

FMO Approach in [4 + 2] Cycloadditions. Kinetic Studies with 1,2-Dimethylenecyclopentane

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Kinetic measurements on [4 + 2] cycloadditions of 1,2-dimethylenecyclopentane (**1**) as a model diene for normal Diels-Alder reactions are described. This diene was selected in order to check whether a synperiplanar diene is a good test case for the FMO model. Using HOMO and LUMO energies from semi-

empirical quantumchemical calculations, we indeed obtained a good linear correlation between the $\lg k_2$ values and $1/(E_{\text{HOMO}} - E_{\text{LUMO}})$. The cycloadditions of *E/Z* isomeric dienophiles to **1** are stereospecific. These reactions are best described in terms of concerted processes.

The frontier molecular orbital (FMO) theory is the most widely accepted approach to explain reactivity in [4 + 2] cycloadditions^[1,2]. While it works satisfactorily on a qualitative basis, most attempts to apply it quantitatively to Diels-Alder reactions have proved unsuccessful. Thus, rather poor quantitative correlations between $\lg k_2$ and the first ionization potentials as a measure of the HOMO energy of the diene were obtained for cycloadditions of substituted 1,3-butadienes to maleic anhydride or tetracyanoethylene^[3]. A better agreement between this simplified theory and experiments was found for the classic cycloadditions of cyclopentadiene to cyano-substituted olefins^[4]. Rather poor correlations resulted for cycloadditions of substituted anthracenes to maleic anhydride^[5], whereas in other examples better correlations were reported^[6]. In 1,3-dipolar cycloadditions, the other important class of $[\pi 4 + \pi 2]$ cycloadditions a much better agreement between this theory and experiments is observed^[7,8].

There are several reasons for the shortcomings in the FMO approach. It derives from the second-order perturbation theory and reduces the full expression for the stabilizing electronic interaction, which includes all occupied and unoccupied MOs of the reactants, to those of the frontier orbitals^[9]. Although these contributions should be greater than those from the interactions of other unoccupied with occupied MOs there is no a priori postulate that such a theory will work in explaining quantitatively reactivity in cycloadditions. On the contrary, it is surprising that the FMO theory functions as good as it does^[10].

Furthermore, the second-order perturbation theory describes only stabilizing electronic interactions. Thus, steric effects which are known to be important in many cases are not considered. More elaborate perturbation theories^[11] do take into account these contributions and constitute, therefore, an improvement. However, also these treatments rely on the quality of the underlying semiempirical SCF procedures like MNDO, AM1, or MNDO-PM3^[12–14].

In the case of Diels-Alder reactions of open-chain dienes the position of the equilibrium between the synperiplanar and antiperiplanar structure, i.e. a conformational situation, is another complicating factor. It is mainly influenced by the number and the size of substituents at different positions of the diene. This complex situation was present in the kinetic study of the cycloadditions of substituted 1,3-butadienes to maleic anhydride and tetracyanoethylene^[3].

Another aspect is that the number and nature of substituents on a dienophile or diene can change the reaction mechanism. This has to be taken into consideration if general reactivity trends are discussed. It is tempting, but dangerous to describe the reactions of a particular diene with a series of dienophiles or vice versa in terms of a single mechanism. It was shown recently, for example, that *trans*-1-(dimethylamino)-1,3-butadiene reacts with fumaro- and maleonitrile in a concerted fashion whereas the corresponding cycloadditions to dimethyl fumarate, dimethyl maleate, dimethyl dicyanofumarate, and dimethyl dicyanomaleate are clearly two-step in character^[15].

Like cyclopentadiene 1,2-dimethylenecyclopentane (**1**) is one of the systems where conformational contributions to diene reactivity are excluded and where the chance for a common reaction mechanism in the addition to a series of dienophiles is high. This should allow the analysis of pure electronic effects on reactivity. Diene **1** has already been used in a study of the importance of charge-transfer complexes in cycloadditions to strongly electron-deficient dienophiles^[16,17]. In another investigation the influence of methyl groups in the diene on its reactivity has been analyzed^[18].

In order to check the FMO model for its quantitative reliability we have now completed a kinetic study of cycloadditions of 1,2-dimethylenecyclopentane (**1**) to a series of dienophiles which range from methyl acrylate and acrylonitrile to tetracyanoethylene. The kinetic data are interpreted in terms of the FMO model. Quantitative information on frontier orbital energies is obtained from semiempirical quantumchemical calculations.

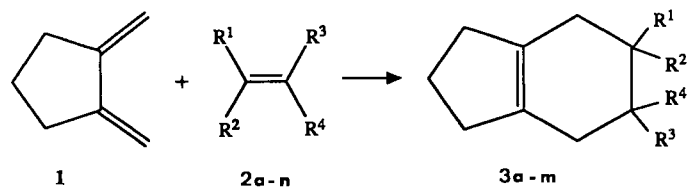
Results and Discussion

Cycloadditions

The reactions were carried out on a mmolar scale in dichloromethane. Products were isolated in 76–94% yields. Dienophiles **2a** to **2h** showed no evidence of charge-transfer complex formation on mixing equimolar solutions (ca. 10%) of the reactants. In the cases **2k** to **2p** a transient color indicated the formation of a CT complex which disappeared rapidly. In Scheme 1 the isolated yields of cycloadducts are

given. In those cases where *E/Z* isomeric olefins were used as dienophiles (**2c**, **2d**, **2e**, **2f**, **2l**, **2m**) no sign of a non-stereospecific cycloaddition could be detected. On this basis it is concluded that **1** undergoes a concerted cycloaddition to all dienophiles.

Scheme 1



	R ¹	R ²	R ³	R ⁴	Yield (%)
2a	CO ₂ CH ₃	H	H	H	3a 81
b	CN	H	H	H	b 86
c	CO ₂ CH ₃	H	H	CO ₂ CH ₃	c 92
d	CO ₂ CH ₃	H	CO ₂ CH ₃	H	d 76
e	CN	H	H	CN	e 90
f	CN	H	CN	H	f 86
g	CN	H	CO ₂ CH ₃	CO ₂ CH ₃	g 92
h	CO ₂ CH ₃	H	CO ₂ CH ₃	CO ₂ CH ₃	h 94
i	CN	CN	H	CO ₂ CH ₃	i 88
k	CN	CN	CO ₂ CH ₃	CO ₂ CH ₃	k 86
l	CO ₂ CH ₃	CN	CN	CO ₂ CH ₃	l 90
m	CO ₂ CH ₃	CN	CO ₂ CH ₃	CN	m 75
n	CN	CN	CN	CN	

Kinetic Measurements

Kinetic measurements were carried out UV spectrophotometrically. The decay of the diene, dienophile, or CT absorption was followed in dichloromethane as solvent at 20.0°C. Measurements were performed under pseudofirst-

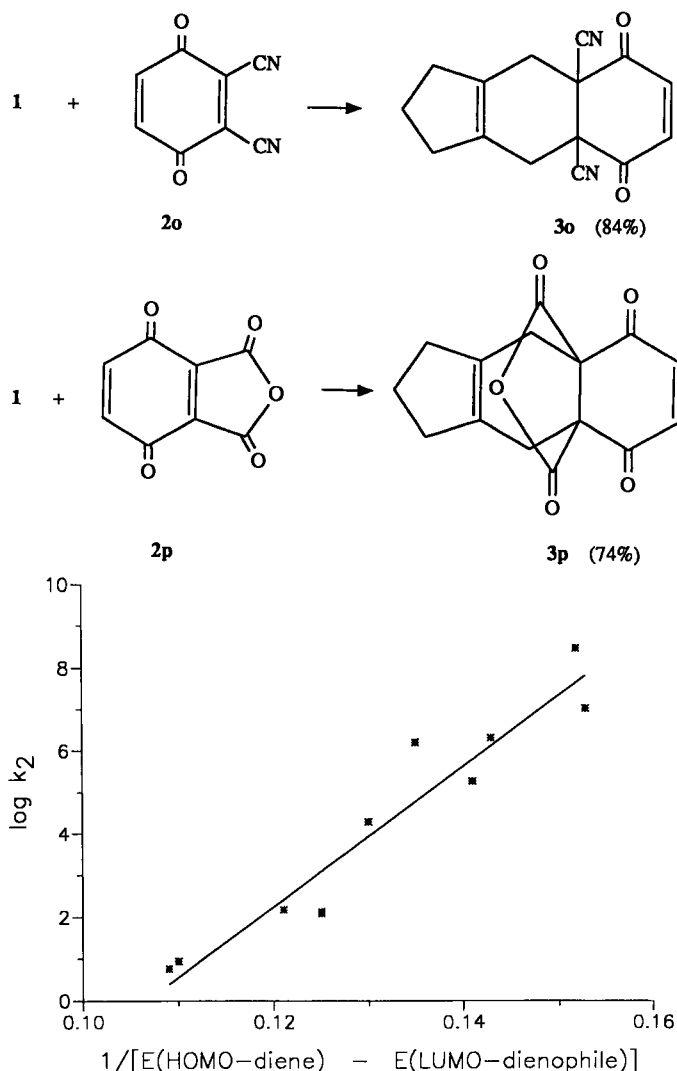


Figure 1. Plot of $\lg k_2$ values ($\text{l mol}^{-1} \text{s}^{-1}$) vs. $1/(E_{\text{HOMO-diene}} - E_{\text{LUMO-dienophile}})$ (eV^{-1}) for cycloadditions of 1,2-dimethylenecyclopentane (**1**) to dienophiles **2a-p**

Table 1. Kinetic data, LUMO energies, and FMO interactions for cycloadditions of 1,2-dimethylenecyclopentane (**1**) to dienophiles **2**

Dienophile	$10^4 \cdot k_2$ [$\text{l mol}^{-1} \text{s}^{-1}$]	k_{rel} [$\text{l mol}^{-1} \text{s}^{-1}$]	LUMO [eV]	$1/(E_{\text{HOMO}} - E_{\text{LUMO}})^{[a]}$ [eV^{-1}]
Tetracyanoethene (2n)	2 888 000	49 000 000	-2.68	-0.152
2,3-Dicyano- <i>p</i> -benzoquinone (2o)	104 500	1 780 000	-2.71	-0.153
<i>trans</i> -1,2-Dicyano-1,2-bis(methoxycarbonyl)ethene (2l)	20 570	350 000	-2.26	-0.143
1,1-Dicyano-2-(methoxycarbonyl)ethene (2i)	15 970	270 000	-1.82	-0.135
1,1-Dicyano-2,2-bis(methoxycarbonyl)ethene (2k)	1 850	31 000	-2.13	-0.141
2-Cyano-1,1-bis(methoxycarbonyl)ethene (2g)	195	3 300	-1.52	-0.130
Dimethyl fumarate (2c)	1.5	25.6	-0.98	-0.121
Maleonitrile (2f)	1.35	23.3	-1.21	-0.125
Fumaronitrile (2e)	1.21	20.7	-1.27	-0.125
Acrylonitrile (2b)	0.0878	1.5	-0.18	-0.110
Methyl acrylate (2a)	0.0585	1.0	-0.09	-0.109

^[a] $\text{HOMO}_{\text{diene}} = -9.24 \text{ eV}$.

order conditions, the pseudofirst-order rate constants were converted to second-order values.

In Table 1 the rate constants are displayed together with the frontier molecular orbital energies and $1/(E_{\text{HOMO}} - E_{\text{LUMO}})$ values. The orbital energies were taken from MNDO calculations on **1** and the dienophiles. Geometrical variables were optimized in all cases. In Figure 1a graphical representation of $\lg k_2$ values vs. $1/(E_{\text{HOMO}} - E_{\text{LUMO}})$ shows that there is a linear correlation ($r = 0.96$). Taking into account the simplifications of the model and that the frontier molecular orbital energies are obtained from semiempirical quantumchemical calculations the quality of the correlation is very satisfactory, indeed.

In the introduction it was stated that reactivity in [4 + 2] cycloadditions is based on a number of individual factors.

A quantitative validation of the FMO model is only possible if other contributions to reactivity are kept constant, conditions which seem to be fulfilled in these cycloadditions. The results of this investigation show that a reasonable linear correlation between the $\lg k_2$ values as a measure of the activation parameters and $1/(E_{\text{HOMO}} - E_{\text{LUMO}})$ is obtained.

Although the FMO model is approximate and has to be applied cautiously it still seems to be the simplest way to rationalize reactivity in concerted cycloadditions. If used with the appropriate caution and with the knowledge of its limitations it fulfills a valuable purpose even though it has been criticized strongly^[19]. There does not seem to be any other theory which can be applied so easily and which fulfills the needs of the experimental chemist so convincingly.

Table 2. Cycloadditions of **1** to dienophiles **2a–p** in dichloromethane at room temperature

1 g [mmol]	dienophile g [mmol]	solvent H ₂ CCl ₂ reaction time	% isolated pure product mp, recryst. from	mol. weight	C	H	N
0.47 (5.0)	0.43 (5.0)	10.0 ml, 21d	81, oil	C ₁₁ H ₁₆ O ₂ 180.2	calcd.	73.33	8.88
					found	73.35	9.20
0.40 (4.3)	0.33 (4.3)	5.0 ml, 8d	86, oil	C ₁₀ H ₁₃ N 147.2	calcd.	81.63	8.84
					found	81.48	8.90
0.36 (3.8)	0.55 (3.8)	10.0 ml, 2d	92, 109 diethyl ether	C ₁₃ H ₁₈ O ₄ 238.3	calcd.	65.54	7.56
					found	65.86	7.97
0.47 (5.0)	0.72 (5.0)	5.0 ml, 56d	87, oil	C ₁₃ H ₁₈ O ₄ 238.3	calcd.	65.54	7.56
					found	65.19	7.57
0.40 (4.3)	0.33 (4.3)	10.0 ml, 6d	90, 96 diethyl ether	C ₁₁ H ₁₂ N ₂ 172.2	calcd.	76.74	6.97
					found	77.00	7.24
0.40 (4.3)	0.33 (4.3)	5.0 ml, 4d	86, oil	C ₁₁ H ₁₂ N ₂ 172.2	calcd.	76.74	6.97
					found	76.65	6.99
0.23 (2.4)	0.41 (2.4)	15.0 ml, 3h	92, 69 diethyl ether	C ₁₄ H ₁₇ NO ₄ 263.3	calcd.	63.87	6.46
					found	63.52	6.81
0.30 (3.2)	0.64 (3.2)	10.0 ml, 16d	94, oil diethyl ether	C ₁₅ H ₂₀ O ₆ 296.3	calcd.	60.81	6.76
					found	60.31	6.80
0.41 (4.3)	0.59 (4.3)	30.0 ml, 5h	88, 68 diethyl ether	C ₁₃ H ₁₄ N ₂ O ₂ 230.3	calcd.	67.82	6.08
					found	67.49	6.41
0.37 (3.9)	0.76 (3.9)	30.0 ml, 5h	86, 118 diethyl ether	C ₁₅ H ₁₆ N ₂ O ₂ 288.3	calcd.	62.50	5.55
					Found	62.49	5.65
0.40 (4.3)	0.83 (4.3)	20.0, 2h	90, 140 n-hexane/diethyl ether	C ₁₅ H ₁₆ N ₂ O ₂ 288.3	Calcd.	62.50	5.55
					Found	62.39	5.70
0.18 (1.9)	0.37 (1.9)	30.0 ml, 2h	75, 110 n-hexane/diethyl ether	C ₁₅ H ₁₆ N ₂ O ₂ 288.3	Calcd.	62.50	5.55
					Found	62.56	5.70
0.20 (2.1)	0.34 (2.1)	35.0 ml, 2h	84, 139-140 ethanol	C ₁₅ H ₁₂ N ₂ O ₂ 252.3	Calcd.	71.43	4.76
					Found	71.05	4.76
0.23 (2.2)	0.39 (2.2)	30.0 ml, 5h	65, 136 benzene/cyclohexane	C ₁₅ H ₁₂ O ₅ 272.3	Calcd.	66.18	4.41
					Found	66.40	4.70

Table 3. Spectroscopic data of cycloadducts 3a–p

com- pound	MS /70 eV; m/z (%)	¹ H NMR (CDCl ₃) δ	¹³ C NMR (CDCl ₃) δ
3a	180 (M ⁺ , 24), 121 (35), 120 (100), 92 (30), 91 (44), 79 (34), 55 (12), 41 (16)	3.65 (s, 3H), 2.51 (m, 1H), 2.20 (m, 6H), 2.01 (m, 4H), 1.80 (quint, 2H, ³ J = 7.3 Hz)	176.26(s), 138.83 (s), 132.56 (s) 51.41 (q), 40.07 (t), 35.61 (t), 24.9 (d), 21.81 (t)
3b	147 (M ⁺ , 15), 175 (55), 118 (100), 117 (30), 91 (29), 41 (12)	1.43 - 2.38 (broad m)	134.25 (s), 130.85 (s), 122.56 (s), 29.50 (t), 35.77 (t), 35.62 (t) 26.20 (t), 25.30 (d), 21.98 (t)
3c	238 (M ⁺ , 13), 178 (60), 119 (100) 118 (30), 91 (50), 41 (13)	3.69 (s, 6H), 2.88 (t, 2H), 2.22 (m, 8H), 1.78 (quint, 2H, ³ J = 7.3 Hz)	175.54 (s), 132.58 (s), 51.81 (d), 42.20 (q), 35.35 (t), 28.62 (t), 22.01 (t)
3d	238 (M ⁺ , 11), 178 (51), 119 (100) 118 (28), 91 (45), 41 (13)	3.76 (s, 6H), 3.03 (t, 2H), 2.21 (m, 8H), 1.80 (quint, 2H, ³ J = 7.6 Hz)	173.99 (s), 132.68 (s), 51.79 (d), 40.75 (q), 35.61 (t), 26.51 (t), 21.88 (t)
3e	172 (M ⁺ , 55), 171 (22), 155 (30), 144 (32), 118 (34), 94 (44), 92 (31) 79 (100), 77 (24), 56 (40), 39 (28)	1.58 - 2.05 (broad m)	131.09 (s), 119.01 (s), 28.07 (d) 35.33 (t), 27.43 (t), 21.49 (t)
3f	172 (M ⁺ , 51), 145 (23), 144 (43), 132 (22), 118 (37), 117 (22), 91 (32) 79 (100), 77 (31), 56 (34), 41 (24)	3.15 (t, 2H), 2.48 (m, 4H), 2.26 (m, 4H) 1.95 (quint, 2H, ³ J = 7.3 Hz)	131.19 (s), 118.45 (s), 28.21 (d), 28.21 (d), 35.24 (t), 27.39 (t), 21.47 (t)
3g	263 (M ⁺ , 46), 232 (12), 204 (48), 203 (100), 177 (70), 144 (60), 117 (70), 91 (26), 77 (18), 59 (40), 41 (26)	3.84 (s, 3H), 3.82 (s, 3H), 3.67 (t, 1H), 2.72 (bs, 2H), 2.01 - 2.55 (m, 6H), 1.87 (quint, 2H, ³ J = 7.3 Hz)	168.77 (s), 132.58 (s), 130.29 (s), 120.02 (s), 55.79 (s), 53.40 (q) 53.30 (q), 35.53 (t), 35.20 (t), 30.61 (d), 29.73 (t), 27.61 (t) 21.80(t)
3h	296 (M ⁺ , 16), 236 (18), 204 (21), 177 (100), 176 (27), 145 (26), 117 (28), 105 (27), 91 (18), 59 (20)	3.72 (s, 3H), 3.69 (s, 3H), 3.66 (s, 3H), 3.52 (t, 1H) 2.71 (m, 4H), 2.35 (m, 4H), 1.78 (quint, 2H, ³ J = 7.6 Hz)	173.01 (s), 171.53 (s), 170.31 (s), 131.86 (s), 131.82 (s), 56.47 (s), 52.83 (d), 52.61 (q), 51.92 (q), 43.81 (t), 35.43 (t), 35.30 (t), 31.19 (t), 26.15 (t), 21.81 (t)
3i	230 (M ⁺ , 54), 198 (66), 171 (66), 170 (78), 144 (100), 143 (46), 142 (34), 116 (36), 91 (32), 77 (36), 59 (42), 41 (34), 39 (43)	3.84 (s, 3H), 3.12 (d, 1H), 2.23 - 3.01 (m, 8H), 1.93 (quint, 2H, ³ J = 7.3 Hz)	169.91 (s), 123.97 (s), 128.63 (s), 115.56 (s), 114.07 (s), 52.91 (q), 45.98 (d), 35.87 (t), 35.23 (t), 35.01 (t), 32.50 (t), 26.50 (s), 21.73 (t)
3k	288 (M ⁺ , 40), 257 (26), 230 (58), 225 (100), 197 (26), 171 (23), 156 (16) 115 (16), 79 (15), 59 (36), 39 (14)	3.84 (s, 6H), 2.87 (s, 4H), 2.31 (bs, 4H), 1.90 (quint, 2H, ³ J = 7.3 Hz)	166.58 (s), 133.51 (s), 128.50 (s), 144.56 (s), 58.52 (s), 53.98 (q), 35.94 (t), 35.45 (t), 35.28 (t), 35.06 (t), 30.47 (s), 21.91 (t)
3l	288 (M ⁺ , 84), 257 (48), 256 (100), 229 (76), 202 (84), 197 (55), 176 (36), 170 (60), 169 (98), 158 (48), 142 (43), 115 (33), 91 (26), 79 (43), 59 (78), 41 (36)	3.85 (s, 6H), 2.81 (s, 4H), 2.35 (m, 4H), 1.95 (quint, 2H, ³ J = 7.3 Hz)	167.16 (s), 132.00 (s), 116.10 (s), 54.93 (s), 52.77 (q), 35.56 (t), 34.83 (t), 22.59 (t)
3m	288 (M ⁺ , 41), 257 (35), 256 (52), 229 (42), 224 (44), 197 (31), 170 (35), 169 (100), 158 (25), 142 (26), 115 (23), 79 (26), 59 (58)	3.78 (s, 6H), 2.94 (m, 4H), 2.26 (m, 4H), 1.84 (quint, 2H, ³ J = 7.6 Hz)	165.77 (s), 130.60 (s), 117.13 (s), 54.88 (s), 47.53 (s), 35.54 (t), 33.49 (s), 22.14 (t)
3o	252 (M ⁺ , 49), 235 (27), 224 (51) 223 (27), 207 (22), 196 (23), 169 (25), 141 (15), 115 (24), 91 (31), 82 (71), 79 (38), 77 (35), 54 (100), 53 (20), 39 (36)	7.02 (s, 2H), 2.83 (m, 4H), 2.32 (t, 4H, ³ J = 7.0 Hz), 1.97 (quint, 2H, ³ J = 7.0 Hz)	185.81 (s), 137.77 (d), 130.20 (s), 115.22 (s), 52.22 (s), 35.18 (t), 30.33 (t), 21.46 (t)
3p	272 (M ⁺ , 7), 200 (18), 111 (100), 110 (76), 78 (84), 69 (25), 52 (18), 32 (30)	5.80 (s, 2H), 2.31 (s, 4H), 1.79 (t, 4H, ³ J = 7.3 Hz), 1.43 (quint, 2H, ³ J = 7.3 Hz)	187.56 (s), 166.69 (s), 138.78 (d), 131.33 (s), 60.61 (s), 35.23 (t), 27.95 (t), 21.37 (t)

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Experimental

¹H- and ¹³C-NMR (internal standard TMS): Varian XL 200 and EM 360 A. — MS: Finigan MAT 312/188.

Reagents: 1,2-Dimethylenecyclopentane (**1**)^[18], Methyl acrylate (**2a**), acrylonitrile (**2b**), fumaronitrile (**2e**), dimethyl fumarate (**2c**), and dimethyl maleate (**2d**) were purchased from Aldrich and purified either by distillation or recrystallization prior to use. Malconitrile was obtained from fumaronitrile according to ref.^[20]. 2-Cyano-1,1-bis(methoxycarbonyl)ethene (**2g**)^[21,22], tris(methoxycarbonyl)ethene (**2h**)^[21], 1,1-dicyano-2-(methoxycarbonyl)ethene (**2i**)^[21,23], 1,1-dicyano-2,2-bis(methoxycarbonyl)ethene (**2k**)^[22], *trans*-1,2-dicyano-1,2-bis(methoxycarbonyl)ethene (**2l**)^[24], *cis*-1,2-dicyano-1,2-bis(methoxycarbonyl)ethene (**2m**)^[25], 2,3-dicyano-*p*-benzoquinone (**2o**)^[26,27], *p*-benzoquinone-2,3-dicarboxylic anhydride (**2p**)^[28,29].

Cycloadditions were carried out in dichloromethane at room temp. Equimolar solutions of reagents (2–4 mmol) were mixed and allowed to react for the time indicated in Table 2. Removal of the solvent in vacuo and recrystallization (solvents see Table 2) gave pure products. No further purification was necessary in the case of oily products. The cycloadducts were characterized spectroscopically (¹H and ¹³C NMR, MS) and by elemental analysis. Data are given in Table 3.

Kinetic Measurements: Rate constants for the cycloaddition of **1** to dienophiles **2a–c**, **2e–g**, **2i–l**, **2n** and **2o** were measured under pseudofirst-order conditions at 20.0 ± 0.2 °C in dichloromethane. The first-order rate constants were converted to second order. Each measurement was repeated at least three times. The slower reactions were followed kinetically with a CARY 219 UV/VIS spectrometer which was modified in such a way that the sample, being in a fused silica cell in a thermostat, was connected to the spectrometer by optical wave guides. The data were collected in an attached micro-computer and analyzed by conventional methods. The kinetic model assumed a bimolecular reaction for product formation, neglecting any contribution of CT complexes in those cases where such complexes could be observed. The cycloadditions of the more reactive dienophiles were monitored with a cryostopped-flow spectrofluorimeter (model SF 40 of HI TECH Scientific^[30]) which has been described earlier^[10]. For dienophiles **2a–c** and **2e–g** the cycloaddition was followed at 250 nm (diene disappearance), for **2i** (λ = 390 nm), **2k** (λ = 380 nm), and **2l** (λ = 402 nm) the disappearance of CT absorptions was analyzed, for **2n** and **2o** the observation wavelengths were 270 and 300 nm. In those cases where

both diene and dienophile showed absorptions at the wavelengths of the measurement this was taken into account in the analysis.

Quantum Chemical Calculations: The MOPAC^[31] program package was used to carry out MNDO calculations on ground states of reagents. All geometrical variables were optimized. HOMO and LUMO energies were taken from these calculations.

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