ether (100 ml). After stirring for an additional 20 min, water was cautiously added; the solution was filtered, and the water layer was separated. The ethereal phase was washed with 2 *N* sodium hydroxide and water. Removal of solvent gave 2.2 g (81%) of liquid 6,6-dimethyl-1,8-octanediol 4-ethylene thioketal (**7a**) which was used without further purification as follows. To diol ethylene thioketal **7a** (1.0 g) in acetone (30 ml) was added cadmium carbonate (2.0 g) followed by mercuric chloride (1.0 g). The mixture immediately became yellow and tlc indicated that all starting material had been replaced by a less polar product. After solid material was removed (filtration), the acetone was evaporated. The residue was dissolved in chloroform and washed with aqueous potassium iodide and water. Removal of solvent at room temperature and distillation of the liquid product gave 0.23 g (36%) of spiroketal **8**: bp 60° (bath) (0.2 mm); ir (CCl_4) 1045 and 815 cm^{-1}; pmr ($CDCl_3$) δ 0.93 (s, 3), 1.15 (s. 3), 1.30 (m), 1.54 (s), 1.85 (m), 3.80 ppm (m, 4); mass spectrum (rel intensity), 171 (M + 1, 11), 170 (52), 169 (3), 156 (12), 155 (82), 152 (7), 148 (10), 147 (8), 142 (7), 140 (20), 139 (3), 138 (2), 137 (29), 130 (2), 129 (48), 127 (3), 126 (19), 125 (49), 114 (20), 113 (43), 112 (19), 111 (36), 109 (4), 105 (5), 98 (8), 97 (2), 96 (3), 95 (4), 93 (4), 91 (5), 89 (3), 88 (29), 87 (100), 86 (51), 85 (29), 84 (86), 83 (33), 81 (4), 79 (5), 77 (6), 72 (9), 71 (14), 70 (16), 69 (88), 68 (18), 67 (20), 59 (12), 58 (8), 57 (22), 56 (91), 55 (48), 54 (25), 53 (15), 45 (31), 44 (22), 43 (56), 42 (30), 41 (56), 40 (22), 39 (33).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65. Found: C, 70.43; H, 10.53.

2-(3′-Hydroxypropyl)-4,4-dimethyltetrahydropyran (9a). To a stirred mixture of lithium aluminum hydride (0.50 g) and aluminum chloride (6 g) in dry ether (100 ml) at room temperature was added (5 min) spiroketal **8** (0.23 g) in 20 ml of ether. The reaction mixture was maintained at room temperature 1.5 hr and heated at reflux for 30 min. Water and 6 *N* hydrochloric acid were cautiously added until two clear layers appeared. The ether layer was separated and washed with saturated sodium bicarbonate and water. Removal (*in vacuo*) of solvent afforded a quantitative yield of alcohol **9a** as a clear liquid. Distillation gave an analytical sample: bp 54° (bath) (0.014 mm); ir (CCl_4) 3440, 1112, and 1075 cm^{-1}; pmr ($CDCl_3$) δ 0.97 (s, 3), 1.02 (s, 3), 1.40 (m, 8, br), 3.60 (m, 5, br), 4.15 ppm (s, 1, br); mass spectrum (see Table I).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.55; H, 12.03.

2-(3′-Hydroxypropyl)-4,4-dimethyltetrahydropyran-*2-d* (9b). Deuteration of alcohol **9a** was accomplished using lithium aluminum deuteride in place of the hydride as described in the preceding experiment. The product **9b** boiled at 70° (bath) (0.03 mm); ir (neat) 3400, 2100, 1075, and 1050 cm^{-1}; pmr ($CDCl_3$) δ 0.97 (s, 3), 1.02 (s, 3), 1.40 (m, 8, br), 2.70 (m, 1, br), 3.65 ppm (m, 4).

An Analysis of Ketene Cycloadditions by Self-Consistent Perturbation Theory

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Received January 24, 1972

Abstract: The significance of the carbonyl group in ketene and the influence of substituents in ketenophiles are investigated by self-consistent perturbation theory (MINDO and CNDO/2 approximation) and by a variation perturbation treatment which is based on SCF wave functions (CNDO/2 approximation). The stabilization through the interaction of the ketenophile π system with the carbonyl π bond plays a dominant role in the orthogonal $({}_\pi 2_s + {}_\pi 2_a)$ approach of the two reactants. This interaction is also responsible for the addition at the carbon–carbon double bond compared to a reaction at the carbonyl group of ketene. The high reactivity of "electron rich" and unsymmetrical ketenophiles is explained by the stabilization through the interaction with the unoccupied carbonyl π orbital and by electrostatic interactions.

The interpretation of ketene cycloadditions in terms of orbital symmetry remained controversial for several years. However, the formulation as a $({}_\pi 2_s + {}_\pi 2_a)$ process[1] together with the subsequent experimental proof of the orthogonal approach by stereochemical investigations[2-4] and kinetic data[5] seemed to provide a satisfactory explanation. The concerted nature of the reaction which should be an attribute of the $({}_\pi 2_s + {}_\pi 2_a)$ process was proven for several cases.[5-7]

Although the carbonyl group of ketene forms the arrowhead of the reaction, as is pointed out by Woodward and Hoffmann,[1] this qualitative picture does not elucidate its significance for the $({}_\pi 2_s + {}_\pi 2_a)$ reaction path. Furthermore, there is no *a priori* reason why the cycloaddition normally occurs at the carbon–carbon double bond and not at the carbonyl group. Thermal (2 + 2) cycloadditions of carbonyl groups to olefins and acetylenes are known.[8,9] It was found only recently that the cumulated double bond of carbon dioxide adds to ynamines.[10] Cycloaddition at the carbonyl group was observed for the reaction of bis(trifluoromethyl)ketene with enol ethers or enol esters,[11] for diphenylketene with ynamines,[12] for ethoxyketene with cyclohexene,[13] and for the reaction of ketene with tetramethoxyethylene.[14] Another poorly understood aspect of this

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cycloaddition is the influence of substituents in the ketenophile on the rate of addition.[15] Electron-rich, especially unsymmetrically substituted olefins exhibit the highest reactivity whereas electron-deficient double bonds do not react. The change in mechanism as a function of substituents should be connected to this reactivity pattern.[16]

Self-consistent perturbation theory[17] in semiempirical form has proven to be useful for problems in chemical reactivity.[18] The selection of appropriate molecular complexes and the identification of the dominant interactions allow us to derive a qualitative representation of the reaction path. Besides the original MINDO/11 version of the self-consistent perturbation theory,[18] we use the MINDO/2[19] and the CNDO/2[20] approximation. In addition, a variation perturbation procedure in the CNDO/2 approximation is tested which is based on SCF wave functions but is not self-consistent. This latter theory originally proposed by Pople for one-electron perturbations in π-electron systems[21] has been extended to two-electron perturbations and was successfully applied to hydrogen bonding.[22]

Results

Computational Procedures. In the perturbation calculations the first- and second-order energy changes are evaluated. The first-order energy in which the change in nuclear repulsion has been incorporated and which is identical for all semiempirical procedures is given by

$$\delta E^{(1)} = \sum_k \sum_l (q_k q_l \gamma_{kl} + (\gamma_{N_k N_l} - \gamma_{kl}) C_k C_l \times \exp(-\alpha_{kl} R_{kl})) \quad (1)$$

Here $q_{k(l)}$ represent the excess charges of the atoms $k(l)$ in the subsystems K and L; γ_{kl} is the repulsion between electrons at atoms k and l. The second term in eq 1 describes the difference between a point charge repulsion $\gamma_{N_k N_l}$ and the electron repulsion γ_{kl} at the distance R_{kl}. This is multiplied by the core charges $C_{k(l)}$ and an exponential. α_{kl} are bond parameters for MINDO/11[23] and MINDO/2 determining the amount of point-charge character which is given to the nuclear repulsion. The full point-charge repulsion enters the CNDO/2 treatment; *i.e.*, α_{kl} is set at zero. The first term in eq 1 is proportional to the excess charges and will be significant only if the electron distribution in both subsystems is highly nonuniform or if the interaction of charged particles is investigated. It will be called "charge interaction." The second term, also coulombic in nature, includes most of what a chemist considers to be steric hindrance and will therefore be called "steric interaction."

The variation perturbation treatment differs from the self-consistent perturbation theory[17,18] by the expression for the second-order energy. The expansion of the perturbed wave function as linear combination of the ground-state wave function and singly excited singlet state wave functions leads in the CNDO/2 approximation to eq 2.[24] The first two terms in eq 2 which are a

$$\begin{aligned}\delta E^{(2)} = {} & -2\sum_{u}^{\text{occ}} \sum_{p}^{\text{unocc}} \left[\sum_{\mu} \sum_{\lambda} c_{u\mu} c_{p\lambda} \beta_{\mu\lambda} \right]^2 E_u{}^{p-1} - \\ & 2\sum_{p}^{\text{occ}} \sum_{u}^{\text{unocc}} \left[\sum_{\lambda} \sum_{\mu} c_{p\lambda} c_{u\mu} \beta_{\lambda\mu} \right]^2 E_p{}^{y-1} - \\ & 2\sum_{u}^{\text{occ}} \sum_{v}^{\text{unocc}} \left[\sum_{\mu} \sum_{l} c_{u\mu} c_{v\mu} \gamma_{\mu l} q_l \right]^2 E_u{}^{v-1} - \\ & 2\sum_{p}^{\text{occ}} \sum_{q}^{\text{unocc}} \left[\sum_{\lambda} \sum_{k} c_{p\lambda} c_{q\lambda} \gamma_{\lambda k} q_k \right]^2 E_p{}^{q-1}\end{aligned} \quad (2)$$

function of the resonance integrals $\beta_{\mu\lambda}$ and depend on charge-transfer excitation energies[21,22] represent the covalent interaction of the systems K and L. This is analogous to independent electron perturbation theory.[25] The two other terms which are divided by local excitation energies display a second-order electrostatic interaction. Their contribution should be negligible as long as the interaction of uncharged particles is studied.

The different formalisms were programmed in FORTRAN IV. In the self-consistent perturbation calculations normally two or three iterations were carried out, corresponding to a convergence limit of ≤ 0.001 for the change of an element of the perturbed first-order density matrix. Carrying the convergence to higher limits will affect the magnitude of the second-order energy slightly but will not influence the relative magnitude of individual energy components.

Interaction of Two Ethylenes. In order to appreciate the special features of ketene cycloadditions, a comparison with the interaction of two ethylenes in a parallel ($_{\pi}2_s + {}_{\pi}2_s$) (**1**) and an orthogonal ($_{\pi}2_s + {}_{\pi}2_a$) orientation (**2**) seemed to be necessary. The total energies of the MINDO perturbation calculations (Table I) show that at a separation of 3.0 Å the parallel alignment **1** is favored by several kilocalories per mole (9.318 and 10.847 kcal/mol as compared to 17.402 and 16.867 kcal/mol for **2**). The high repulsive contribution of the hydrogen atoms 3 and 5 in **2** (3.065 and 2.061 kcal/mol for MINDO/11 and MINDO/2; Table II) which is almost entirely due to "steric interactions" reveals the origin of the preference for **1**. However, for **1** no bonding second-order contribution from the p_{π} atomic orbital pairs is observed, their interaction being zero. Because it is impossible to overcome the repulsive first-order energy without concomitant stabilization from the p_{π} interactions, the new carbon–carbon bonds cannot be formed by this mode of approach. Even though in **2** the finite bonding contribution from the π systems is small at 3.0 Å, it will increase rapidly at shorter distances.

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[24] We use the following index convention: u, v = molecular orbitals of K; p, q = molecular orbitals of L; μ = atomic orbitals in K; λ = atomic orbitals in L; k, l = atoms in K and L.

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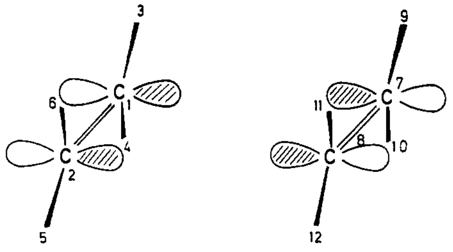

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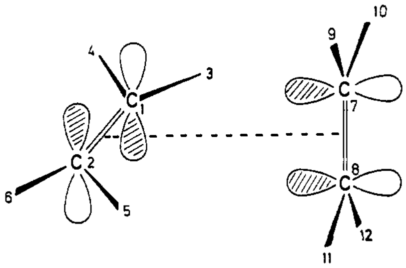

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Table I. Perturbation Energies of Molecular Complexes between Two Ethylenes (**1**–**2**) and Ethylene and Ketene (**3**–**5**)

Complex	1st order[a] 2nd order[a] Total[a]	SCF perturbation procedures MINDO/11	 MINDO/2	 CNDO/2	Variation perturbation procedure CNDO/2
1	1	9.878	12.486	1.356	1.356
	2	−0.560	−1.639	−1.163	−1.186
	T	9.318	10.847	0.193	0.170
2	1	20.111	27.539	3.736	3.736
	2	−2.709	−10.673	−3.003	−3.064
	T	17.402	16.867	0.733	0.672
3	1	9.423	13.220	1.385	1.385
	2	−0.684	−1.461	−1.422	−1.465
	T	8.739	11.759	−0.037	−0.081
4	1	10.908	15.865	1.455	1.455
	2	−1.412	−4.287	−2.800	−2.905
	T	9.496	11.578	−1.345	−1.450
5	1	8.069	11.848	1.107	1.107
	2	−1.009	−1.332	−1.533	−1.541
	T	7.060	10.517	−0.426	−0.434

[a] kcal/mol.

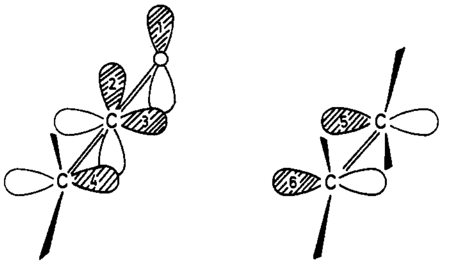
The perturbation calculations based on the CNDO/2 approximation underestimate the first-order repulsion. This becomes apparent from the total energies which fail to produce a perceptible energy barrier and from the total contributions of the hydrogen atoms 3 and 5 in **2** (−0.412 kcal/mol) which are bonding (Table II). However, the interpretation of the second-order energy leads to the same conclusions as in the other calculations.

Interaction of Ketene and Ethylene. A parallel complex **3** and an orthogonal complex **4** where the carbon–carbon double bond of the olefin is located perpendicular to the central ketene carbon atom were investigated at a separation of 3.0 Å. Whereas the MINDO treatments produce repulsive total energies (8.739 and 11.759 kcal/mol for **3**; 9.496 and 11.578 kcal/mol for **4**), CNDO/2 gives no barrier of activation (−0.081 kcal/mol for **3**; −1.450 kcal/mol for **4**) (Table I). A comparison of the total energies for **3** and **4** with those of **1** and **2** reveals that the steric preference for the parallel orientation is no longer present. This is primarily due to the substitution of two hydrogen atoms of ethylene by oxygen.

Table II. Atom Contributions to the Perturbation Energies of the Orthogonal (**1**) and Parallel (**2**) Complex of Two Ethylenes

Complex	Atom[d]	Perturbation method	1st order[e]	2nd order[e]	1st + 2nd order[e]
1	1=2=7=8	*a*	0.949	−0.024	0.925
		b	1.238	0.016	1.254
		c	0.269	−0.274	−0.005
	3=4=5=6	*a*	0.760	−0.058	0.702
	9=10=11=12	*b*	0.942	−0.213	0.729
		c	0.035	−0.008	0.027
2	1=2	*a*	0.886	0.244	1.130
		b	1.163	0.809	1.972
		c	0.232	0.379	0.611
	3=5	*a*	3.964	−0.899	3.065
		b	5.508	−3.447	2.061
		c	0.691	−1.103	−0.412
	4=6	*a*	0.177	−0.024	0.153
		b	0.214	−0.030	0.184
		c	0.011	−0.027	−0.016
	7=8	*a*	2.150	−0.419	1.731
		b	3.327	−0.778	2.549
		c	0.726	−0.753	−0.027
	9=10=11=12	*a*	1.439	−0.129	1.310
		b	1.779	−0.945	0.834
		c	0.104	0.001	0.105

[a] MINDO/11. [b] MINDO/2. [c] CNDO/2. [d] Numbering as in **1** and **2**. [e] kcal/mol.



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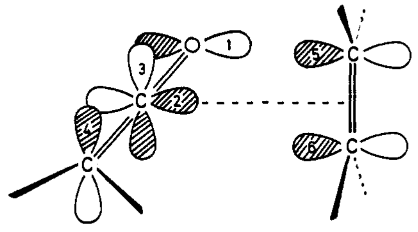


4

As the two carbon atoms of ketene are not identical, a finite bonding interaction of the p_π atomic orbitals of the carbon–carbon double bonds results for **3** (interaction 3–5 and 4–6 for **3** in Table III). A further consequence of the parallel orientation is that no interaction of the ethylene π system with the carbonyl π bond is possible (interaction 1–5(6) = 2–5(6) of Table III). The orthogonal orientation displays significant differences. Besides interactions of the carbon–carbon bonds which are similar as in **3** (3–5(6) and 4–5(6) in Table III), an additional high stabilization stems from the interaction of the olefin π electrons with the carbonyl p orbital of the central carbon atom in ketene (2–5(6) in Table III). The variation perturbation treatment traces this extra stabilization for **4** back to the interaction of HOMO ethylene and the molecular

Table III. Orbital Pair Contributions for the Complexes between Ketene and Ethylene (**3**–**5**)

Complex	Orbital pair[a]	SCF perturbation procedures MINDO/11[b]	MINDO/2[b]	CNDO/2[b]
3	1-5(6) = 2-5(6)	0.0	0.0	0.0
	3-5	−0.043	−0.076	−0.191
	4-6	−0.011	−0.073	−0.263
4	1–5(6)	0.023	0.054	0.177
	2–5(6)	−0.168	−0.311	−1.050
	3-5(6)	−0.011	−0.026	−0.099
	4–5(6)	−0.007	−0.016	−0.061
5	1-5(6)	−0.002	−0.004	−0.016
	2–5(6)	−0.006	−0.016	−0.069
	3-5(6)	−0.110	−0.214	−0.703
	4–5(6)	0.038	0.076	0.272

[a] Orbital numbering as in **3**–**5**. [b] kcal/mol.

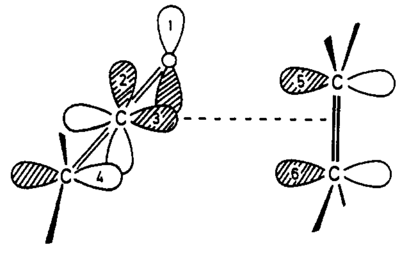
orbital of ketene which corresponds most closely to the unoccupied carbonyl π orbital. The relevant charge-transfer stabilizations are given in Table IV. It can be seen that the difference in total energy between **3** and **4** is due almost entirely to this interaction (−1.355 kcal/mol).

Table IV. HOMO–LUMO* Interactions for the Complexes of Ketene and Ethylene by the Variation Perturbation Treatment

Molecular orbitals ketene–ethylene	Charge-transfer stabilizations[a] **3**	**4**	**5**
C=C → C=C*	−0.285	−0.118	0.000
C=O → C=C*	0.0	0.000	−0.007
C=O* ← C=C	0.0	−1.355	0.000
C=C* ← C=C	−0.052	0.000	−0.728

[a] kcal/mol.

In order to elucidate the preferred addition of ketenes at the carbon–carbon bond as compared to the carbonyl bond, an orthogonal complex **5** for a (${}_{\pi}2_s + {}_{\pi}2_a$) carbonyl addition at a separation of 3.0 Å was evaluated. The parallel alternative will suffer from the same disadvantages as **3** and was therefore disregarded. The reactivity difference between the two types of ketene double bonds can be explained by the orbital pair contributions of Table III. The interaction of the ethylene p orbitals with those of the carbonyl π bond (1–5(6) and 2–5(6) for **5** in Table III) is smaller than the stabilization through the interaction of the p orbitals of ethylene with those of the carbon–carbon double bond of ketene in **4** (3–5(6) and 4–5(6) in Table III). However, more important is the reduced bonding of the olefin π system with the carbon–carbon double bond of ketene (3–5(6) and 4–5(6) in Table III) which is equivalent to the stabilization through the carbonyl group in **4** (1–5(6) and 2–5(6)). The variation perturbation procedure leads to the same conclusion (Table IV); the interaction of the occupied olefin π orbital with the unoccupied carbon–carbon double bond orbital in ketene (−0.728 kcal/mol) is smaller than the HOMO ethylene–LUMO ketene carbonyl orbital stabilization in **4** (−1.355 kcal/mol). As a consequence, cycloaddition at the carbonyl group of ketene is less favorable than reaction at the carbon–carbon double bond.



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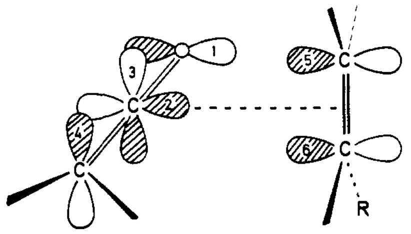
Substituent Effects. A detailed analysis of the interaction of ketene with aminoethylene (**6**), with methyl vinyl ether (**7**), and with methyl acrylate (**8**) was carried out assuming orthogonal complexes at a separation of 3.0 Å. The total energies (Table V) for the CNDO/2 perturbation calculations are net attractive, becoming more negative from methyl acrylate (−0.462 and −0.478 kcal/mol) to aminoethylene (−1.331 and −1.425 kcal/mol). This is entirely due to decreasing first-order energies. The second-order energies in the MINDO approximation also do not show perceptible differences for **6**–**8**; yet, the first-order energies are such that a total destabilization results (lines *a* and *b* in Table V).

Table V. Perturbation Energies for Orthogonal Complexes of Ketene and Substituted Ethylenes ($H_2C{=}CHR$)

Complex	Perturbation method	1st order[e]	2nd order[e]	1st + 2nd order[c]
6, R = NH_2	*a*	11.197	−1.497	9.800
	b	16.647	−4.433	12.214
	c	1.518	−2.849	−1.331
	d	1.518	−2.943	−1.425
7, R = OCH_3	*a*	13.229	−1.452	11.197
	b	18.621	−4.331	14.290
	c	2.070	−2.818	−0.748
	d	2.070	−2.881	−0.811
8, R = CO_2CH_3	*a*	12.528	−1.437	11.091
	b	17.821	−4.126	13.695
	c	2.405	−2.868	−0.462
	d	2.405	−2.883	−0.478

[a] MINDO/11. [b] MINDO/2. [c] CNDO/2. [d] Variation perturbation CNDO/2. [e] kcal/mol.



6, R = NH_2
7, R = OCH_3
8, R = CO_2CH_3

The second-order π-orbital interactions in Table VI demonstrate that independent of the semiempirical method the highest interactions of the ketenophile occur with the carbon p orbital of the carbonyl system (interaction 2–5 and 2–6 in Table VI). The magnitude of this stabilization furthermore parallels the experimental reactivity trend. An unsymmetrical transition state is indicated by the stronger 2–5 as compared to the 2–6 interaction (see **6**–**8**). The variation perturbation treatment also shows that the highest stabilization derives from the interaction of the highest occupied π orbital of the ketenophile with the unoccupied car-

Table VI. Second-Order Orbital Interactions in kcal/mol for the Complexes of Ketene and Substituted Ethylenes ($CH_2{=}CHR$)

Orbital pair[a]	SCF perturbation procedures								
	MINDO/11	MINDO/2	CNDO/2	MINDO/11	MINDO/2	CNDO/2	MINDO/11	MINDO/2	CNDO/2
	R = NH_2 (**6**)			R = OCH_3 (**7**)			R = CO_2CH_3 (**8**)		
1–5	0.0265	0.0614	0.2065	0.0248	0.0594	0.1643	−0.0346	0.0049	0.1579
1–6	0.0207	0.0514	0.1608	0.0201	0.0513	0.1913	0.0465	0.0694	0.1800
2–5	−0.1868	−0.3499	−1.1792	−0.1724	−0.3370	−1.0968	−0.1545	−0.2746	−1.0040
2–6	−0.1615	−0.3035	−1.0020	−0.1586	−0.3040	−1.0128	−0.0078	−0.1732	−0.9495
3–5	−0.0108	−0.0250	−0.0946	−0.0106	−0.0254	−0.0972	−0.0135	−0.0310	−0.1154
3–6	−0.0099	−0.0224	−0.0878	−0.0110	−0.0239	−0.0941	−0.0130	−0.0275	−0.0981
4–5	−0.0050	−0.0114	−0.0408	−0.0074	−0.0138	−0.0518	−0.0089	−0.0203	−0.0693
4–6	−0.0068	−0.0153	−0.0567	−0.0060	−0.0164	−0.0603	−0.0060	−0.0159	−0.0596

[a] The numbering of the orbitals is indicated in **6–8**.

Table VII. Charge-Transfer Interactions for the HOMO's and LUMO's* in the Complexes of Ketene and Substituted Ethylenes

Molecular orbitals Olefin–ketene		R = NH_2 **6**	R = OCH_3 **7**	R = CO_2CH_3 **8**
C=C → C=O*	a[a]	−0.755	−0.723	−0.321
	b[b]	11.185	12.815	13.792
C=C → C=C*	a	−0.014	−0.003	−0.003
	b	13.447	15.077	16.090
C=C* ← C=C	a	−0.101	−0.112	−0.085
	b	14.589	13.879	11.213
C=C* ← C=O	a	−0.001	0.000	−0.011
	b	18.529	17.822	15.129

[a] Charge-transfer stabilization (kcal/mol). [b] Charge-transfer excitation (eV).

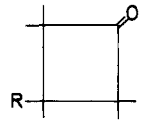
Table VIII. Charge Interactions in the Complexes of Ketene and Substituted Ethylenes ($H_2C{=}CHR$)

Fragments	SCF perturbation procedures[e]								
	MINDO/11	MINDO/2	CNDO/2	MINDO/11	MINDO/2	CNDO/2	MINDO/11	MINDO/2	CNDO/2
	R = NH_2 (**6**)			R = OCH_3 (**7**)			R = CO_2CH_3 (**8**)		
A[a]–C[c]	1.266	2.440	1.997	0.371	1.523	0.972	−1.592	−1.866	−0.655
A–D[d]	−1.619	−2.861	−2.335	−0.532	−1.856	−1.167	1.917	2.135	0.723
B[b]–C	−1.225	−2.227	−1.732	−0.544	−2.302	−0.952	0.995	1.124	−0.199
B–D	1.707	2.606	1.866	2.453	3.040	1.326	0.044	−0.601	0.341
A–(C + D)	−0.353	−0.421	−0.338	−0.161	−0.333	−0.195	0.325	0.269	0.068
B–(C + D)	0.483	0.379	0.134	1.909	0.738	0.374	1.040	0.523	0.142
(A + B)–(C + D)	0.132	−0.042	−0.204	1.748	0.405	0.179	1.365	0.792	0.210

[a] Methylene group of ketene. [b] Carbonyl group of ketene. [c] Methylene group of ketenophile. [d] Remaining ketenophile. [e] kcal/mol.

bonyl π orbital of ketene (Table VII). The energy gain through this charge-transfer stabilization decreases from **6–8**, a result which is in accordance with the opposite trend of the charge-transfer excitation energies (Table VII).

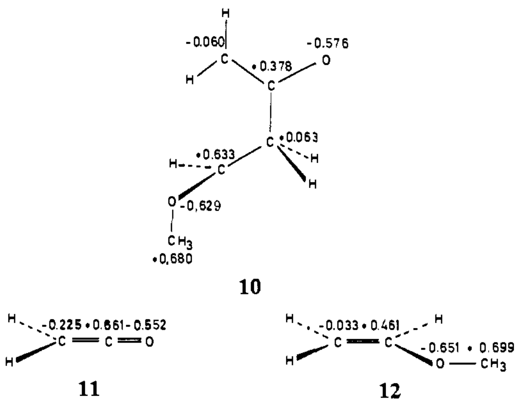
The cycloaddition of enamines and enol ethers leads to cyclobutanones with the substituent in the 3 position (**9**). Table VI makes it clear that the observed regiospecificity for enamines and enol ethers is not only favored by the interaction of the ketenophile p orbitals with the carbonyl p orbitals (interaction 2–5(6) in Table VI) but also by the interaction with the p orbitals of the carbon–carbon double bond of ketene (interaction 3–5 is > 4–6 in Table VI). The experimental orientation is further substantiated if one separates the molecules in individual groups and analyzes their charge interactions (Table VIII). The methylene groups of aminoethylene and methyl vinyl ether are attracted electrostatically by the carbonyl group of ketene (B–C), the interaction with the methylene group of ketene being repulsive (A–C). The opposite holds for the remaining part of the ketenophile: attraction by the methylene group (A–D) and repulsion by the carbonyl group of ketene (B–D). Although the total charge interactions in the orthogonal complexes are small at 3.0 Å, the individual terms demonstrate the presence of an electrostatic force which pushes the molecules in the correct orientation. Looking at ketene as a unit the methylene group of the ketenophiles **6** and **7** is attracted (A–(C + D) in Table VIII) and the remaining molecule is repelled. This points to an unsymmetrical transition state which is more pronounced for methyl vinyl ether than for aminoethylene. Methylacrylate behaves differently because neither the segment A nor B of the ketenophile is attracted by ketene. As a consequence, methyl acrylate should be less reactive than the other ketenophiles. In the case that addition would take place, the methoxycarbonyl group of methyl acrylate should appear in the 2 position of the cyclobutanone as is shown by the electrostatic interactions (A–C and B–D are more favorable than B–C and A–D in Table VIII).



9

Discussion

The perturbational investigation of molecular complexes between ketene and olefins and between two ethylenes allows us to recognize three features by which ketene cycloadditions are different from the ethylene dimerization. (1) As a consequence of the substitution of two hydrogen atoms by oxygen, the steric hindrance decreases and the orthogonal approach is facilitated. (2) The orthogonal orientation gains considerably from the interaction with the carbonyl π bond of ketene. (3) In the parallel orientation bonding results through



10

11

12

Figure 1. Excess charge densities for **10**–**12**.

the p orbitals of the carbon–carbon double bonds of ketene and ethylene.

The important influence of the carbonyl group raises the question whether the molecules would follow an orthogonal pathway if it were not assisted by this group. Because of the smaller steric hindrance it seems possible that (2 + 2) cycloadditions of highly unsymmetrical reactants having no opportunity of an extra stabilization like the carbonyl group do occur by a parallel or quasiparallel approach.

The normally preferred addition of olefins at the carbon–carbon π bond in ketenes follows from the less favorable interaction of the occupied olefin π molecular orbital in **5** with the unoccupied carbon–carbon double bond in ketene as compared to the same interaction in **4** with the unoccupied carbonyl π orbital. This result may offer an understanding of the different behavior of bis(trifluoromethyl)ketene[11] where both carbonyl and carbon–carbon double bond cycloaddition have been observed. As a consequence of the strongly electron-withdrawing substituents, the carbon–carbon double bond becomes similar to a carbonyl π system and therefore an orthogonal complex like **5** should gain in stability.

It seems as if the additional stabilization through the bond which in general is not directly involved in the reaction is responsible for the reactivity pattern. The influence of electron-releasing and electron-withdrawing substituents on the rate of addition leads to similar conclusions. These results may be rationalized by a simple one-electron perturbation model. The interaction of the highest occupied molecular orbitals with the lowest unoccupied ones of the two reactants will give the most important contribution to the intermolecular stabilization, the magnitude of this interaction being inversely proportional to the orbital separation. The qualitative energy level diagram for ketene and an electron-rich olefin shows that the HOMO of the olefin and the unoccupied carbonyl π orbital does have the smallest separation and therefore should yield the dominant stabilization. In order to take advantage of this energy gain the molecules have to approach orthogonally. Electron-releasing substituents in the ketenophile will raise its HOMO energy level and as a consequence of the reduced HOMO–LUMO separation increase the reactivity. Electron-withdrawing substituents will have the opposite effect on the orbital energy and therefore reduce the reactivity. This is exactly what is found for ketene cycloadditions. The same rationalization can be given for the interaction of the occupied and unoccupied molecular orbitals of the carbon–carbon double bonds. However, their separation is greater and therefore their interaction will provide less stabilization as is borne out by the perturbation calculations. Similarly, substituents in the ketene will influence the orbital pattern. To a first approximation only the carbon–carbon double bond will be affected. Electron-withdrawing substituents will lower both the occupied and unoccupied molecular orbital in energy, hence increasing the interaction of HOMO olefin with LUMO of the carbon–carbon bond in ketene. Therefore ketenes with electron-withdrawing substituents should exhibit higher reactivity toward electron-rich olefins than does ketene itself. As was pointed out earlier, a consequence of electron-attracting substituents in ketenes should be the competition of the carbonyl bond with the carbon–carbon double bond; bis(trifluoromethyl)ketene seems to be an example. The importance of HOMO–LUMO interactions for the reactivity pattern in cycloadditions has recently been stressed.[26,27] Also, in the case of vinyl cation interacting with olefins[28] and acetylenes,[29] the leading influence of these contributions has been recognized.

The greater reactivity of unsymmetrical ketenophiles which is exhibited by a rate factor of 250 between dihydrofuran and 1,3-dioxole[15] demonstrates that the above reactivity model does not take care of all factors. Electrostatic interactions due to the nonuniform electron distribution in the reactants which are given by the charge interactions seem to be responsible. The electrostatic attraction of the methylene groups of aminoethylene and methyl vinyl ether by the ketene carbonyl group and by ketene as a whole increases the total bonding interaction and therefore these polarized unsymmetrical ketenophiles exceed the symmetrical 1,3-dioxole in reactivity. In the latter case such favorable electrostatic interactions are not possible. This result indicates that the ring closure starts preferably at the carbonyl carbon atom.

The perturbational analysis was performed without making assumptions about a one-step or a multistep reaction. All complexes can in principal yield the adducts in a concerted fashion. Whether they will follow this possibility or prefer a multistep reaction will depend on the stability of feasible intermediates and the ease by which they can be formed. The initial approach of the molecules and therefore the interpretation of the perturbation calculations should not be affected by the mechanistic uncertainty. Unsymmetrical charge interactions and unsymmetrical covalent interactions will assist the formation of intermediates. In this respect enol ethers should exhibit a less symmetric transition state than enamines. Another factor important for the distinction between a one-step or a multistep addition is the amount of charge separation necessary to form a dipolar intermediate. Therefore a MINDO/1 variational calculation using standard bond lengths and bond angles[30] was performed for a hypothetical dipolar intermediate (**10** in Figure 1). The small additional

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(26) R. Sustmann, *Tetrahedron Lett.*, 2717 (1971).

(27) R. Sustmann, *ibid.*, 2721 (1971).

(28) H.-U. Wagner and R. Gompper, *ibid.*, 4061 (1971).

(29) H.-U. Wagner and R. Gompper, *ibid.*, 4065 (1971).

(30) "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.*, No. 11 (1958); *Suppl.*, No. 18 (1965).

charge separations which occur in comparison to the parent molecules **11** and **12** (Figure 1) seem to facilitate the formation of an intermediate. This finding makes the experimental distinction between a one-step or a multistep reaction difficult. Only a rather small rate change is expected if the solvent polarity is altered and this even if the reaction takes place by way of an intermediate. The observation of a rate factor of 36 for cyclohexane and acetonitrile as solvents in the concerted reaction and one of 560 for the multistep addition of dimethylketene to pyrrolidinoisobutene confirms the assumption.[16] The superposition of the two rate factors yields a total solvent dependence of 79. This is smaller than the value of 160 for the cycloaddition of diphenylketene and butyl vinyl ether which presumably add exclusively in a concerted fashion.

SCF perturbation theory and the variation perturbation treatment seem to be suited to interpret problems in chemical reactivity. The semiempirical schemes show distinct differences. The CNDO/2 approximation underestimates the repulsive forces between molecules and therefore is unable to account for steric effects. The MINDO/11 and the MINDO/2 procedures compensate this disadvantage by their treatment of nuclear repulsions. MINDO integrals are smaller (about 20%) than the same CNDO/2 integrals over Slater orbitals.[19,20] An analysis of term 2 in eq 1 shows that the difference between electron repulsion and exact point charge repulsion is greater for MINDO/11 and MINDO/2 than for CNDO/2. Even though this difference is multiplied by an exponential, the magnitude of the MINDO α parameters ensures higher repulsive interactions. As far as the second-order energy is concerned, all procedures lead to the same qualitative interpretation. The variation perturbation treatment is attractive because it enables an interpretation of the results analogous to Hückel perturbation theory. The different programs written for an IBM 360/50 computer will be available from QCPE.[31]

Acknowledgments. This work was supported by the Deutsche Forschungsgemeinschaft. Computer time was made available by the computer center of the University in Münster.

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Excited-State Geometries of the Singly Substituted Methylpropenals. III.[1a] Geometry, Substituent Interaction, Fermi Correlation, and Spin–Orbit Coupling in $T_1(n,\pi^*)$

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Contribution from the Hall-Atwater Laboratories, Wesleyan University, Middletown, Connecticut 06457. *Received March 15, 1972*

Abstract: The nature of the first excited n,π* triplet states of acrolein, crotonaldehyde, methacrolein, and methyl vinyl ketone was investigated using low and medium resolution vibrational electronic spectroscopy, and molecular orbital and spin–orbit coupling calculations. The spectroscopic analysis and singlet–triplet splitting calculations indicate that the n,π* triplet is planar and is hence of n,π*(π) character. This observation is discussed with reference to recent *an initio* calculations which indicate that acrolein's n,π* triplet relaxes to a nonplanar geometry of y,π* orbital nature. The prominent Fermi correlative mechanism in the n,π* triplet state involves delocalization of the spin-unpaired electrons rather than charge separation, indicating that the n,π* triplet should be less photoreductive than the corresponding n,π* singlet. Oscillator strengths for the $S_0 \rightarrow T_1$ transition in the three aldehydes were experimentally observed and compared to values calculated using spin–orbit coupling theory. These calculations, based on the McClure central field approach utilizing a one-electron Hamiltonian, successfully predict the relative ordering of the oscillator strengths. The principal perturbing singlet is found to be $S_2(\pi,\pi^*)$, but mixing of the ground-state singlet into $T_1(n,\pi^*)$ is also found to be significant because of the relatively large ground-state dipole moments observed for acrolein and its singly substituted methyl derivatives.

In the first two parts of this three-part investigation,[2,3] the vibrational electronic spectrum of $S_1(n,\pi^*(\pi))$ was analyzed and used in a discussion of substituent interaction in the first excited singet state. The methyl group was found to perturb the energy of the ground-state nonbonding electrons on oxygen and the excited state π* orbital *via* similar mechanisms involving "hyperconjugative" charge redistribution. The amount of methyl group electron donation was found to be of lesser importance than the position of the localized electron density within the molecular orbital.[3] The present report investigates substituent interaction in the first excited n,π* triplet manifold to find what effect methyl group position has on the energy and geometry of T_1 and the intensity of the spin-forbidden $S_0 \rightarrow T_1(n,\pi^*)$ transition.

A summary of important experimental and calculated parameters for the triplet states of acrolein and its singly substituted methyl derivatives is given in Table I. The observed singlet–triplet splittings (~1600

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[1] (a) The Nature of the n → π* Transition. III. (Abstracted from a portion of the Ph.D. Thesis of R. R. B., Wesleyan University, 1972.) For parts I and II, see ref 2 and 3, respectively. (b) Deceased Aug 16, 1971.

[2] R. R. Birge, W. C. Pringle, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **93**, 6715 (1971).

[3] R. R. Birge and P. A. Leermakers, *ibid.*, **93**, 6726 (1971).