the *exo*-2,4-addition product is considerably favoured by the steric



(30) R = H

(31) R = Me

(27) and, although the covalent terms act in the opposite direction, the steric effects clearly dominate. Considering only the two forms (18) and (19), the former is favoured both by steric and covalent effects, and indeed the *endo*-form (18a) is correctly predicted as the preferred product.

term and the *endo*-2,6- by the covalent term. Here no ring inversion is possible for the *exo*-2,4-adduct, which consequently is isolated as such and not as the *endo*-stereoisomer (as for the acyclic pentadiene analogue).

*Site and Regioselectivity of Fulvene Cycloadditions.*— This is a complex problem. *exo*- and *endo*-Additions at



TABLE 12

Transition state interaction energies (a.u.) for the addition of buta-1,3-diene (30) to 1-(pyrimidin-2-yl)-3-oxidopyridinium

Eqn.	Reaction at 2,6-position of betaine				Reaction at 2,4-position <i>s-cis</i> -Diene —0.0550 3.77 3.41 100% (32) <sup>a</sup>
	<i>s-trans</i> -Olefin		<i>s-cis</i> -Olefin		
	(18)	(19)	(18)	(19)	
(1)	—0.0445	—0.0415	—0.0434	—0.0407	
(4)	3.46	3.60	3.61	3.71	3.77
	<i>endo</i>				3.41
	<i>exo</i>		4.03	3.99	
Exp. %					

<sup>a</sup> Ref. 20.

seven orientations give a total of fourteen possible adducts. Furthermore the HOMO of fulvene has zero

*Conclusions.*—We have demonstrated the FMO method to be a powerful tool for the explanation, rationalisation,

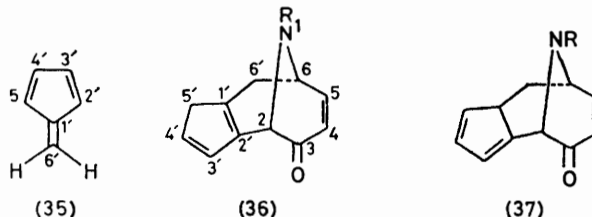
TABLE 13

Transition-state interaction energies (a.u.) for the addition of cyclopentadiene (33) to 1-(pyrimidin-2-yl)-3-oxidopyridinium

Eqn.	Reaction at 2,6-position of betaine		Reaction at 2,4-position
	[ <i>as</i> (26)]	[ <i>as</i> (27)]	
(1)	—0.0409	—0.0386	—0.0535
(4)	4.50	4.48	4.54
	<i>endo</i>		4.33
	<i>exo</i>	4.93	
Exp. %	33% [ <i>as</i> (26a)] <sup>a</sup>		67% <i>exo</i> (34) <sup>a</sup>

<sup>a</sup> Ref. 3.

coefficients at the 1- and 6-positions and therefore calculations including the SOMO have also been carried out (Table 14).



and prediction of peri-, site, regio-, and stereo-selectivity and for the quantitative correlation of kinetic rate data within the various thermal cycloadditions to 3-oxidopyridiniums.

TABLE 14

Transition state energies (a.u.) for addition of fulvene (35) to 1-(pyrimidin-2-yl)-3-oxidopyridinium [equation (1)]

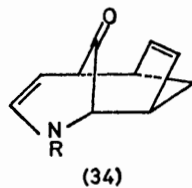
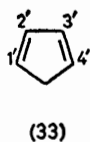
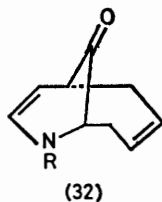
Regioisomer <sup>a</sup>	H <sub>B</sub> L <sub>F</sub>	L <sub>B</sub> H <sub>F</sub>	L <sub>B</sub> S <sub>F</sub>	T	<i>exo</i>	<i>endo</i>
2,2'-6,6'	—0.0288	—0.0073	—0.0044	—0.0405	5.35	4.94
2,6'-6,2'	—0.0342	—0.0064	—0.0053	—0.0459	5.39	4.82
2,2'-6,3'	—0.0174	—0.0190	—0.0044	—0.0308	5.39	4.92
2,3'-6,2'	—0.0169	—0.0186	—0.0047	—0.0402	5.42	4.84
2,1'-6,6'	—0.0216	—0.0000	—0.0213	—0.0429	4.86	4.86
2,6'-6,1'	—0.0285	—0.0000	—0.0216	—0.0501	4.76	4.76
2,2'-4,5'	—0.0174	—0.0299	—0.0000	—0.0473	4.28	4.92

<sup>a</sup> Exp. 2,2'-6,6', 20% (36) (ref. 3). Only adducts of the type 2,  $\alpha$  - 6,  $\gamma$  [ $\nu$ (C=O) 1 680—1 690 cm<sup>-1</sup>] were formed in the reaction between 6-(4-methoxyphenyl)fulvene and 1-(pyrimidin-2-yl)-3-oxidopyridinium. No adducts of the type 2,2'-4,5' [ $\nu$ (C=O) 1 740 cm<sup>-1</sup>] were detected.

We cannot presently explain experimental results for the fulvene addition: we believe that the product found

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experimentally (36) does not derive from kinetic control, but from (37) by a 1,5 hydrogen shift.

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