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THE REGIOSELECTIVITY OF α,β-ENONE PHOTOANNELATION WITH MONOSUBSTITUTED ACETYLENES: A POSSIBLE EFFECT OF DIPOLE–DIPOLE INTERACTIONS

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Abstract—The Raman and ^1H NMR-spectra of mixtures of 2-cyclopentenone and 2-cyclohexenone with 1-hexyne show that the enone-alkyne association in the ground state is weak and cannot account for the difference in the regioselectivity observed in photocycloadditions of enones to alkynes and alkenes. The comparison of dipole moments and the calculation of π-electronic charges on the interacting orbitals of both enone and substrate lead to the conclusion that the regioselectivity of enone-alkyne photoannelation may be controlled by the dipole–dipole interactions between the $_3(\pi, \pi^*)$ state of the enone and the ground state of the substrate. This effect is the stronger, the weaker are π-donating capacity and polarization of the multiple bond in the substrate.

A large majority of the mixed [2 + 2] photocycloadditions involving α,β-enones and unsymmetrically substituted olefins obey the so-called Corey rule.[1] The latter stipulates that the regioselectivity of a cycloaddition is determined at the stage of formation of a π-complex between the triplet state of the enone and the ground state of the substrate. Since the polarization of the enone double bond in the triplet state is believed to be opposite to its polarization in the ground state, the reaction with alkenes possessing electron-donating groups should lead mainly to the head-to-tail cycloaddition while the reaction with olefins possessing electron-withdrawing groups should lead mainly to the head-to-head cycloadducts. Such orientation arises from Coulombic interaction between the π-orbitals concerned (see Chart 1).

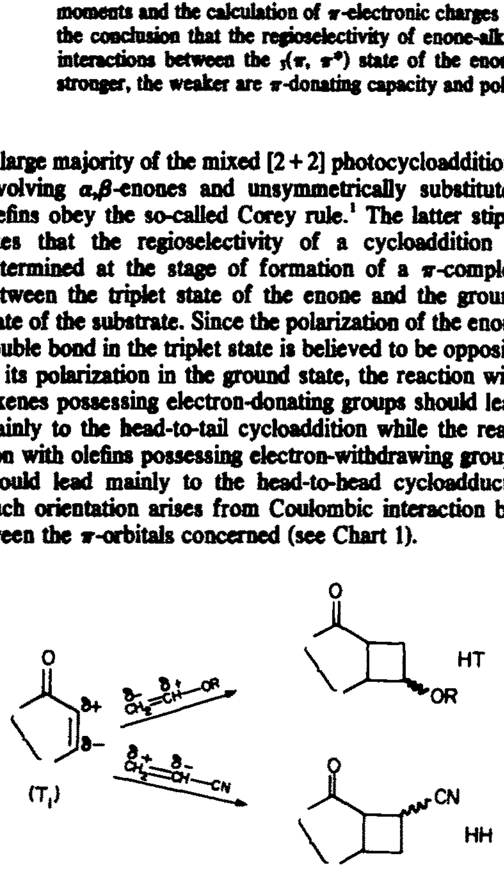


Chart 1.

Until recently, the deviations from Corey's rule were reported mostly for the cases of enone photocyclodimerization.[2–7] Such deviations normally occur in nonpolar solvents, are due to dipole–dipole interactions and may be quantitatively characterized by the Kirkwood–Onsager equation. The effects of the medium on the regioselectivity of mixed photocycloadditions[8,9] are certainly of the same nature.

Another case where the orientation rule is disobeyed was later found in the photocycloaddition of α,β-enones to 1-alkynes. Thus, while 2-cyclopentenone **1** and 2-cyclohexenone **2** react with terminal alkenes to give mainly HT-cycloadducts,[1,10] the addition of **1** to 1-hexyne[11] **3** and other 1-alkynes[12] gives rise mainly to HH-cycloadducts; their predominance is even more pronounced when **2** or its 3-alkyl-derivatives react with 1-hexyne.[12] As the polarization of the π-bond in 1-alkenes and 1-alkynes is qualitatively the same, this difference in the regioselectivity of photoannelation at first sight appears as striking.

With the exception of one rather peculiar case,[13] the photocycloaddition of α,β-enones to vinyl ethers leads almost exclusively to HT-adducts, but when **1** reacts with ethoxy-acetylene **4** the content of the HT-cycloadduct (and the secondary products thereof) does not exceed 60% of the products mixture.[12] The addition of α,β-enones to the acrylic acid derivatives gives rise to HH-adducts,[1,14–17] while the reaction of **1** with methyl propiolate **5** affords nearly equal amounts of the HH- and HT-compounds.[12] These facts are also difficult to explain on the basis of Corey's postulate. Since the photocycloaddition of α,β-enones to alkynes proceeds via the low triplet state of the enone,[11,12] i.e. in the same manner as to alkenes,[18] there is no possibility that the difference in the regioselectivity might be due to the difference in the multiplicity of the excited species.

This communication is concerned with experimental and computational verification of the previously suggested hypotheses[12] about the possible reasons for different regioselectivity of enone photocycloaddition to alkenes and alkynes.

Hypothesis I: *Unequal stability of associates formed between the reactants in their ground state*

The simplest explanation of the differences observed in the regioselectivity of cycloaddition of α,β-enones to alkenes and alkynes might be found in different stability (and thus different contribution to the outcome of the reaction) of oriented π-complexes or dipole–dipole associates formed by *the ground state* of the enone with a substrate. Since monosubstituted acetylenes are a great deal more polar than their analogs in the olefinic series,[19] it would be natural if their association with the S_0-states of α,β-enones were stronger than in the case of alkene-enone systems. Such ground-state association might explain why the reactions of **1** or **2** with **3** or **4** give rise to high proportions of HH-cycloadducts while the reaction between **1** and **5** affords large amounts of the HT-cycloadduct (see Chart 2).

As a test for the validity of this hypothesis we choose the effect of 1-hexyne **3** and 1-hexene **6** on the Raman and ^{1}H-NMR spectra of enones **1** and **2** in carbon tetrachloride. It is known that the formation of π-complexes brings about the alteration in the stretching frequencies of olefins or acetylenes;[20] such alterations are more or less proportional to the strength of association. It is also known that benzene produces considerable changes in ^{1}H NMR spectra of α,β-enones by way of complexation.[21] Similar effects should be expected upon complexation of enones **1** and **2** with olefinic or acetylenic π-donors. Although the sign and the magnitude of such an effect will depend on magnetic anisotropy of a given π-donor, the efficiency of the enone-substrate association may be deduced from the "saturating" concentration of the substrate, i.e. from such a concentration of the π-donor at which the changes in the spectrum of the enone reach their maximum. On this premise we investigated the dependence of enone C=C stretching frequencies and the dependence of chemical shifts of enone olefinic protons on the concentration of acetylenic or olefinic substrates. Enones **1** and **2**, 1-hexyne **3** and 1-hexene **6** were used as models.

A study of Raman and ^{1}H NMR spectra for the systems **1** + **3**, **2** + **3**, **1** + **6** and **2** + **6** in carbon tetrachloride (see Experimental Section) both at room temperature and at −20° showed that the formation of enone-alkyne or enone-alkene associates could not be reliably detected by these spectral means. The Raman spectra of all four systems differ from the spectra of pure enones **1** and **2** only by a slight increase in the intensity of the enone C=C stretching bands. In the ^{1}H NMR spectra of these four systems the changes observed for the chemical shifts of the enone olefinic protons, H_α and H_β (in respect to the chemical shifts of these protons in pure **1** and **2**), are small and nearly of the same order as the accuracy of measurement. From this negative evidence one may conclude that the formation of oriented associates between the ground states of reactants is rather weak and cannot explain the differences observed in the photocycloaddition of enones **1** and **2** to the terminal alkenes and alkynes.

Hypothesis II: Unequal strength of dipole–dipole interactions between an enone triplet and olefinic or acetylenic substrates

Another explanation of these differences may be that dipole–dipole interaction between the triplet state of the enone and the ground state of the substrate becomes more important in the case of acetylenic substrates.

This hypothesis brings about the problem of the identity of the reactive triplet. From the phosphorescence spectra of polycyclic α,β-enones it follows that the energy levels of their $_3(n, \pi^*)$ and $_3(\pi, \pi^*)$ states are very close or nearly degenerated.[22] The relative position of these states may be altered by substitution[22a,f] medium[22e,23] and, possibly, by temperature.[22c,g] Therefore, the extrapolation of the data obtained from the low-temperature emission spectra onto reactions occurring at ambient temperatures is somewhat risky. On the other hand, both spectroscopic and kinetic evidence seem to imply that simple cyclic enones such as **1** or **2** after excitation and intersystem crossing relax as π,π^*- rather than n,π^*-triplets.[4b,22e]

The closeness of both triplet levels is in a good agreement with the quantum mechanical data obtained for acrolein either without[24] or with taking into account the polarizability of σ-bonds.[25] All variants of quantum mechanical calculations for acrolein[24–26] or cyclohexenone **2** and its analogs[26] indicate that the C=C bond of enones in the π,π^*- state is more electron-deficient and in the n,π^*-state is more electron-rich than in the ground state. From this fact an important conclusion can be drawn which is valuable just because of the difficulty to distinguish n,π^*-triplets from π, π^*-triplets under normal conditions of enone photoannelation. Namely, if in a reaction involving enone low triplets the C=C bond

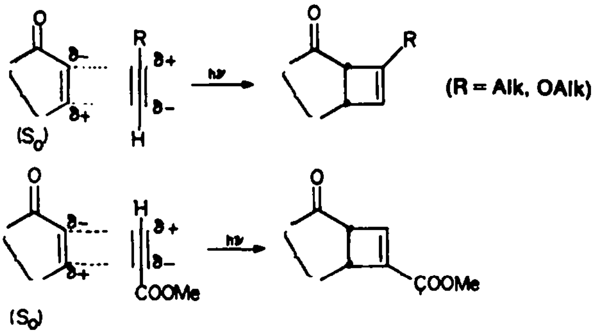
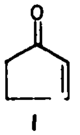
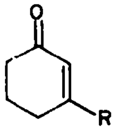


Chart 2.



1



2: R = H
9: R = Me
10: R = Bu-tert
11: R = Ph

R—C≡CH

3: R = C_4H_9-n
4: R = OEt
5: R = COOMe

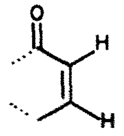
R—CH=CH$_2$

6: R = C_4H_9-n
7: R = OEt
8: R = COOMe

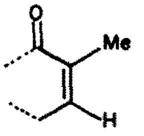
of the enone behaves as an electrophile, such a reaction must proceed via the $_3(\pi, \pi^*)$-rather than $_3(n, \pi^*)$-state of the enone.

Now the comparison of the relative[1,14,27] or absolute[12,28] rates of photocycloaddition of α,β-enones to various olefins and acetylenes shows that this reaction represents an electrophilic attack of the enone triplet on the π-bond of the substrate. Combining these results with quantum mechanical calculations of α,β-enones[24–26] one can identify the reactive triplet as $_3(\pi, \pi^*)$ form.

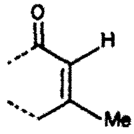
Thus, when speaking about the effect of dipole–dipole interactions on the regioselectivity of photoannelation one has to take into account the dipole moment and the π-electronic charge distribution in the enone $_3(\pi, \pi^*)$ state. For this purpose we calculated with use of CNDO/2 technique the magnitude and the direction of molecular dipole moments as well as the distribution of π-electronic charge in the ground, $_3(n, \pi^*)$- and $_3(\pi, \pi^*)$-states of the model systems **A**, **B**, **C** and **D**, approximating unsubstituted, α-alkyl substituted, β-alkyl substituted and β-aryl substituted α,β-enones, respectively. As these systems were considered as the fragments of the corresponding cyclic enones, the calculations were performed only for s-trans-conformers.



A



B



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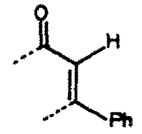


D

The results of calculations for enone systems **A**, **B**, **C** and **D** are collected in Table 1.

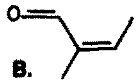
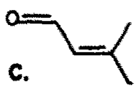
In all four cases the magnitude and the direction of the calculated dipole moments in the $_3(\pi, \pi^*)$-state are rather close to the corresponding characteristics of the ground state while those of the $_3(n, \pi^*)$-state do not display such similarity. From the magnitude of $\vec{M}_{calc.}$ one may conclude that dipole–dipole interactions for the $_3(\pi, \pi^*)$ state of enones must be much stronger than for its $_3(n, \pi^*)$ counterpart.

In accordance with previous calculations [24–26] in systems **A**, **B** and **C** the π-electronic deficit of the C=C bond decreases in the order $_3(\pi, \pi^*) > S_0 > {}_3(n, \pi^*)$, i.e. $_3(\pi, \pi^*)$-state is the most electrophilic. In system **D**, where this bond makes part of an extended conjugated system, its electrophilicity in the $_3(\pi, \pi^*)$ state appears to be lower than in the ground state; however, the full calculation of π-electronic density shows that as a whole the former is more electrophilic. In all four systems, **A**, **B**, **C** and **D**, the reacting π-bond is polarized in such a manner that C-2 (α-position) represents the positive and C-3 (β-position)—the negative pole of a local dipole. Nevertheless, the direction of the full molecular dipole in the $_3(\pi, \pi^*)$ state of systems **A**–**D** remains approximately the same as is their ground state. Hence, the orientation effect produced by the dipole–dipole interactions must be practically the same for both the ground and the $_3(\pi, \pi^*)$ states of α,β-enones.

Interestingly, π-electronic deficit in the $_3(\pi, \pi^*)$ state of system **B** is by no way smaller than in the case of systems **A** and **C**. This implies that the compounds like 2 - methyl - 2 - cyclohexenone in their $_3(\pi, \pi^*)$ state are no weaker electrophiles than other cyclic enones. The sluggishness of the former in photoannelation reactions[1,12] should therefore be due to other factors—for instance, to the reversal of stability levels for $_3(\pi, \pi^*)$ and $_3(n, \pi^*)$ states caused by the substitution pattern (cf. the case of propellane systems[22f]) or to the different stability of 1,4-diradicals intermediates.

The data from Table 1 have to be compared with the ground-state dipole moments and π-electronic charges of the structurally similar olefinic and acetylenic substrates R–CH=CH$_2$ (**6**, **7**, **8**) and R–C≡CH (**3**, **4**, **5**). The experimental values of $\vec{M}$ for terminal olefins and acetylenes

Table 1. Dipole moments and π-charge distribution in α,β-enones (CNDO/2 method)

Enone model	State	$\vec{M}_{calc}$ (D)	θ°_{calc} (Angle between $\vec{M}$ and C=C)	π-Charge distribution 0	C$_1$	C$_2$	C$_3$
 A.	S$_0$	3.42	175	−0.220	+0.162	−0.055	+0.088
	$_3(n, \pi^*)$	1.60	170	−0.840	−0.048	−0.046	−0.083
	$_3(\pi, \pi^*)$	2.96	176	−0.097	−0.017	+0.078	−0.031
 B.	S$_0$	3.07	173	−0.213	+0.158	−0.025	+0.046
	$_3(n, \pi^*)$	1.47	171	−0.836	−0.059	−0.023	−0.107
	$_3(\pi, \pi^*)$	3.43	154	−0.167	−0.015	+0.094	−0.036
 C.	S$_0$	4.05	174	−0.238	+0.167	−0.096	+0.117
	$_3(n, \pi^*)$	1.83	162	−0.852	−0.037	−0.072	−0.065
	$_3(\pi, \pi^*)$	3.25	171	−0.111	−0.012	+0.078	−0.040
 D.	S$_0$	3.06	167	−0.203	+0.158	−0.035	+0.064
	$_3(n, \pi^*)$	1.23	121	−0.754	−0.041	−0.078	−0.077
	$_3(\pi, \pi^*)$	4.19	154	−0.188	+0.065	+0.041	−0.030

The values of $\vec{M}$ for the ground states of enone models can be compared with those experimentally found for related systems.[29] Thus, for 2-cyclopentenone $\vec{M}_{exp} = 3.44$D (in benzene) and for 3,5,5-trimethyl-2-cyclohexenone $\vec{M} = 3.96$D (in dioxan), which is in good agreement with the values calculated for systems A and C.

Table 2. Dipole moments and π-charge distribution in terminal alkenes and alkynes (CNDO/2 method)

R	$\vec{M}_{exp}$ (D)		θ°_{calc} (Angle between $\vec{M}$ and C——C)		π-Charge density			
					C_α		C_β	
	$RCH{=}CH_2$	$RC{\equiv}CH$	$RCH{=}CH_2$	$RC{\equiv}CH$	$RCH{=}CH_2$	$RC{\equiv}CH$	$RCH{=}CH_2$	$RC{\equiv}CH$
CH_3	0.35	0.76	8°	0°	+0.029	+0.013	−0.044	−0.029
OMe	1.26[a]	1.79	178°	105°	+0.036	+0.023	−0.081	−0.069
COOMe	1.67	2.08[b]	169°	108°	−0.026	−0.012	+0.060	+0.032

[a] For R = OEt; for ethoxyacetylene 4 $\vec{M}_{exp}$ = 1.98D.

[b] For R = COOH; the difference between $\vec{M}$ of acids and their methyl esters normally lies within 0.15D.

All values of $\vec{M}_{exp}$ are borrowed from the compilation in Ref. 29.

are easily available.[29] The direction of dipole moments and the distribution of π-electronic charge in the ground state of substrates were obtained with use of CNDO/2 method. These data are represented in Table 2.

Not unexpectedly, the π-charge distribution is qualitatively the same for both olefinic and acetylenic substrates. On the other hand, the magnitude of $\vec{M}$ is considerably greater for acetylenes than for their olefinic analogs. It seems thus plausible that the photocycloaddition of α,β-enones to unsymmetrical acetylenes should be more sensitive to dipole–dipole interactions. Another point of interest is the direction of the molecular dipole. If in simple alkenes (such as **6**) and simple alkynes (such as **3**) the angle Θ between the molecular dipole vector and the bond C_α—C_β is nearly the same, in the case of functionally substituted substrates the difference is much greater. In vinyl ethers and in alkyl acrylates this angle is close to 180° while in alkoxy-acetylenes and in alkyl propiolates Θ is much nearer to 90° than to 180°. In other words, the molecular dipole vector in **4** or **5** is quasiperpendicular to the triple bond.

Hypothesis III: *Lower π-electronic density and weaker polarization of the π-bond of alkynes in respect to alkenes*

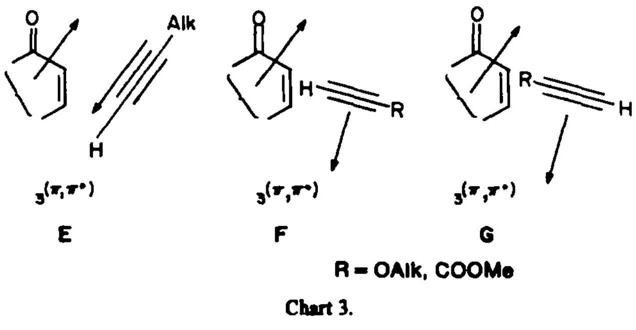
This hypotheses is, in fact, a corollary to the previous one. The lower is π-electronic density and the weaker is polarization of the π-bond in a substrate, the weaker should be the orientation effect postulated by Corey and, respectively, the greater should be the effect of dipole–dipole interactions. As can be seen from Table 2, both electronic density and polarization of the π-bond in acetylenic substrates $RC{\equiv}CH$ are considerably smaller than in their olefinic analogs $RCH{=}CH_2$. Hence the formation of an oriented π-complex between the enone triplet and $RC{\equiv}CH$ will be not so important as in the case of enone-alkene photocycloaddition.

Another consequence of lower electronic density and weaker polarization of the acetylenic π-bond may consist in a relatively greater importance of steric effects. Symptomatically, the regioselectivity of cycloaddition of **1** to 3,3-dimethyl-1-butyne is much higher than in the case of reaction between **1** and linear 1-alkynes.[12]

These considerations are but a particular case of the general concept, according to which the regioselectivity of a reaction is determined by interplay of orbital, dipole–dipole and steric interactions or, rather, by their relative importance. On the basis of this concept one may offer the following explanation for "abnormal" regioselectivity observed earlier[11,12] in the photocycloaddition of α,β-enones to monosubstituted acetylenes:

(a) The cycloaddition of enones **1** and **2** (modelled by system A) or their 3-alkylsubstituted analogs such as 3-methyl- and 3-tert-butyl-2-cyclohexenones **9** and **10** (modelled by system C) is oriented mainly by intermolecular dipole–dipole interactions.† The main cycloadduct corresponds to the minimum of these interactions, i.e. to the situation where the molecular dipole vectors of the enone $_3(\pi, \pi^*)$ state and the substrate ground state tend to become anti-parallel. This can be schematically represented by situations **E**, **F** and **G** (see Chart 3) which show, why the addition of **1**, **2**, **9** or **10** to 1-alkynes gives rise mainly to the HH-cycloadducts while the addition of **1** to **4** or **5** proceeds with partial or complete loss of regioselectivity.

A certain decrease in regioselectivity observed upon transition from **2** to its analogs **9** and **10** may be due to a small change in the direction of molecular dipole vector in the $_3(\pi, \pi^*)$ state of system C in respect to system A (see Table 1).



R = OAlk, COOMe

Chart 3.

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†Elementary calculations based on dipole–dipole approximation show that the difference in the energy of dipole–dipole interaction ($2M_1 \cdot M_2\, L^{-3}$) should be about 1–2 kcal mole^{-1} when the distance between two molecular dipoles of such magnitude becomes close to 4 Å. Such energy difference is large enough to account for the observed regioselectivity of enone-alkyne cycloaddition.

(b) The cycloaddition of 3-phenyl-2-cyclohexenone (11, modelled by system D) to 1-alkynes is oriented mainly by π-orbital interaction between the substrate and the $_3(\pi, \pi^*)$ state of the enone. Only one cycloadduct is formed and its HT-structure corresponds to Corey's rule; in this case the regioselectivity of cycloaddition is the same as in the case of reaction between 11 and 2-methylpropene.[14] One of possible reasons of this discrepancy between enones 1, 2, 9 and 10 on one hand and enone 11—on the other might be the softening of dipole–dipole interactions by the aromatic π-system (the latter effect may be likened to the effect of polar solvents on the regioselectivity of enone photoannelation,[2–9,12] when in more polar solvents the reaction proceeds in a better agreement with Corey's rule).

The relative importance of π-orbital and dipole–dipole interactions for the regioselectivity of enone photocycloaddition to olefinic and acetylenic substrates can be qualitatively estimated by non-dimensional index r showing the contribution of the reacting π-bond to the total dipole moment of a substrate molecule.

$$r = \frac{|a_\alpha - a_\beta| \times 4.8 \times l_{C—C}}{|\vec{M}|}$$

where a_α and a_β are the coefficients of p-orbitals at C_α and C_β in the substrates of type $R\overset{\alpha}{C}H{=}\overset{\beta}{C}H_2$ or $R\overset{\alpha}{C}{\equiv}\overset{\beta}{C}H$, $l_{C—C}$—the length of the multiple bond (~1.33 Å for alkenes and ~1.20 Å for alkynes) and $[\vec{M}]$—scalar value of molecular dipole moment; the multiplier 4.8 relates to the charge of an electron. As can be seen from Table 3, compiled on the basis of data given in Tables 1 and 2, for all acetylenic substrates r is 2–4 fold smaller than for their olefinic analogs with the same substituents. Evidently, the smaller is r, the weaker is the effect of π-orbital interaction and, respectively, the greater is the influence of dipole–dipole interactions upon the regioselectivity of photoannelation.

Thus, among olefinic substrates the lowest r corresponds to acrolein (R=CHO). The latter represents the family of unsubstituted α,β-enones (system A) for which the regioselectivity of photo-cyclodimerization strongly depends on the polarity of the solvent and, consequently, on dipole–dipole interactions. On the other hand, for cinnamic aldehyde (i.e. system D) r is nearly twice as large (0.206) as for acrolein; this is in line with the observation[30] that the regioselectivity of cyclodimerization of 3-aryl-2-cyclohexenones is not solvent-dependent and always corresponds to Corey's rule.

Table 3. π-Bond polarization and its contribution to molecular dipole moments in the substrate

R	$RCH=CH_2$ ($l_{C=C}$ = 1.33 Å)			$RC{\equiv}CH$ ($l_{C\equiv C}$ = 1.20 Å)		
	$\lvert a_\alpha - a_\beta\rvert$	$\vec{M}$	r*	$\lvert a_\alpha - a_\beta\rvert$	$\vec{M}$	r*
CH_3	0.073	0.35	1.33	0.042	0.76	0.32
EtO[(a)]	0.117	1.26	0.59	0.092	1.94	0.27
COOMe	0.086	1.67	0.33	0.044	2.08[(b)]	0.121
CHO	0.050	2.8	0.11	—	—	—

*Index $r = (|a_\alpha - a_\beta| \times 4.8 \times l_{C—C}/|\vec{M}_D|)$.

(a)The values of $|a_\alpha - a_\beta|$ correspond to methoxy-homologs (see Table 2).

(b)For R = COOH (see Table 2).

Table 4.

(a) Raman spectra (20°, CCl_4)

Sample (concentration)	$\nu_{C=C}$ (cm^{-1}) in the enone	Rel. intensity
1 (0.25 M)	1597	1.00
1 (0.25 M) + 3 (2.50 M)	1597	1.86
1 (0.25 M) + 6 (2.50 M)	1597	1.75
2 (0.25 M)	1620	1.00
2 (0.25 M) + 3 (2.50 M)	1620	1.70
2 (0.25 M) + 6 (2.50 M)	1620	1.61

(b) ^1H NMR spectra (−20°, CCl_4)†

Sample (concentration)	$\delta_{H_\beta(c/s)}$	$\delta_{H_\alpha(c/s)}$
1 (0.30 M)	463.50 and 450.12	370.18 and 365.80
1 (0.30 M) + 3 (1.50 M)	461.90 and 446.17	366.20 and 361.08
1 (0.30 M) + 6 (1.50 M)	461.12 and 445.83	365.17 and 359.14
2 (0.25 M)	417.11 and 406.86	355.41 and 345.52
2 (0.25 M) + 3 (1.25 M)	417.11 and 407.22	355.59 and 348.89
2 (0.25 M) + 6 (1.25 M)	416.56 and 406.49	355.41 and 345.15

†The position of the two most intense lines in the complex signals of the enone olefinic protons are indicated.

It must be pointed out, as a concluding remark, that our approach, different from the earlier ones based on PMO theory considerations,[31,32] is only a rough approximation since it neglects the full geometry of reactants and steric effects derived from it. The closer the dimensions of a molecule are to the critical distance of intermolecular interaction or the greater is concentration of positive and negative poles in reacting molecules, the less certain will be prognosis of regioselectivity made on the basis of dipole–dipole interactions concept (see the regioselectivity of enone photoannelation with 1-hexyne in the case of 2 and 11). Index r should not be used as an absolute criterium in the estimates of regioselectivity. Thus, from the data of Table 3 one might conclude that the addition of simple α,β-enones to methyl acrylate ($r = 0.33$), just as in the case of 1-alkynes ($r = 0.32$), should have been controlled by dipole–dipole interactions and therefore should lead mainly to HT-cycloadducts. Actually, α,β-enones and acrylic acid derivatives react to give mainly HH-cycloadducts. A more precise estimate of orientation effects arising from π-orbital and from dipole–dipole interactions requires the knowledge of the full geometry of reactants. As for r, it may be used as a guide either within each series of substrates ($RC\equiv CH$ and $RCH{=}CH_2$) or for a rough comparison of these. A simple test for the validity of r as a criterion appears to lie in the study of solvent effects: the regioselectivity of enone photocycloaddition to propiolic or acrylic acid derivatives should be more solvent-dependent than in the case of their addition to 1-alkynes and 1-alkenes.

EXPERIMENTAL

Raman spectra were recorded in abs CCl_4 at 20° with Speks-Ramalog 6 instrument. ^1H NMR Spectra were taken in the same solvent at −20° with a computerized Spectrospin-Bruker 60 MHz instrument. The data are presented in Table 4.

The calculations were performed by the CNDO/2 method[33] with the program of the authors. The half-electron method designed by Dewar[34] was used to account for two uncoupled electrons in both triplet states. For systems A, B and C the characteristics of the excited states were obtained by optimisation of interatomic distances $O–C_{(1)}–C_{(2)}–C_{(3)}$ in cis-crotonic aldehyde and its α- and β-methylsubstituted analogs. For system D, approximated as cinnamic aldehyde, geometric parameters of all states were assumed to be equal to their values in the ground state.

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