248. Competitive Formation of Ylide and Carbene Intermediates from $^1\pi,\pi^*$-Excited α,β-Unsaturated γ,δ-Epoxyketones[1])

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Summary

Laser flash photolyses ($\lambda = 265$ mm) of the γ,δ-epoxyenones **1–3**, **7** and **8**, the α,β-unsaturated γ,δ-epoxy ester **6**, and the epoxytriene **9** at ambient temperature produced short-lived transients with broad absorption maxima in the visible region, which are identified as carbonyl ylides. Comparison of the rather long-wavelength absorption maxima with the results of standard PPP SCF SCI calculations suggests that some degree of twisting is present in all the ylides studied. The lifetimes of the order of hundreds of ns of these intermediates and *Stern-Volmer* analysis of the trapping of the carbonyl ylide derived from **2** with CH_3COOH provide conclusive evidence that the carbene products are not formed *via* the carbonyl-ylide intermediate *(Scheme 3).*

1. Introduction. – In recent years the photochemistry of α,β-unsaturated γ,δ-epoxyketones has been investigated systematically. From these studies, it has been disclosed that, in general, on $^1n,\pi^*$-excitation, substrates of type **I** undergo *(E)/(Z)*-isomerization and/or product formation *via* C(γ), O-cleavage of the oxirane (**I** → **a**) [2]. Selective $^1\pi,\pi^*$-excitation, however, also causes reactions which include cleavage of the C(γ), C(δ)-bond of the oxirane, leading to ylide and carbene intermediates of type **b**, **c** and **d** *(Scheme 1)* [2] [3] [4].

The distribution of the isolated products depends markedly on R^2 and on the solvent [3] [4]. Thus, $^1\pi,\pi^*$-excitation ($\lambda = 254$ mm, CH_3CN) of epoxyenone **1** gives rise to product formation *via* carbene intermediate **c** [2b], while **2** mainly gives products arising from C(δ)-carbene intermediate **d**, and only to a small extent products from a C(γ)-carbene **c** [3]. On the other hand, irradiation of **3** ($\lambda = 254$ nm, CH_3CN) exclusively leads to products of an ylide intermediate **b** [4].

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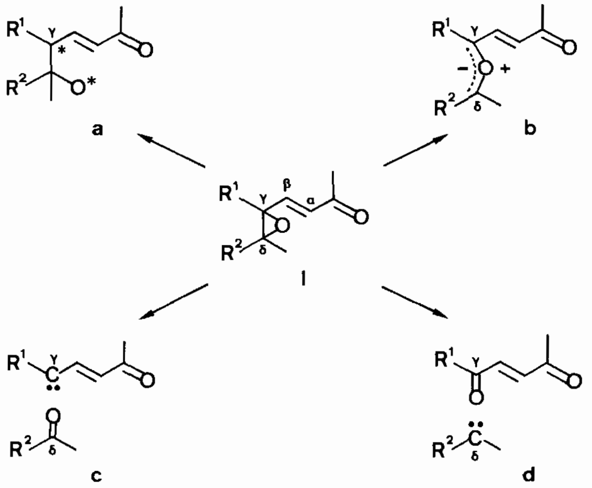
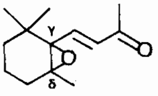
[1]) 131st Communication of the series '*Photochemical Reactions*' 130th Communication see [1].

Scheme 1



In the irradiation of **2**, attempts to trap carbene intermediates with CH_3OH were not successful, instead ylide trapping occurred [3]. Furthermore, an optically pure sample of the epoxyenone **2** was rapidly photoracemized *via* a carbonyl-ylide intermediate on the time scale of the conversion to photoproducts [5].



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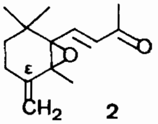

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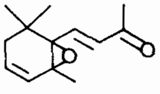

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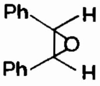
These findings led us originally to postulate that, on $^1\pi,\pi^*$-excitation of **2**, a carbonyl ylide is formed, which either returns to starting material or undergoes cleavage to carbene intermediates of type **c** and **d**. This hypothesis finds precedent in the photolysis of aryl-substituted oxiranes of type **4** which also undergo photocleavage to carbenes and carbonyl ylides [6]. These carbenes have been trapped by alcohols, and the carbonyl ylides have been observed by UV/VIS spectroscopy at low temperature [7] and trapped by common dipolarophiles at ambient temperature [8]. Investigating the mechanism of the carbene formation in this reaction, *Griffin et al.* showed that the rate of carbene formation from aryldicyanooxiranes of structure **5** may be enhanced using a double-irradiation technique (UV/VIS) indicating photolytic cleavage of the carbonyl ylide [9]. On the other hand, it



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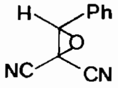

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has also been recognized that the thermal generation of carbonyl ylides is not accompanied by the formation of carbene products [10][2].

The aim of the present investigation was to monitor directly the postulated carbonyl ylides from various epoxyenones and dienes of the ionone series by laser flash photolysis and low-temperature techniques. To determine whether or not the ylide **b** is in fact the precursor of the carbene intermediates **c** and **d**, compound **2** was considered as a prime candidate for kinetic investigations as it yields exclusively carbene products on photolysis in CH_3CN and yet the ylide intermediate can be trapped in CH_3OH.

2. Results and Discussion. – Laser flash photolyses ($\lambda = 265$ nm) of the epoxy compounds **1–3** and **6–9** at ambient temperature in various solvents produced short-lived transients with broad absorption bands in the visible region. The same species were formed as persistent blue photoproducts by 254-nm irradiation of compounds **1–3** and **6–9** dissolved in an EPA glass (Et_2O/i-pentane/EtOH 5:5:2) at 77 K. The UV/VIS spectrum of the carbonyl ylide derived from **2** is shown in *Fig. 1*. The lifetimes (τ) and the λ_{max}-values of the transients, which are identified as carbonyl ylides [6–8] [12–13], are given in *Table 1*. Flash photolysis at 353 nm (n,π^*-transition of the epoxyenones) produced only very small amounts of the transient ylides, φ_{ylide} (353 nm) $\leqq 0.1 \cdot \varphi_{ylide}$ (265 nm), in accord with earlier conclusions from preparative work (see *Introduction*).

The ylides derived from the epoxides **2**, **3**, and **6**, which incorporate an additional double bond in ε-position, show absorption maxima at 660–690 nm, whereas the λ_{max} of the ylides derived from the bisepoxyenone **7** and the methano-epoxyenone **8** are blue-

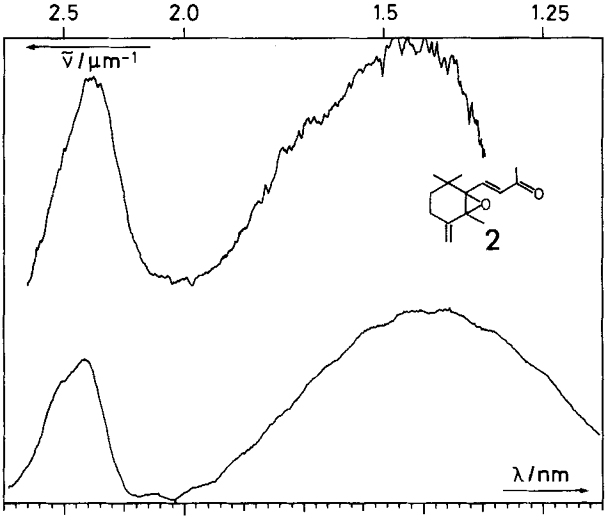

Fig. 1. *Absorbance of the carbonyl-ylide derived from* **2** *(arbitrary ordinate scale; solvent EPA)*. Upper curve: transient spectrum at r. t. after laser excitation at 265 nm; lower curve: spectrum recorded at 77 K after 254 nm irradiation.

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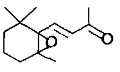
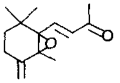
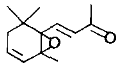
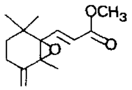
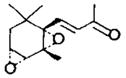
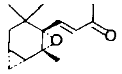
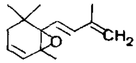
[2] However, it was recently reported that the thermal fragmentation of methoxy-substituted ylides to carbenes had been discovered [11].

Table 1. *Lifetimes τ and λ_{max} of the Carbonyl Ylides Obtained on Irradiation of the Epoxides*

Compound		τ/ns) at room temperature a)		λ_{max}/nm in EPA at 77 K b)	
1		7000 ± 500 (Et$_2$O/N$_2$)c) 22000 ± 3000 (CH$_3$CN/N$_2$)c) 11000 ± 1000 (pentane)e)	3000 ± 500 (Et$_2$O) 3000 ± 500 (CH$_3$CN/O$_2$)d) 1200 ± 500 (pentane)f)	770	*ca.* 300
2		158 ± 10 (Et$_2$O) 370 ± 20 (Et$_2$O/CH$_3$OH 1:1)	250 ± 10 (CH$_3$CN) 120 ± 10 (hexane)	720	420
3		185 ± 10 (Et$_2$O)	229 ± 10 (CH$_3$CN)	655	416
6		160 ± 10 (Et$_2$O)		690	420
7		33 ± 3 (Et$_2$O)		620	370
8		2700 ± 200 (Et$_2$O/N$_2$)c)	10000 ± 1000 (CH$_3$CN)c)	620	350
9		42 ± 5 (CH$_3$CN)		500	

a) After laser excitation at 265 nm. b) After 254 nm irradiation. c) Flushed with N$_2$. d) Flushed with O$_2$. e) Degassed. f) Saturated with O$_2$.

shifted to 620 nm (see *Table 1*). On the other hand, the ylide derived from the epoxytriene **9**, incorporating a diene side-chain instead of an enone, exhibits its absorption maximum at shorter wavelength.

The carbonyl ylide derived from **1** behaves exceptionally. Though it is the least conjugated it absorbs at the longest wavelength. Also its lifetime is greately shortened by the presence of O$_2$ (k_q(Et$_2$O) = *ca.* $5 \cdot 10^7 s^{-1} M^{-1}$; the O$_2$-concentration was taken as $3.9 \cdot 10^{-3}$ M (under air) according to [15]), whereas the other ylides of this study proved to be insensitive to O$_2$ within their natural lifetimes and the limits of error. The absorption at longer wavelength may be explained by a twisted conformation of the carbonyl-ylide moiety (*cf.* **e**), since it can be seen from *Dreiding* models that a planarization of the carbonyl-ylide moiety is inhibited by steric repulsion between the geminal CH$_3$-groups and the H-atoms in the 4-position[3]) (*cf.* **f**), whereas compounds **2**–**9** allow the ylides to

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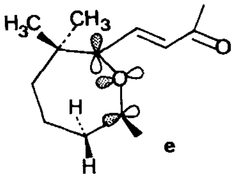
[3]) In ionone derivatives, numbering according to the carotinoid nomenclature is used [16].



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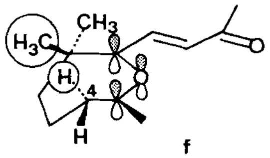

f

adopt a planar conformation without steric interaction[4]). The hypothesis of a twisted carbonyl ylide derived from **1** was confirmed by the study of the epoxyenone **10**, which has no *gem*-dimethyl group. In this case, the ylide may adopt a planar conformation without steric repulsion and, indeed, the absorption maximum of the ylide derived from **10** (see *Fig. 2)* is now at 660 nm ($\tau = 6.8 \pm 0.5\,\mu s$ in Et_2O at room temperature).

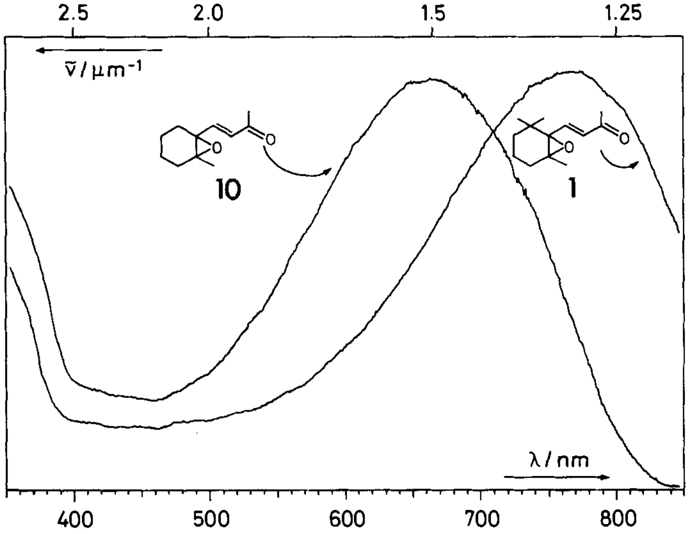

Fig. 2. *Absorbance of the carbonyl ylides derived from* **1** *and* **10**. Both spectra were recorded after 254-nm irradiation of the epoxy precursors in an EPA glass at 77 K (arbitrary ordinate scales).

Comparison of the remarkably long-wavelength ylide absorption spectra *(Table 1, Fig. 1* and *2)* with the results of standard PPP SCF SCI calculations *(Table 2)* nevertheless suggests that some degree of twisting is present in all the ylides studied here, presumably due to the angle strain in the seven-membered ring. It is known from both experiment [10] [18] and calculations [19] that the rotational barrier of carbonyl ylides is low. If we assume a fully planar geometry, the first two electronic transitions are predicted to lie at much higher energies than is observed. Furthermore, the distinct bathochromic shift of the first band upon replacement of the terminal methylene group by a carbonyl

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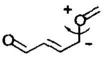
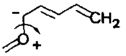
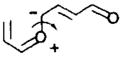
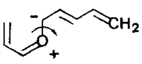
[4]) The twisted ylide has a reduced energy gap between the HOMO and the LUMO, thus, causing a red-shift in the absorption spectrum of the ylide [17].

Table 2. *Results of PPP SCF SCI Calculations*[a])

Model compound	Planar geometry	Twisted geometry[b])
	409 (1.46)	492 (1.06)
	298 (0.03)	329 (0.10)
	234 (0.40)	256 (0.56)
	407 (1.57)	471 (1.26)
	323 (0.01)	355 (0.07)
	244 (0.52)	266 (0.68)
	520 (1.18)	627 (0.88)
	323 (0.04)	341 (0.09)
	283 (0.01)	303 (0.00)
	258 (0.27)	268 (0.44)
	518 (1.27)	599 (1.07)
	345 (0.01)	369 (0.04)
	286 (0.01)	308 (0.00)
	271 (0.37)	278 (0.58)

[a]) Standard parameters were used [20]. The first transitions are quoted in nm (oscillator strength).

[b]) A twist around the C,O-bond marked with an arrow was simulated by reducing the corresponding resonance integral to one half its standard value of – 2.318 eV.

O-atom (**9** → **3**) is not reproduced by the calculations. These discrepancies are largely removed by simulating a nonplanar ylide geometry in the calculations with the use of a reduced resonance integral β_{CO} for one of the ylide C,O-bonds.

Due to the dipolar nature of the ylides, their lifetimes increase with the solvent polarity (*cf.* **1**, **2** and **3**, *Table 1*). The lifetimes of the carbonyl ylides derived from the epoxyenones are in the region of hundreds of ns, whereas the corresponding ylides derived from the epoxydienes are more short-lived (compare **3** and **9**), in some cases beyond the time resolution of the laser system (*ca.* 20 ns). Thus, there were no ylides detectable on laser flash photolysis of the epoxydienes derived from the enones **7** and **8** though on preparative photolyses carbonyl ylide products were isolated [21].

The knowledge of the carbonyl ylide lifetimes allows us to draw some mechanistic conclusions about the formation of the carbene products (see *Scheme 1*) isolated on preparative photolyses of these epoxyenones and -dienes. The ylides are too short-lived to be cleaved photochemically to carbenes under the conditions of preparative photolyses[5]). This is further born out by the preparative results with the epoxydienes, which generally yield more carbene products than the corresponding epoxyenones, although their ylide-lifetimes are shorter. Moreover, on irradiation of these ylides at 77 K with a powerful light source in the visible region, bleaching of the samples occurred only slowly, indicating considerable photostability of the ylides to visible light.

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[5]) A low-pressure Hg immersion lamp (*Hanau TNN 15/32*) was used with an output of *ca.* $5 \cdot 10^{20}$ photons $\cdot$ s^{-1} $\cdot$ m^{-2} (254 nm) at the inner surface of the solution. As a conservative upper limit we assume that the extinction coefficient ε (254 nm) is less than 10^5 $M^{-1} \cdot cm^{-1}$ (the PPP calculations predict only relatively weak transitions, $\varepsilon \leqq 10^4$ $M^{-1}cm^{-1}$, in the UV region below 300 nm) corresponding to a molecular cross section of less than $2 \cdot 10^{-20}$ m^2. Thus the probability that an ylide produced at the inner surface will absorb a second photon during its lifetime ($\leqq 1$ µs) is less than 10^{-5} and lower still within the solution.

Having found strong evidence that the carbene products are not formed by photochemical cleavage of carbonyl ylides, we wanted to obtain experimental proof as to whether or not the carbene products arise from carbonyl ylides. It was provided by a *Stern-Volmer* analysis of the trapping of the carbonyl ylide. Compound **2** was chosen as a substrate for the kinetic experiments as it yields exclusively carbene products when photolyzed in CH_3CN, but ylide-trapping products are obtained on irradiation in CH_3OH [3]. Searching for a suitable trapping agent we found by laser flash photolysis that the carbonyl-ylide lifetimes were effectively reduced by the addition of CH_3COOH[6]. Kinetic quenching experiments were carried out by measuring the lifetimes τ of the ylide in CH_3CN in the presence of various CH_3COOH-concentrations (see *Exper. Part*). The results are depicted in *Fig. 3*.

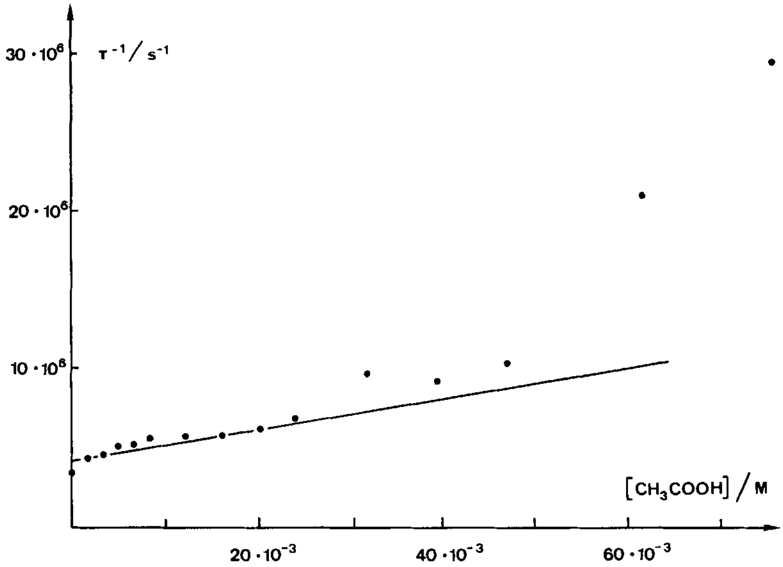

Fig. 3. *Plot of 1/τ of the ylide derived from* **2** *in* CH_3CN *as function of the concentration of* CH_3COOH

The plot of τ^{-1} against the CH_3COOH-concentration produced a straight line at low CH_3COOH-concentrations[7]) and, from the *Stern-Volmer* equation $\tau_{expt}^{-1} = \tau_o^{-1} + k_q[Q]$, a bimolecular quenching constant $k_q = 1.0 \cdot 10^8 \pm 0.2 \cdot 10^8\ \text{M}^{-1}\ \text{s}^{-1}$ could be determined in this concentration range.

To characterize the ylide-trapping product, the epoxyenone **2** was irradiated ($\lambda = 254$ nm) in neat CH_3COOH on a preparative scale (*Scheme 2*).

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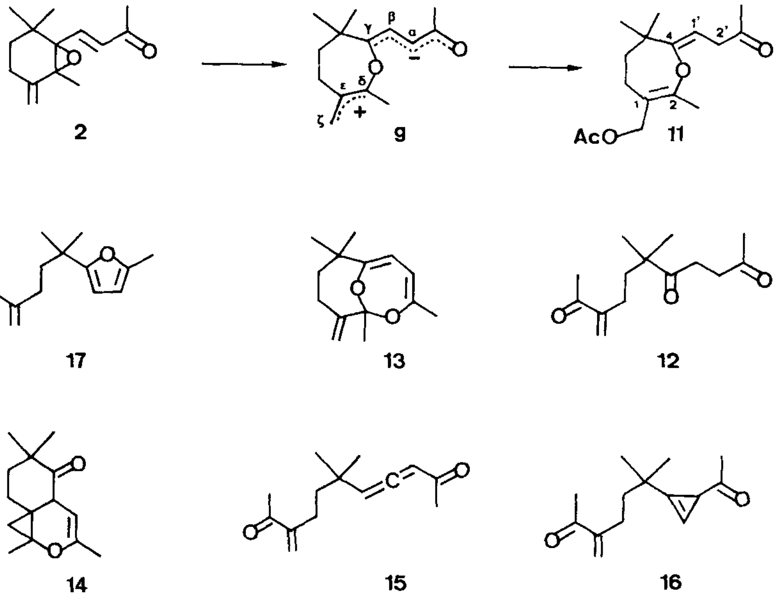
[6] CH_3OH proved not to be a suitable trapping reagent, since it was observed that addition of small amounts of CH_3OH increased the lifetime of the ylide.

[7] The nonlinearity of the slope at higher CH_3COOH-concentrations might be due to the formation of acetic acid dimers; a similar effect was recently described for the trapping of carbenes with CH_3OH [22]. However, the curvature of the slope could also arise from a ground state complexation of the enone by CH_3COOH.

Scheme 2



As the main products, the acetate **11** (23 %) and the hydrolysis product **12** (18 %) were isolated. Thus, the ylide **g** is trapped by protonation at C(α) and addition of the acetate to C(ζ). The bicyclic enolether **13**(14 %) obtained as the only product in 75 % yield on ^{1}n,π*-excitation of **2** in pentane [3] is here assumed to be formed *via* ylide **g**. In addition to the previously obtained [3] carbene products **14** (1 %), **15** (4 %) and **16** (3 %), the furan **17** [23] (10 %) was isolated, formed presumably by acid-catalyzed rearrangement of the (*Z*)-isomer of **2** (*cf.* [24]).

The structure of the acetate **11** is established by spectral data. In particular the oxo-butylidene side chain is evidenced in the ^{1}H-NMR spectrum by a *d* at 3.11 ppm and a *t* at 5.11 ppm (J = 7 Hz) for the 2H–C(2') and the H–C(1'), respectively. The AcOCH$_2$-moiety is indicated by characteristic signals (in the ^{1}H-NMR spectrum a *s* at 4.45 ppm, in the ^{13}C-NMR spectrum a *t* at 66.5 ppm and an IR band at 1735 cm^{-1}). The bis-enolether moiety is evidenced in the ^{13}C-NMR spectrum by 2*s* at 153.9 and 163.4 ppm for C(2) and C(4) and an upfield-shifted *d* at 104.7 and a *s* at 110.6 ppm for C(1') and C(1). Moreover, compound **11** was hydrolyzed (70% aq. CH$_3$COOH) to the acyclic triketone **12** [24] in 78% yield, which was also obtained on hydrolysis of **13** in 88% yield.

Conclusive evidence whether or not the ylide **g** is the precursor of the carbene intermediates **h** and **i** (*Scheme 3*) was provided by the determination of the CH$_3$COOH-concentration dependence of the relative quantum yields (Φ_{rel}) for the ylide-trapping and carbene products, respectively, upon 254-nm irradiation of **2** in CH$_3$CN. The results are shown in *Fig. 4.*

This *Stern-Volmer* plot shows that the quantum yield of the ylide-trapping products[8]) increases with increasing CH$_3$COOH-concentration, whereas the quantum yield of

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[8]) Total ylide-trapping product was taken as total product minus carbene products. A more accurate determination was not possible, since, unlike the carbene products **14**–**16** the ylide-trapping product **11** could not be detected by capillary GC (*Ucon*).

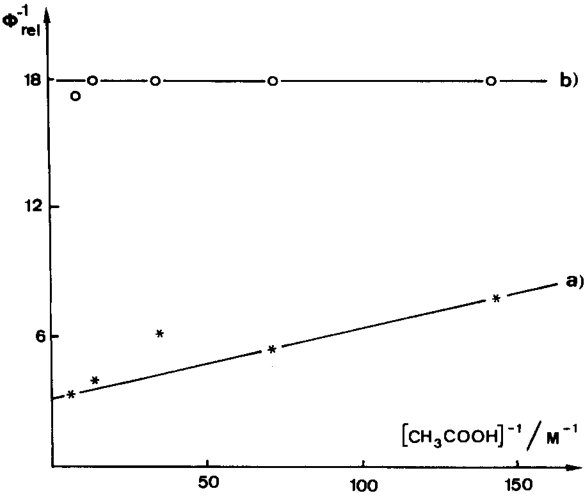
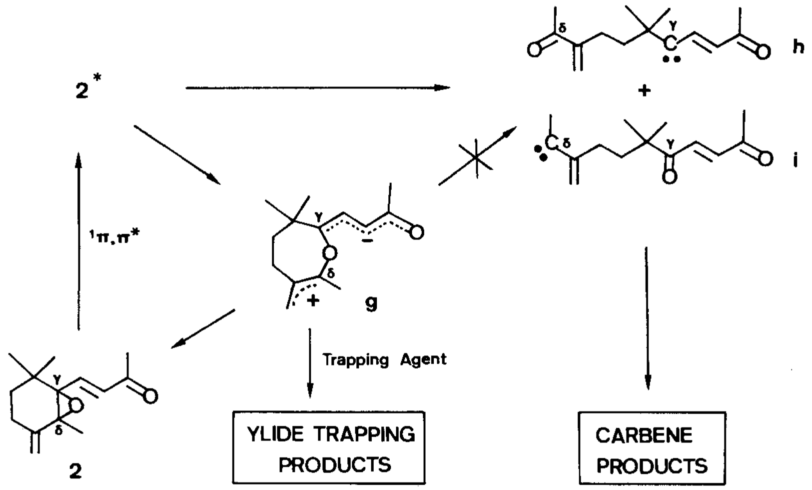


Fig. 4. *Plot of the reciprocal relative quantum yields* $1/\Phi_{rel}$ *of ylide-trapping (a) and carbene products (b) as function of the reciprocal* CH_3COOH*-concentrations*

carbene products is not dependent on the CH_3COOH-concentration. Thus, the carbene products are not formed *via* the carbonyl-ylide intermediate which is trapped with CH_3COOH.

On the basis of these results we are now able to present the following mechanistic scheme for the photoreactions of the epoxyenone **2** (see *Scheme 3*). The main pathway (*ca.* 85%) of π,π^*-excited **2** leads to the ylide g, which, in the absence of a trapping agent, recloses to the starting material. This pathway was also brought to evidence by optically

Scheme 3



active **2**, which under photolytic conditions was shown to undergo rapid racemization [5]. Only a minor pathway (*ca.* 15 %) of the excited epoxyenone leads to carbene products, which are the only isolable photoproducts on photolysis in CH_3CN or pentane. In the presence of an ylide-trapping agent such as CH_3COOH, CH_3OH or H_2O, however, the formation of ylide-trapping products competes effectively with the formation of carbene products. Since *Stern-Volmer* analysis indicates that *carbene products are not formed from the ylide intermediate* **g**, they must arise from a different pathway. Most likely alternatives are a direct cycloelimination from the excited epoxyenone or a fragmentation of the *excited* carbonyl-ylide, both of which have been discussed in [6] [17].

Although we have obtained experimental proof for the independent formation of carbonyl-ylide and carbene intermediates by *Stern-Volmer* analysis with the epoxyenone **2** only, we conclude that the mechanism outlined in *Scheme 3* is applicable to all epoxides studied here. However, they seem to behave differently from aryl-substituted epoxides, since it has been reported that the formation of carbenes also proceeds *via* photolytic cleavage of the carbonyl-ylide intermediates [9][9]).

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Experimental Part

1. *Epoxy compounds* **1** [26], **2** [3], **3** [27], **6** [28], **7** [29], **8** [21], **9** [30] and **10** [31] were prepared as described elsewhere.

2. *Low-temperature UV/VIS spectra* were recorded after 254-nm irradiation of solutions of the epoxides in EPA at 77 K on an UV/VIS/NIR spectrophotometer *Beckmann UV5240* and transferred to a PDP11/60 computer for processing and display.

3. *Laser flash photolysis experiments* were carried out at ambient temp. in rectangular quartz cells (10 × 10 × 40 mm) using excitation pulses (*ca.* 30 mJ/pulse at 265 nm, 20 ns duration) from a *JK2000* frequency-quadrupled Nd-glass laser. The monitoring system allowed for the simultaneous detection of the kinetics (at a given wavelength) and the transient spectrum (at a given delay time) in digital form. Details shall be given elsewhere [32].

The concentrations of the epoxides studied were chosen so as to give an absorbance of *ca.* 1 at 265 nm. The lifetimes were determined at 620 nm.

4. *Determination of the Lifetime τ of the Ylide Derived from* **2** *as a Function of the CH_3COOH-Concentration.* To samples of a CH_3CN-solution of **2**, which had an absorbance of *ca.* 1 at 265 nm were given various amounts of CH_3COOH, and the lifetimes τ of the ylide were determined by the laser flash technique as given in *Table 3.*

Table 3. *Lifetimes τ of the Ylide Derived from* **2** *as Function of the CH_3COOH-Concentration in CH_3CN*

$[CH_3COOH]$ (M)	τ (ns)	$[CH_3COOH]$ (M)	τ (ns)	$[CH_3COOH]$ (M)	τ (ns)
0	282 ± 5	$8.25 \cdot 10^{-3}$	171 ± 5	$3.20 \cdot 10^{-2}$	99 ± 5
$1.67 \cdot 10^{-3}$	228 ± 5	$1.23 \cdot 10^{-2}$	170 ± 5	$3.97 \cdot 10^{-2}$	102 ± 5
$3.33 \cdot 10^{-3}$	210 ± 5	$1.63 \cdot 10^{-2}$	162 ± 5	$4.72 \cdot 10^{-2}$	91 ± 5
$4.97 \cdot 10^{-3}$	188 ± 5	$2.03 \cdot 10^{-2}$	150 ± 5	$6.17 \cdot 10^{-2}$	46 ± 5
$6.61 \cdot 10^{-3}$	184 ± 5	$2.42 \cdot 10^{-2}$	146 ± 5	$7.57 \cdot 10^{-2}$	31 ± 5

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[9]) During the preparation of this manuscript Prof. *A.M. Trozzolo* has kindly called our attention to his laser flash photolysis experiments with aryl-substituted oxiranes using an excimer laser (λ = 248 nm). These experiments have shown that carbenes are also formed directly from oxiranes without the intermediacy of an ylide [25]. His observations and interpretation are consistent with and complementary to our results.

The plot of τ^{-1} *vs.* [CH_3COOH] yielded a curve which is approximately linear for [CH_3COOH] $< 4 \cdot 10^{-2}$ M *(*see *Fig. 3)* with a slope of $1.0 \cdot 10^8 \pm 0.2 \cdot 10^8$ $M^{-1}s^{-1}$.

5. *Photolysis of* **2** *in CH_3COOH.* A solution of **2**[3] (1.22 g, 5.5 mmol) in CH_3COOH (120 ml) was irradiated with a low-pressure Hg-lamp in a water-cooled quartz vessel. The reaction was followed by capillary GC analysis of aliquots, which were neutralized with sat. $NaHCO_3$ and worked up in Et_2O pentane. After chromatography (SiO_2; Et_2O/pentane 1:2 to 2:1) the following product distribution was determined by ^{1}H-NMR and GC analysis of the fractions (based on converted starting material): **11**(23%), **12**[24](18%), **13**[24](14%), **14**[3](1%), **15**[3](4%), **16**[3](3%) and **17**[23](10%).

[4-(3'-Oxo-1'-butylidene)-2,5,5-trimethyl-3-oxa-1-cycloheptenyl]methyl acetate (**11**). B.p. 100°/0.03 Torr. IR 3080 *w*, 3070 *w*, 3005 *w*, 2965 *s*, 2942 *s*, 2928 *s*, 2870 *m*, 2840 *w*, 1735 *s*, 1720 *s*, 1668 *s*, 1465 *m*, 1458 *m*, 1445 *m*, 1432 *m*, 1415 *m*, 1380 *s*, 1372 *s*, 1355 *s*, 1335 *m*, 1317 *m*, 1275 *m*, 1225 br. *s*., 1160 *s*, 1155 *s*, 1105 *s*, 1048 *s*, 1013 *s*, 952 *s*, 940 *s*, 920 *w* sh, 900 *w*, 890 *w*, 845 *w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.15 (*s*, 2CH_3–C(5)); 1.50–1.70 (3H) and 1.90–2.40 (1H) (*m*, 2H–C(7), 2H–C(6)); 2.00, 2.03, 2.14 (3 *s*, 3H–C(4'), H_3C–C(2), CH_3COO); 3.11 (*d*, *J* = 7, 2H–C(2')); 4.45 (*s*, $AcOCH_2$); 5.11 (*t*, *J* = 7, H–C(1')). ^{13}C-NMR (20 MHz, $CDCl_3$): 17.4, 20.7, 27.3, 29.0 (4 *q*, 2 at 27.3, 5 CH_3); 26.1, 39.4, 40.3 (3 *t*, C(6), C(7), C(2')); 66.5 (*t*, $AcOCH_2$); 104.7 (*d*, C(1')); 39.6 (*s*, C(5)); 110.6 (*s*, C(1)); 153.9, 163.4 (2 *s*, C(2), C(4)); 170.8 (*s*, CH_3COO); 206.0 (s, C(3')). MS: 220 (13, M^+–CH_3CO_2H), 177 (58), 135 (31), 123 (10), 121 (11), 119 (12), 107 (21), 93 (18), 91 (12), 79 (26), 77 (18), 69 (22), 55 (20), 45 (11), *43* (100), 41 (22), 39 (13).

$C_{16}H_{24}O_4$ (280.35) Calc. C 68.54 H 8.63% Found C 68.67 H 8.68%

6. *Hydrolysis of* **11** *and* **13.** *a)* A solution of **11** (39 mg, 0.139 mmol) in 70% aq. CH_3COOH (5 ml) was stirred over night. Workup as described above gave according to ^{1}H-NMR analysis pure **12**[24] (26 mg, 78%). *b)* Analogous treatment of **13** (43 mg, 0.195 mmol) gave **12** (41 mg, 88%).

7. *Determination of the Relative Quantum Yield of the Ylide-Trapping and Carbene Products as Function of the CH_3COOH-Concentration.* To 6 aliquots (10 ml) of a *ca.* 5 mM CH_3CN-solution of **2** and hexadecane as an internal standard for GC analysis definite amounts of CH_3COOH were added, and the solutions were irradiated with a low-pressure Hg-lamp in a merry-go-round apparatus. By GC analysis of the samples the following fractions of the carbene products and of converted **2** were determined.

Table 4. *Relative Quantum Yields Φ_{rel} of Ylide-Trapping and Carbene Products as Function of the CH_3COOH-Concentration*

[CH_3COOH] (mM)	Fraction of converted **2**	Φ_{rel} Carbene products	Φ_{rel} Ylide-trapping products
0	0.11	0.058	0
7	0.24	0.055	0.13
14	0.29	0.055	0.18
29	0.27	0.055	0.16
72	0.36	0.055	0.25
145	0.40	0.051	0.29

The relative quantum yields, Φ_{rel}, of the ylide-trapping product were taken as Φ_{rel} of total product minus Φ_{rel} of total product at [CH_3COOH] = 0. The plot of Φ_{rel}^{-1} *vs.* [CH_3COOH]$^{-1}$ gave straight lines with a slope of 0 for the carbene products and with a slope of $21 \cdot 10^{-3}$ M^{-1} and an intercept of 4.7 for the ylide-trapping product, respectively *(*see *Fig. 4)*.

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