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PHOTOCHEMICAL [2+2]-CYCLOADDITION OF CYCLIC α,β-ENONES TO MONOSUBSTITUTED ACETYLENES

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Abstract—The photo addition of cyclic α,β-enones to monosubstituted acetylenes gives substituted bicyclo[3,2,0]hept-6-en-2-ones and bicyclo[4,2,0]oct-7-en-2-ones. The addition of 2-cyclopentenone to different substrates of type RC≡CH (where R is alkyl, CH_2X, OEt, COOMe and also Ph) and addition of 2-cyclohexenones to 1-hexyne show a linear correlation between the σ-constants of substituents and the rates of cycloaddition. The reaction can be qualified as a moderately electrophilic attack of the enone triplet on the acetylenic bond ($|\rho| \sim 1.5$). Temperature and solvent effects on the rates and regioselectivity were also studied. The regioselectivity of addition of these α,β-unsaturated ketones to 1-alkynes does not correspond to what might be expected on the basis of Corey's orientation rule. The addition of 2-cyclopentenone to ethoxyacetylene (**3g**) and to methyl propiolate (**3h**) proceeds with surprisingly low regioselectivity while phenylacetylene (**3i**) undergoes only dimerization under photoannelation conditions.

Photo-induced [2+2] cycloaddition of α,β-enones to alkenes and alkynes has been studied from a mechanistic point of view; a large part of this work is covered by several reviews.[1–5] However, in nearly all studies the emphasis was put only on the enone-alkene photoannelation. The addition of α,β-enones to alkynes[6–14] till recently was limited only to the symmetrically substituted acetylenes. Nevertheless, the photocycloaddition of α,β-enones to the monosubstituted acetylenes[12,14] deserves special attention for two reasons: (i) due to the high symmetry of the acetylenic bond and to the rigid geometry of the cyclobutene ring formed in the reaction, the problems of stereochemistry are here greatly reduced in comparison with the case of enone-alkene photoannelation, and this may offer a better opportunity for the study of regioselectivity; (ii) the comparison of the cycloaddition of α,β-enones to the similarly substituted terminal olefins and acetylenes may reveal factors influencing the rates and regioselectivity of the reaction. These considerations prompted us to investigate the cycloaddition of some representative α,β-enones to the monosubstituted acetylenes upon n,π^*-excitation.

Two groups of reactions were studied: the photoannelation of 2-cyclopentenone **1** with different monosubstituted acetylenes[15] and the addition of 2-cyclohexenone **2** or its substituted derivatives to 1-hexyne.[16] This communication provides additional data concerning the mechanism of enone-alkyne photoannelation and summarizes the work done in our laboratory on that problem.

The addition of 2-cyclopentenone to monosubstituted acetylenes

The reaction of **1** with linear 1-alkynes (**3a–c**), 3,3-dimethyl-1-butyne **3d**, propargyl chloride **3e**, propynol **3f**, ethoxyacetylene **3g** and methyl propiolate **3h** upon irradiation with $\lambda \geqslant 316$ nm gives rise to two isomerically substituted bicyclo[3,2,0]hept-6-en-2-ones: head-to-head adducts (**4a–h**) and head-to-tail adducts (**5a–h**). When the reaction is induced by the light with $\lambda \geqslant 300$ nm, these products are usually accompanied by the 1-substituted isomers (**6a–c, e–h**) arising from the photo-isomerisation of the head-to-tail adducts of type **5**. Both **5** and **6** interconvert to each other to give equilibrium mixtures with predominance of **5**; this interconversion represents a case of the well-known 1,3-acyl shift of β,γ-enones.[6,12,17,18] Head-to-head adducts **4**, where this rearrangement must be degenerated, are not isomerized (with the exception of **4g**, see below).

This difference in the photochemical behaviour of HH- and HT-adducts was used earlier[12] as a probe for structural assignment; an alternative method is mass spectrometry.[19] The separation of cycloadducts could be achieved either by preparative TLC (for cases **1**+**3d** and **1**+**3h**) or by preparative GLC (for all other cases). The large-scale experiments, performed with $\lambda \geqslant 300$ nm, are summarized in Table 1.

The structures of the products follow from spectral evidence (see Table 2) and from their response to the light with $\lambda \geqslant 300$ nm. The HH-adducts **4a–f** and **4h** undergo only slow photo-decomposition and compound **4g** isomerises irreversibly to 1-ethoxytricyclo[3,1,1,$0^{6,7}$]heptan-2-one **7**, but neither of them is capable of 1,3-acyl shift. On the contrary, the HT-adducts **5a–c** and **5e–g** rearrange easily to the corresponding isomers of type **6**. Interconversion **5g** ⇌ **6g** is complicated by the irreversible oxa-di-π-methane rearrangement (cf Ref. 17) to tricycloheptanone **8** while in the system **5h** ⇌ **6h** the equilibrium is shifted strongly in favour of the conjugated isomer **5h**. In other equilibria the ratio **5**:**6** is close to 2:1.

In this series the addition of **1** to **3g** is the most complicated. Initially, only adducts **4g** and **5g** are formed in a ratio ~2:3, but later it changes due to the secondary isomerisations **4g**→**7**, **5g**→**8** and **5g** ⇌ **6g**. In all cases crystalline mixtures of cyclopentenone dimers were also obtained the yield of which (3–10%) increased as the rate of the mixed cycloaddition was decreasing. When ether was used as solvent, the previously described[20] solvent adducts **9** could also be obtained in small amounts.

The reaction of **1** with phenylacetylene **3i** instead of cycloaddition products gives only 1-phenylazulene **10** and 1-phenylnaphtalene **11** in low yield. Since the absorbancy of **3i** above 316 nm is quite low, a mechanism of cyclopentenone-sensitized dimerization of **3i** seems not unlikely; similar result was observed earlier[21] in the case of 2-en-1,4-diones.

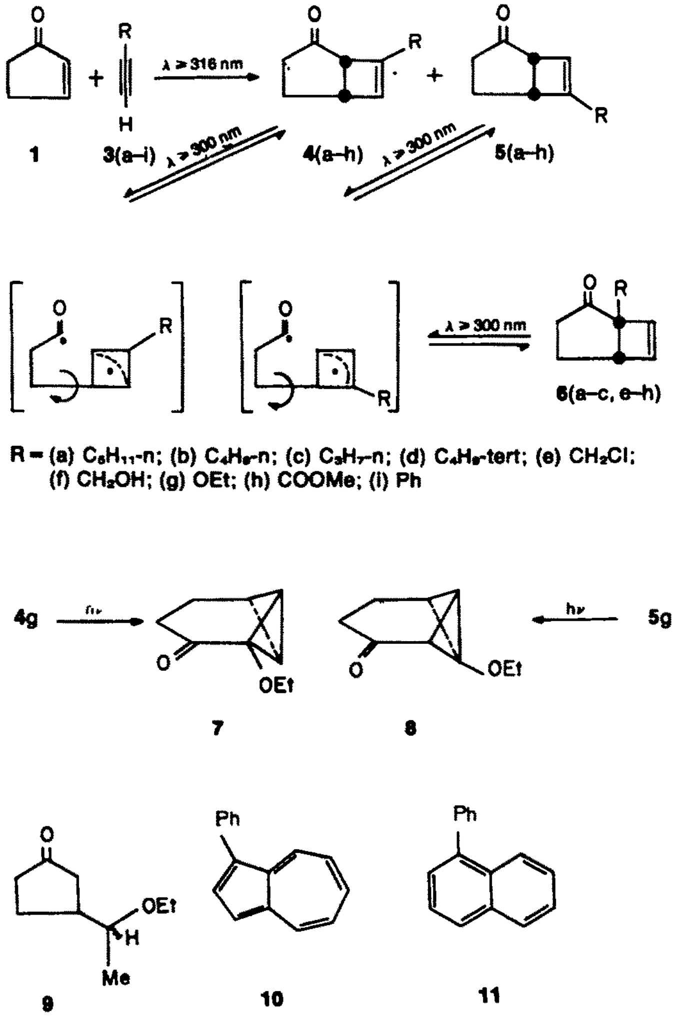

Chart 1.

Table 1. Photocycloaddition of cyclopentenone to RC≡CH (3a–h) (initial enone concentrations ~1%)

R	Conditions Molar ratio 1:3	 Solvent	 Time (hr)	Total yield of adducts (% %)	Products and their ratio after photolysis†
a. n-C_5H_{11}	1:15	—	58	40–44‡	6a, 4a, 5a (6:70:24)
b. n-C_4H_9	1:15	—	70	32–38‡	6b, 4b, 5b (12:69:19)
c. n-C_3H_7	1:20	—	63	25–30‡	6c, 4c, 5c (9:61:30)
d. Tert-C_4H_9	1:5	Ether§	40	24–26	4d, 5d(87:13)
e. CH_2Cl	1:5	Ether§	42	26–32	6e, 4e, 5e (9:72:19)
f. CH_2OH	1:10	C_6H_6	48	6–9	6f, 4f, 5f (11:69:20)
g. OC_2H_5	1:10	c-C_6H_{12}	40	17–23	6g, 4g, 5g, 7, 8 (5:24:27:16:28)
h. $COOCH_3$	1:3	C_6H_6	52	6–8	6h, 5h, 4h (2.5:49:48.5)

†Cited in the order of increasing retention times. The ratios (in brackets), determined by GLC both before and after the removal of solvents and volatile products, were practically identical. In the latter case the ratios were also checked by ^{1}H NMR. Both GLC and NMR gave similar results.

‡The yields are increased by 10–12% when 1 is slowly added to a concentrated solution of 3a, b, c in benzene.

§Small amounts of 9 are obtained as a side product in this solvent.

Table 2. ^{1}H NMR data of isomeric bicyclo[3,2,0]hept-6-en-2-ones (olefinic protons only, δ in CCl_4)

R	4	5	6
a. n-C_5H_{11}	5.87 (broad s, 1H)	5.80 (broad s, 1H)	5.99 and 6.31 (2H, J_{AB} = 3 c/s)
b. n-C_4H_9	5.85 (broad s, 1H)	5.70 (broad s, 1H)	—
c. n-C_3H_7	5.80 (s, 1H)	5.70 (s, 1H)	5.93 and 6.27 (2H, J_{AB} = 3 c/s)
d. Tert-C_4H_9	5.81 (d, 1H, J = 1.1 c/s)	—	—
e. CH_2Cl	6.23 (s, 1H)	6.00 (s, 1H)	5.89 and 5.92 (2H, J_{AB} = 3 c/s)
f. CH_2OH†	6.08 (s, 1H)	5.81 (broad s, 1H)	6.05 and 6.31 (2H, J_{AB} = 2.8 c/s)
g. OC_2H_5	4.60 (broad s, 1H)	4.50 (broad s, 1H)	6.17 and 6.35 (2H, J_{AB} = 2.9 c/s)
h. $COOCH_3$	6.79 (s, 1H)	7.13 (s, 1H)	5.93 and 6.06 (2H, J_{AB} = 2.8 c/s)

†For 4f, 5f and 6f, in $CDCl_3$.

The addition of 2-cyclohexenone and its analogues to 1-hexyne

This series comprises 2 as well as 2 - methyl - 2 - cyclohexenone 12, 3 - ethoxy - 2 - cyclohexenone 13 and a number of 3-substituted enones with carbon-to-carbon attached substituents: 3-methyl 14a, 3-tert-butyl 14b, 3-methoxycarbonyl 14c, 3-cyano 14d and 3 - phenyl - 2 - cyclohexenone 14e. All large-scale experiments here were performed with λ ≥ 300 nm. The products were isolated either by chromatography on silica-gel (in the cases 12+3b, 14d+3b and 14e+3b) or by preparative GLC. The summary of reactions is given in Table 3, the spectral data of the products in Table 4.

Unlike their lower homologs, all bicyclo[4,2,0]oct-7-en-2-ones obtained in this series were stable to the light with λ ≥ 300 nm, a fact that had been already noted.[18] Moreover, the presence of angular substituents in the position 6 does not allow to make unambiguous structural assignments on the basis of mass spectrometrical evidence. Therefore, the structures of isomeric cycloadducts were established by ^{1}H NMR with use of $Eu(dpm)_3$ and especially by ^{13}C NMR which reliably differentiates HH-adducts from HT-adducts by chemical shifts of olefinic carbon atoms C-7 and C-8 (δ 135 and 145 vs δ 155 and 125 ppm, respectively).[22] On this ground a structure can be attributed even to those adducts which were isolated without the isomeric counterpart.

The addition of 2 to 3b takes place with much greater regioselectivity than in the case 1+3b and affords in 26–28% yield a mixture of two cycloadducts—head-to-head 15 and head-to-tail 16 in a ratio ~7:1. Much worse proceeds the addition of 12 to 3b. In this case the yield does not exceed 5%. The mixture of products contains essentially two isomeric compounds in a ratio ~1.4:1. The predominant isomer was identified as 2 - methylene - 3 - (1' - hexenyl) - cyclohexanone 17 on the basis of its

Table 3. Photocycloaddition of cyclohexenone and its analogs to 1-hexyne (for all cases [enone]:[alkyne] = 1:20)

Enone†	Solvent and temperature	Time (hr)	Total yield of adducts (% %)	Products and their ratio after photolysis‡
2	C_6H_6, 18–22°	7	26–28	15, 16 (7.0:1)
12	C_6H_6, 18–22°	25	3–5	17, 18 (1.4:1)
13	C_6H_6, 18–22°	35	0	None
14a (R' = CH_3)	C_6H_6, 18–22°	8	40–42	19a, 20a (5.5:1)
14b (R' = tert-C_4H_9)	C_6H_6, 18–22°	16	55–57	19b, 20b (4.2:1)
14c (R' = $COOCH_3$)	C_6H_6, 18–22°	2	58–60	20c, 19c (2:1)
14d (R' = CN)	Ether, −50°	0.5	2§	20d (not isolated)
14e (R' = C_6H_5)	C_6H_6, 18–22°	7.5	42–45	20e (single isomer)

†Initial concentration for 14e—1%, for all others—5%.

‡Cited in the order of increasing retention times. Analysis by GLC before and after the removal of benzene and, in the latter case, by ^{1}H NMR gave coinciding results.

§The yield of the cyano alcohol 21 isolated upon borohydride reduction.

Table 4. ^{1}H NMR and ^{13}C NMR data of isomeric bicyclo[4,2,0]oct-7-en-2-ones (olefinic protons and carbons only, δ in CCl_4 and $CDCl_3$, respectively)

HH-isomers			HT-isomers		
Adduct	^{1}H NMR	^{13}C NMR	Adduct	^{1}H NMR	^{13}C NMR
15	5.72 (broad s, 1H)	131.8 and 148.2	16	5.61 (broad s, 1H)	159.6 and 124.8
18	5.77 (broad s, 1H)	—			
19a	5.80 (broad s, 1H)	136.7 and 146.2	20a	5.66 (broad s, 1H)	155.8 and 122.8
19b	5.78 (broad s, 1H)	134.6 and 147.5	20b	5.72 (broad s, 1H)	158.3 and 124.1
19c	5.78 (broad s, 1H)	135.2 and 146.6	20c	5.74 (dd, J 1.4 c/s)	154.1 and 127.7
			21	6.36 (broad s, 1H)	152.5 and 125.5
			20e	5.87 (dd, 1H J 1.4 c/s)	157.1 and 126.1

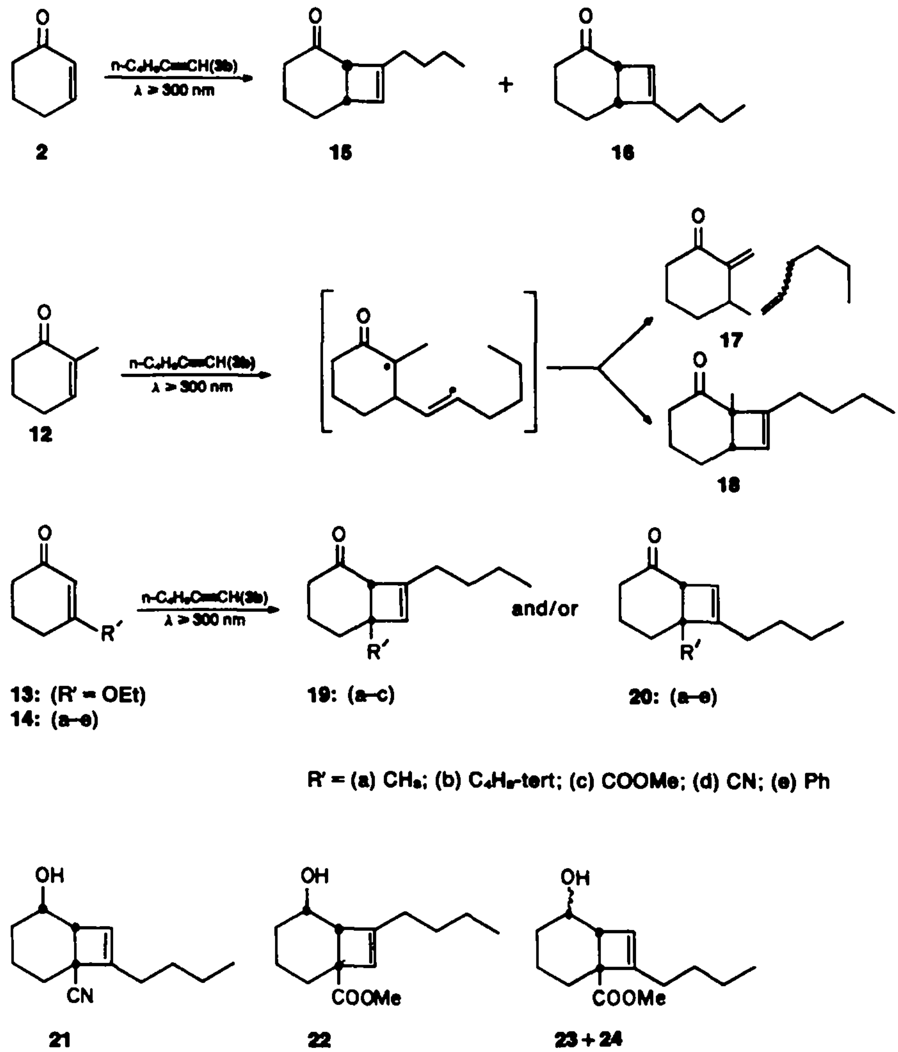

Chart 2.

spectral characteristics (λ 230 nm, ν 1692 and 1618 cm^{-1}, δ 5.14 and 5.89 ppm) closely reminiscent of those recorded for 2-methylene-cyclohexanone.[23] The other isomer corresponds to the normal cycloaddition and, according to its mass spectrum, must possess a HH-structure 18. Both 17 and 18 might arise from the same 1,4-diradical intermediate.

The enol ether 13 does not react with 3b even on prolonged irradiation. On the contrary, enones 14a–e react easily. In spite of somewhat lower rates of addition of 14a and 14b, the yields of the corresponding adducts are higher than in the case of 2; probably, because of the slower dimerization of those enones. In both cases the HH-adducts predominate. The reverse is observed in the addition of 14c to 3b which proceeds very rapidly to give a good yield of cycloadducts where the HT-isomer 20c predominates.

Still quicker occurs the reaction of 14d with 3b since the rate of disappearance of this enone in the presence of 3b is very high. However, the attempts to isolate the corresponding cycloaddrcts failed because of the rapid decomposition of the photolysis products. The enhanced instability of photocycloadducts formed by 14d with olefins had been already noted.[24,25] When the reaction was carried out at −50° in ether the rate of secondary thermal reactions could be diminished; after the low-temperature freeze-pump-thaw evaporation the presence of a 1:1 adduct (M^+ 203) could be detected in the photolysate by combined GLC–MS. The treatment of the photolysate at −30° with a large excess of $NaBH_4$ in MeOH and subsequent preparative TLC afforded a crystalline cyano alcohol 21 whose structure was determined by ^{13}C NMR. The isolation of a single alcohol implies preferential, if not exclusive, formation of the HT-adduct 20d in the reaction of 14d with 3b. The reduction of cycloadducts to the corresponding alcohols was also used for additional confirmation of structures 19c and 20c where the presence of a COOMe grouping capable of complexation with $Eu(dpm)_3$ diminishes the difference in the response of their ^1H NMR spectra to the shifting reagent: in the corresponding alcohols 22 and 23 + 24, obtained from 19c and 20c respectively on treatment with $NaBH_4$ this difference becomes much greater.

The addition of 14e to 3b proceeds smoothly to give the HT-cycloadduct 20e as the only product; its structure relies on ^{13}C NMR data.

Mechanistic aspects

The comparison of the regioselectivity found in the cycloaddition of enones **1** and **2** to monosubstituted acetylenes with the regioselectivity reported for their addition to terminal olefins[1-5,26] shows a remarkable difference between these two cases. Whereas terminal olefins with electron-donating substituents react with **1** or **2** to give mainly HT-cycloadducts, their acetylenic analogs form with **1** and **2** predominantly HH-adducts. Moreover, if the derivatives of acrylic acid and α,β-enones afford with high degree of regioselectivity HH-cyclo-adducts, the reaction between **1** and methyl propiolate **3h** gives nearly equal amounts of HH- and HT-isomers. Obviously, these results do not correspond to what might be expected on the basis of Corey's hypothesis[26] about the effect of the π-bond polarization in the substrate on the regioselectivity of photocycloaddition.

This discrepancy prompted us to investigate certain mechanistic aspects of the enone-alkyne photoannelation.

Kinetics and the reactive species

The quantum yield of the reaction **1** + **3a** → **4a** + **5a** in cyclohexane and **2** + **3b** → **15** + **16** in benzene were measured at 25° in the band of n,π*-transition, the enone–alkyne ratio being 1:10 and 1:20, respectively. The amounts of cycloadducts were determined by GLC from the calibration curves plotted with use of pure samples and n-$C_{19}H_{40}$ as internal standard. In both cases the dependence of the quantum yield of cycloaddition on the substrate concentration could be expressed as a linear correlation between Φ^{-1} and $[\text{alkyne}]^{-1}$. The reaction **1** + **3a** → **4a** + **5a** is described by the equation

$$\frac{1}{\Phi} = 2.57 + 0.517 \times \frac{1}{[\mathbf{3a}]}$$

with r = 0.952 and the reaction **2** + **3b** → **15** + **16**, by the equation

$$\frac{1}{\Phi} = 7.04 + 99.703 \times \frac{1}{[\mathbf{3b}]}$$

with r = 0.996. From these dilution plots it was found that at the infinitely great concentrations of the alkyne $\Phi^{25°}_{\lim}$ are 0.39 and 0.142 mole/Einst for the cases **1** + **3a** and **2** + **3b**, respectively.

The cycloaddition of **1** to **3a** is linearly quenched by 2,3 - dimethyl - 1,3 - butadiene (DMB) according to the equation:

$$\Phi_0/\Phi_i = 1.023 + 2.149[\text{DMB}]$$

with r = 0.971. The effect of DMB on the efficiency of cycloaddition could not be measured in the case **2** + **3b** since **2** and DMB react to give a mixture of 1:1 adducts with M^+ 178 (cf Ref. 27); chemical competition thus prevails over energy-transfer processes. However, the reaction **2** + **3b** → **15** + **16** is linearly quenched by naphthalene according to the equation:

$$\Phi_0/\Phi_i = 0.973 + 7.646\,[\text{Naphthalene}]$$

with r = 0.988. It is well known that DMB and naphthalene are efficient quenchers of triplet states with $E_T > 61$–62 kcal/mole while the most probable value of E_T for **1** and **2** appears to lie at 65–73 kcal/mole.[28] Hence, the cycloaddition of **1** and **2** to 1-alkynes must proceed via the lowest triplet state of the enone, that is, in the same manner as the enone–alkene photoannelation. Therefore, the different regioselectivity of photocycloaddition of these enones to olefins and acetylenes is not due to the differences in the multiplicity of the reacting excited state.

This was further confirmed by the similarity of kinetic parameters for the photoannelation of **1** and **2** with alkenes and alkynes. The triplet state of the reacting enone and, to some extent, the value of reaction constants ρ obtained from the correlation of the cycloaddition rates with σ-constants of substituents (see below) speak in favour of a stepwise mechanism. Therefore, for the cycloaddition of **1** and **2** to alkynes one may adopt the kinetic scheme developed earlier[3,12,29] for the photoannelation of α,β-enones with alkenes:

$$\mathrm{E} \xrightarrow{h\nu} {}_1\mathrm{E}^* \xrightarrow{\text{isc}} {}_3\mathrm{E}^* \quad v_1 = aI_0\Phi_{\text{isc}} \tag{1}$$

$${}_3\mathrm{E}^* \xrightarrow{k_d} \mathrm{E} \quad v_2 = k_d[{}_3\mathrm{E}^*] \tag{2}$$

$${}_3\mathrm{E}^* + \mathrm{A} \xrightarrow{k_r} \{{}_3\mathrm{E}^* \ldots \mathrm{A}\} \quad v_3 = k_r[{}_3\mathrm{E}^*][\mathrm{A}] \tag{3}$$

$$\{{}_3\mathrm{E}^* \ldots \mathrm{A}\} \xrightarrow{k_{\text{prod}}} \mathrm{P} \quad v_4 = k_{\text{prod}}[\{{}_3\mathrm{E}^* \ldots \mathrm{A}\}] \tag{4}$$

$$\{{}_3\mathrm{E}^* \ldots \mathrm{A}\} \xrightarrow{k_{\text{diss}}} \mathrm{E} + \mathrm{A} \quad v_5 = k_{\text{diss}}[\{{}_3\mathrm{E}^* \ldots \mathrm{A}\}] \tag{5}$$

where E-enone, A-alkene or alkyne and $\{{}_3\mathrm{E}^* \ldots \mathrm{A}\}$ is a triplet exciplex or a kinetically equivalent intermediate which partly collapses to an adduct P and partly reverts (with nonradiative dissipation of energy) to the ground state of reactants. In the expression for v_1 the member aI_0 corresponds to the effective part of incident light while the efficiency of intersystem crossing (Φ_{isc}) for enones **1** and **2** is close to unity.[28] Two generalized Stern–Volmer equations can be applied to this scheme; in the absence of triplet quenchers (dilution plot):

$$\frac{1}{\Phi} = \frac{1}{K}\left\{1 + \frac{k_d}{k_r[\mathrm{A}]}\right\}. \tag{I}$$

In the presence of a quencher Q (combined plot):

$$\frac{1}{\Phi} = \frac{1}{K}\left\{1 + \frac{k_d}{k_r[\mathrm{A}]} + \frac{k_q[\mathrm{Q}]}{[\mathrm{A}]}\right\}. \tag{II}$$

Since the difference in the triplet energy of enones (**1**, **2**) and their quenchers (DMB, naphthalene) is about 5 kcal/mole, one may assume[29] that k_q—the rate constant of triplet quenching—is close to the rate constant of diffusion (k_{diff}). The latter amounts to $7.5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ for cyclohexane and $1 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ for benzene.[30] The value of K shows which part of the exciplex is converted to P:

$$K = \frac{k_{\text{prod}}}{k_{\text{prod}} + k_{\text{diss}}}.$$

From the dilution plots, i.e. Φ^{-1} vs $[\text{alkyne}]^{-1}$ follows that the intercept

$$\frac{1}{\Phi_{\text{lim}}} = \frac{1}{K} = \frac{k_{\text{prod}} + k_{\text{diss}}}{k_{\text{prod}}} = 1 + \frac{k_{\text{diss}}}{k_{\text{prod}}} \qquad \text{(III)}$$

while the slope

$$\text{tg}\alpha = \frac{1}{K} \cdot \frac{k_d}{k_r} \qquad \text{(IV)}$$

From these expressions the ratios $k_{\text{prod}}/k_{\text{diss}}$ and $|k_d/k_r|$ can be obtained. Then from the slope of the combined plot Φ^{-1} vs [Q] obtained at permanent concentrations of the substrate and assuming $k_q \approx k_{\text{diff}}$

$$\text{tg}\beta = \frac{1}{K} \cdot \frac{k_q}{k_r[A]} \approx \frac{1}{K} \cdot \frac{k_{\text{diff}}}{k_r[A]} \qquad \text{(V)}$$

one can calculate the value of k_r. Returning to eqn (IV) one obtains k_d and, subsequently, $\tau = 1/k_d$—the lifetime of enone triplets. Kinetic parameters obtained from the dilution and quenching plots by means of eqns (I)–(V) are presented in Table 5.

The values of k_r, k_d and τ thus found are in a good agreement with the corresponding values obtained for the photoannelation of 1 and 2 with alkenes or 3-hexyne.[3,12] The lifetime of the reactive species is about two orders of magnitude greater than that of the lowest n,π^* singlet state of 1 and 2 derived from their UV-spectra.

The data from Table 5 seem to reflect the effect of the ring size on the efficiency of cycloaddition. In the strained enone 1 the energy of excitation must be dissipated mainly by bimolecular collisions while in the conformationally more flexible enone 2 it is the monomolecular deactivation that prevails. Moreover, the ratio $k_{\text{diss}}/k_{\text{prod}}$ in the latter case is greater than in the former; the reason may be that upon the reversion of the exciplex to the ground states of reactants the re-introduction of the double bond into six-membered cycle is more favoured.

The effect of substituents

As the reaction between 1 and 3a proceeds with maximum speed in diethyl ether (see below), the rates of cycloaddition of 1 to the monosubstituted acetylenic substrates 3a and 3d–h were measured in ether at 25°, the concentrations being 0.08 M in enone and 0.40 M in acetylenic substrate. The quantum yields of cycloaddition were determined at the reaction depth amounting to 3–5%. Their values, together with inductive substituent constants and the ratios of isomeric cycloadducts, are given in Table 6.

The plotting of the quantum yields against σ_I values of substituents shows that for all substrates but propynol 3f there exist a linear correlation between the rate of cycloaddition and the electronic characteristic of the substituent. In the case of 3f the deviation from linearity may be *due to hydrogen bonding* (*cf Ref.* 31). *Five* other substrates give a series with a reaction constant $\rho = -1.485$ ($r = 0.985$). The effect of substituents characterizes the reaction as moderately electrophilic towards acetylenic substrate: the more electron-rich is the triple bond, the easier takes place the cycloaddition (see Fig. 1a). Interestingly, the additions of 1 to ethoxyacetylene 3g and to methyl propiolate 3h proceed with comparable speeds, while from the analogy with vinyl ethers and acrylic acid derivatives (cf Refs. 26, 32) one might expect greater difference in the rates of photoannelation. The ethoxy group of 3g behaves as −J rather than +R substituent; this observation is in line with many others[33] indicating that acetylenic bond is much less prone to conjugation than olefinic one. This fact necessitates (or justifies) the use of σ_I rather than σ_p constants for the acetylenic substrates.

The regioselectivity of cycloaddition in this series does not depend explicitly on the electronic nature of substituents. From a sharp increase of the ratio 4:5 upon transition from linear alkynes such as 3a to branched alkynes 3d it can be concluded that the orientation is rather sensitive to steric factors. The largest proportions

Table 6. The effect of substituents in RC≡CH on the rates and regioselectivity of cyclopentenone photoannelation (in ether, 25°)

R	σ_I	$\Phi^{25°}_{n,\pi^*}$	[4]/[5] = HH : HT
n-C_5H_{11} (3a)	−0.04	0.32	2.23
tert-C_4H_9 (3d)	−0.07	0.36	7.80
CH_2Cl (3e)	+0.15	0.19	2.62
CH_2OH (3f)	+0.05	0.14	2.28
OC_2H_5 (3g)	+0.27	0.11	0.79
$COOCH_3$ (3h)	+0.34	0.08	0.97

Table 5. Kinetic parameters for the photocycloaddition of cyclopentenone and cyclohexenone *to* alkynes

	Parameters				
Reaction	$\Phi_{334-366}$§ (mole/Einstein)	$k_r \cdot 10^8$ (M^{-1} sec^{-1})	$k_d \cdot 10^{-8}$ (sec^{-1})	τ (nsec)	$\frac{k_{\text{diss}}}{k_{\text{prod}}}$
1 + 3a (in cyclohexane, 25°)†	0.30 ± 0.05 (0.39)	2.68	0.55	18.00	1.57
2 + 3b (in benzene, 25°)‡	0.048 (0.142)	0.86	12.20	0.82	6.04

†For the reaction of 1 with 3-hexyne (in hexane, 20°) reported:[12] $\Phi_{366} = 0.49$ mole/Einst; $k_r = 1.8\ M^{-1}\ \text{sec}^{-1} \cdot 10^8$; $k_d = 0.23\ \text{sec}^{-1} \cdot 10^8$. From the value of K it follows that $k_{\text{diss}}/k_{\text{prod}} = 1.04$.

‡For the reaction of 2 with 3-hexyne (in heptane, 20°) reported:[12] $\Phi_{366} = 0.048$ mole/Einst; $k_r = 0.23\ M^{-1}\ \text{sec}^{-1} \cdot 10^8$; $k_d = 3.2\ \text{sec}^{-1} \cdot 10^8$. From the value of K it follows that $k_{\text{diss}}/k_{\text{prod}} = 6.70$.

§In brackets, Φ_{lim}.

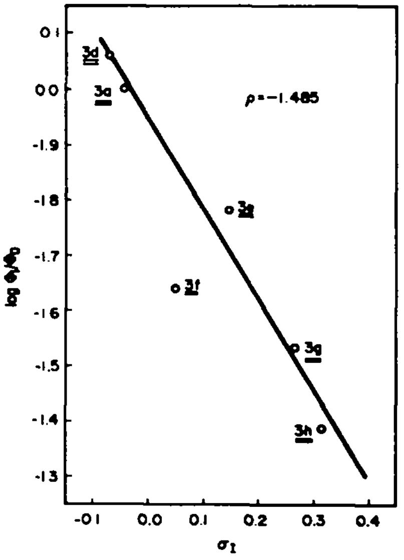

Fig. 1(a). The correlation between Φ^{rel} and σ_I constants of substituents in RC≡CH for the series 1+3(a, d–h). The quantum yield of cycloaddition for the reaction 1+3a→4a+5a is taken as reference.

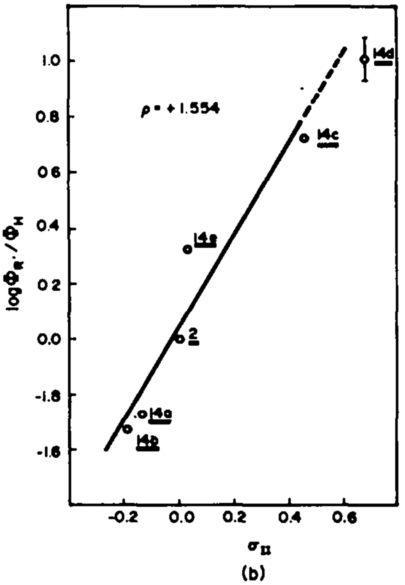

Fig. 1(b). The correlation between Φ_{rel} and σ_π constants of enone substituents R′ for the series 2, 14(a–e) + 1-hexyne.

Table 7. The effect of substituents in different cyclohexenones on the rates and regioselectivity of their cycloaddition to 1-hexyne (in benzene, 25°)

R′	σ_π	$V_{add} \cdot 10^4$ $(M^{-1}\,sec^{-1})$	Φ^{25}_{n,π^*}	[HH]/[HT]
H (2)	0.000	3.52	0.048	7.02
CH_3 (14a)	−0.170	1.87	0.026	5.51
tert-C_4H_9 (14b)	−0.197	1.61	0.022	4.23
$COOCH_3$ (14c)	+0.450	16.87	0.23	0.51
CN (14d)	+0.660	35†	—	§
C_6H_5 (14e)	+0.009	4.26	0.063	0.02‡
OC_2H_5 (13)	−0.250	0.0	0.0	—

†Extrapolated from the rates of disappearance of enones 2, 14c and 14d on the assumption that the cycloaddition proceeds much quicker than all other possible photo-transformations.

‡Deduced from ¹H NMR data.

§Determination not possible. From the reduction experiment HT-cycloaddition seems to prevail.

of HT-adducts are observed for the reactions of 1 with 3g and 3h. If in the case of 3g the predominant formation of 5g, although not strongly pronounced, coincides qualitatively with the regioselectivity of enone cycloaddition to vinyl ethers, in the case of 3h the high proportion of 5h finds no analogy in the regioselectivity of enone cycloaddition to acrylonitrile, which leads mainly to HH-adducts (cf Refs. 26, 32).

The reaction of 2 with 3b proceeds with maximum speed in benzene (see below). Therefore, the rates of cycloaddition of 2 and its analogs (14a–e) to 3b were measured in this solvent at 25°, the concentrations being 0.25 M in enone and 5.0 M in alkyne. The yields of cycloaddition as determined for 3–5% conversions and the initial rates of cycloaddition as obtained from the early parts of the adducts concentration-reaction time curves are given in Table 7 together with normal substituent constants (σ_π) and the HH : HT ratios.

In the case of 14d the amount of cycloadducts could not be determined by GLC because of their thermal instability. The reactivity of 14d was estimated indirectly by the rate of its disappearance in the presence of 3b; this rate was compared with those of enones 2 and 14c under the same conditions. In the absence of 3b the rates of disappearance of 14d or 14c were much lower.

The plotting of the quantum yields against σ_π constants of the enone substituents R′ reveals a linear correlation between the efficiency of cycloaddition and the σ_π values for five (and, possibly, for all six) members of this series. The correlation cannot be extended to 3-ethoxy-2-cyclohexenone 13 which is totally unreactive towards 3b; this is compatible with previous observations that α,β-enones with heteroatomic β-substituents react sluggishly even with most active olefins or do not react at all.[25] Enones 2, 14a, 14b, 14c and 14e give a series with reaction constant $\rho = +1.554$ ($r = 0.998$). The acceleration of cycloaddition by the electron-withdrawing substituents in the enone again characterizes this reaction as moderately electrophilic towards acetylenic substrate: the more electron-deficient is the double bond in the excited enone, the quicker it attacks the π-bond of the substrate (see Fig. 1b).

In this series, as in the former, it is difficult to find a straight-forward connection between the regioselectivity of cycloaddition and the electronic or steric effects of substituents. However, any substituent larger than hydrogen augments the content of the HT-isomer in the cycloadducts mixture. Moreover, in the case of two similarly substituted enones, 14a and 14b, a greater amount of the HT-adduct is formed by the enone with bulkier alkyl substituent.

The comparison of both reaction series obtained for similar reactions carried out under similar conditions shows that the absolute values of ρ in these series are close to 1.5. The value $|\rho| \sim 1.5$ can be considered, although with due reservation, as indirect evidence in favour of a stepwise mechanism of cycloaddition, since the majority of concerted reactions with cyclic electron transfer are characterized by $|\rho| \leq 0.7$, i.e. by a low sensitivity to the effect of substituents.[34]

The linearity of the correlation observed in the second series (Fig. 1b) implies that the mechanism of cycloaddition is the same for all members of this series. This point deserves attention in view of earlier suggestions[3] that such enones as **14c** or **14e** might cycloadd in their singlet rather than triplet states. When the reactions **2** + **3b**, **14c** + **3b** and **14e** + **3b** were carried out in the presence of air oxygen, the rates of photoannelation in all three cases were 2–2.5 times slower than under argon. This result seems to confirm the triplet mechanism of cycloaddition for all members of the series.

Temperature effects

The total quantum yield of cycloaddition for the reaction **1** + **3a** → **4a** + **5a** in ethyl acetate (molar ratio enone:alkyne = 1:10) changes but insignificantly when temperature rises from −23° to +77°. At the same time the regioselectivity, i.e. the ratio **4a**:**5a**, decreases quite remarkably. The same situation is observed when **2** reacts with **3b** in xylol (molar ratio 1:10) at temperatures ranging from −23° to +127°. The data thus obtained and the values of $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ calculated thereof are given in Table 8.

As the mechanism of formation of HH- and HT-isomers is probably the same, the small values of $\Delta\Delta S^{\neq}$ seem to reflect a close similarity between the corresponding transition states. The predominance of the HH-cycloadducts must be caused rather by the difference in the heats of activation. From the synthetic point of view the photocycloaddition at lower temperatures proved to be the most effective way for selective obtention of the HH-isomers.

Solvent effects

The influence of solvents on the rates and regioselectivity of cycloaddition for reactions **1** + **3a** and **2** + **3b** were studied under standard conditions at 26 ± 2°, the concentrations being 0.16 M in enone and 1.60 M in alkyne in the first case and 0.25 M in enone and 2.50 M in alkyne in the second. The relative rates of cycloaddition and the ratios of isomers were determined by GLC as described above. The results are given in Table 9.

As can be seen from Table 9, on the whole there is a tendency for the rates of cycloaddition to decrease on passage from unpolar to more polar solvents. The ratio [HH]:[HT], which characterizes the regioselectivity of addition, is higher in the former and decreases in the latter. In aprotic solvents both reactions show "satisfactory" ($|r| > 0.90$) linear correlation between the logarithm of the ratio [HH]/[HT] and the Kirkwood–Onsager parameter $\Omega = d(\epsilon - 1)/MW(2\epsilon + 1)$ where d-density, ϵ-dielectric constant and MW-molecular weight of the solvent. For the reaction **1** + **3a** → **4a** + **5a** in six aprotic solvents this dependence is described by the equation:

$$\log\frac{[\mathbf{4a}]}{[\mathbf{5a}]} = 0.446 - 0.362 \cdot \Omega \times 100 \quad (r = -0.951).$$

In this series acetonitrile deviates somewhat from the correlation, although general trend remains the same. For the reaction **2** + **3b** → **15** + **16** in all solvents tried the correlation is described by the equation:

$$\log\frac{[\mathbf{15}]}{[\mathbf{16}]} = 0.885 - 0.281 \cdot \Omega \times 100 \quad (r = -0.938).$$

The plots of log [HH]/[HT] vs Ω for both reactions are nearly parallel (see Fig. 2). This implies the identity of the stabilizing solvent effect upon the intermediates and/or transition states for both reactions and hence a close similarity of these species. In solvents capable of forming hydrogen bonds the deviations from the Kirkwood–Onsager equation become possible.[31] Indeed, when **1** reacts with **3a** in tert-BuOH (Ω × 100 = 0.45) the ratio **4a**:**5a** sinks to 1.30 and in 95% aqueous AcOH (Ω × 100 = 0.66) even to 0.70, i.e. the ratio becomes reversed in favour of the HT-isomer.

Table 8. Temperature effects and activation parameters

Reaction	Temp. (°K)	Φ (λ > 316 nm)	[HH]/[HT]	$\Delta\Delta H^{\neq}$ (kcal/mole)	$\Delta\Delta S^{\neq}$ (e.u.)
1 + **3a** (in AcOEt)	250	0.23 ± 0.05	3.35	−1.56	−3.85
	300	0.24 ± 0.05	2.10		
	350	0.25 ± 0.05	1.35		
2 + **3b** (in xylol)	250	0.046	8.58	−0.88	+0.83
	300	0.048	7.02		
	350	0.049	5.55		
	400	—	4.42		

Table 9. The effect of aprotic solvents on the rate and regioselectivity of photoannelation

Solvent	$\Omega = \frac{\epsilon - 1}{2\epsilon + 1} \cdot \frac{d}{MW} \times 10^2$	V_{rel}		[HH]:[HT]	
		1 + **3a**	**2** + **3b**	**1** + **3a**	**2** + **3b**
Cyclohexane	0.18	0.81	0.79	2.30	6.25
Benzene	0.26	0.92	1.00	2.20	7.00
Ether	0.32	1.00	0.83	2.21	6.70
Ethyl acetate	0.38	0.64	0.64	2.08	5.20
Acetone	0.63	0.76	0.72	1.75	4.60
CH_2Cl_2	0.65	0.91	—	1.51	—
Acetonitrile	0.90	0.12	0.59	1.93	4.41

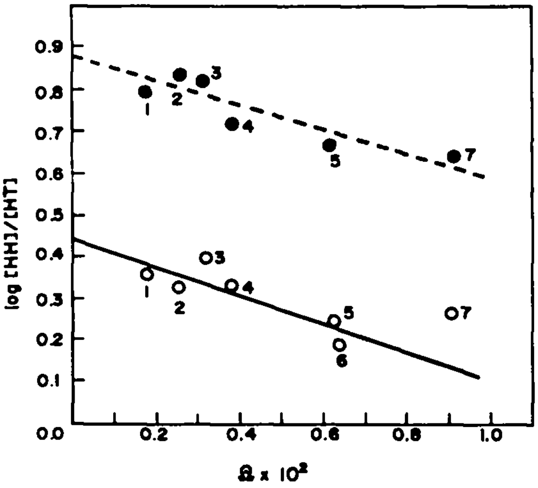

Fig. 2. The effect of aprotic solvents on the regioselectivity of reactions 1 + 3a (solid line) and 2 + 3b (dotted line). Solvents: 1, Cyclohexane; 2, Benzene; 3, Ether; 4, AcOEt; 5, Acetone; 6, CH_2Cl_2; 7, Acetonitrile.

Summary

Mechanistic aspects of the cycloaddition of 5- and 6-membered cyclic α,β-enones to monosubstituted acetylenes can be generalized as follows: (1) The quantum efficiency of photoannelation lies within the same order of magnitude (though somewhat lower) as in the case of the enone–alkene photocycloaddition. In both cases the reaction involves the triplet state of the enone and represents an electrophilic attack of this triplet state on the π-bond of the substrate; (2) The regioselectivity of cycloaddition cannot be predicted on the basis of Corey's hypothesis[26] about the formation of an oriented π-complex between the triplet state of the enone and the ground state of the substrate. All enones studied in this work react with 1-alkynes to give mainly those cycloadducts which correspond to the formation of the most stable 1,4-diradical intermediate; (3) From the solvent effects observed it can be concluded that the intermediates and/or transition states leading to the HT-cycloadducts are somewhat more destabilized by dipole–dipole interactions than those leading to the HH-isomers.

Different regioselectivity observed for the same α,β-enones in their cycloadditions to the structurally similar terminal olefins and acetylenes may have the following explanations, verifiable either experimentally or by calculation:

(A) Different stability of π-complexes or dipole–dipole associates formed between *the ground states* of reactants.

(B) Greater effect of dipole–dipole interactions between enone triplets and alkynes in comparison with the case of enone–alkene photoannelation.

(C) Different density of π-electronic charges in structurally similar alkenes and alkynes and/or a weaker polarization of the π-bond in the latter.

The discussion of these possibilities and of some factors influencing the regioselectivity of enone photoannelation make the subject of the next communication.[35]

EXPERIMENTAL

For the detailed description of preparative-scale experiments; see Refs. 15*a*, 15*c*, 15*d*, 16*b*. Spectral characteristics of the products *loc. cit.*, and also Refs. 19, 22. Kinetics, temperature and solvent effects; see Refs. 15*b*, 15*d*, 16*a*, 16*c*. Medium-pressure mercury lamps DRT-375 w and PRK-4 (2 × 220 w) were used as light source. All photolyses were carried out under dry argon. The isolation of the light with $\lambda \geq 316$ nm was achieved with a glass filter of type UFS-6 with the following transmittance: $\lambda \leq 316$ nm, 0%; λ 334 nm, 48%; λ 366 nm, 73% (maximum). Analytical and preparative GLC was performed with all-glass columns with either 5% PEG-4000 on Chromosorb G (+5% KOH) for the series 1 + 3a–h or with 5% SE-30 on Chromaton N-AW-DMCS (for 2 and its analogs + 3b). Column chromatography—on silicagel L, preparative TLC—on silicagel LG (5–40 μ).

The quantum yields were measured with ferrioxalate actinometer[36] on the assumption that for the decomposition of potassium ferrioxalate $\Phi_{334} = \Phi_{366} = 1.23$. The isolation of the enone n,π^*-transition band was achieved by the combination of UFS-6 filter with conc. $NiSO_4$ solution (thickness 5 mm), the intensities of lines with λ 334 and 366 nm relating as 1 : 4.8. The values of Φ are averaged from 4 to 5 measurements. The quenching experiments were done according to Ref. 28. The data obtained in the study of solvent effects (average from 3–4 runs) correspond in all cases to the same depth of the reaction when 15 ± 3% of the starting enone was consumed. All plots were obtained by the least squares method.

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ADDENDUM

While this paper was in preparation one more case of predominantly head-to-head cycloaddition of α,β-enones to monosubstitutes acetylenes, namely, to trimethyl-silylacetylene was reported [J. Soulie and M. J. Pouet, *Tetrahedron* **33**, 2521 (1977)].