106. The Photochemistry of 2-Cyclopentenyl Methyl Ketones[1])

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Dedicated to Professor *R. B. Woodward* on his 60th anniversary

(20.I.77)

Summary

2-Cyclopentenyl and 3-phenyl-2-cyclopentenyl methyl ketones **(15–18, 30, 31)** undergo a 1,3-acetyl shift on direct irradiation, and the oxa-di-π-methane rearrangement to photochemically non-interconverting *endo* and *exo* bicyclo-[2.1.0]pentyl methyl ketones on triplet sensitization. Exceptions include the 2-methyl-3-phenyl-2-cyclopentenyl methyl ketone **32** and the 1-phenyl-2-cyclopentenyl methyl ketone **44** which are unreactive on direct irradiation and on triplet sensitization, respectively, and the 2-phenyl-2-cyclopentenyl methyl ketones **42** and **43** which do not react under either condition. The reactive triplet of the 3-phenyl-2-cyclopentenyl methyl ketone **30** has been identified as the localized styrene π,π^*-state of $E_T = 59$ kcal/mol by comparison of its phosphorescence at 77 K in rigid glasses with that of 1-phenyl-cyclopentene, and by the independence of the quantum yield on sensitizer energy in the range of 61–74 kcal/mol.

Introduction. – The photochemistry of β,γ-unsaturated ketones has been investigated extensively in recent years [1b] [2]. Our own entry into this field dealt with a study of an optically active cyclopentenyl methyl ketone [3]. The results are summarized in *Scheme 1*. Together with reports by *Ipaktschi* [4] and *Hart* [5] on other β,γ-unsaturated ketones, they had for the first time fully revealed a photochemical selectivity which has since been found characteristic of many such compounds: an allylic 1,3-acyl migration and α-cleavage to acyl and allyl radicals upon direct irradiation, and in triplet-sensitized runs a reaction involving a formal 1,2-acyl shift and three-ring formation (the oxa-di-π-methane (=ODPM) rearrangement). In the case at hand the photoracemization was unequivocally shown to be a fully intramolecular 1,3-acetyl shift rather than the result of free-radical recombination to racemic ketone, and both this isomerization and the radical cleavage proved unaffected by added triplet quenchers and yet subject to competition by bimolecular photoreactions of the starting ketone. On direct population of the triplet state by sensitization with acetone the ketone was found to rearrange

[1]) Taken from the Doctoral Theses by *Gonzenbach* (ETH Zürich, 1973), *Tegmo-Larsson*, and *Grosclaude* (Université de Genève, 1976). – For preliminary communications see [1].

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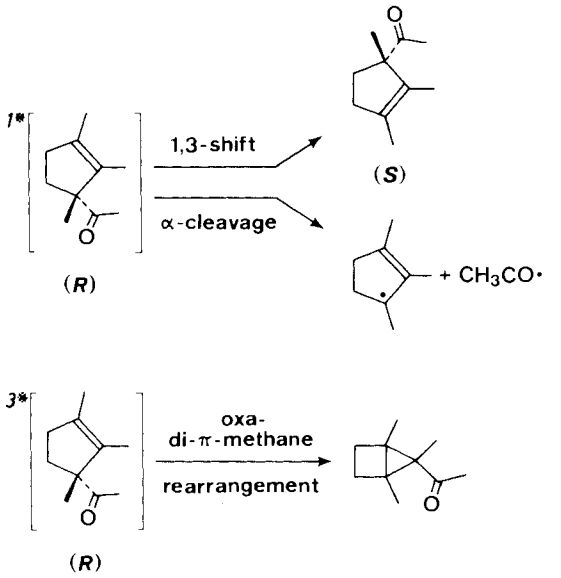
Scheme 1. *Photochemistry of* (R)–(+)-*1,2,3-Trimethyl-2-cyclopentenyl Methyl Ketone:* Summary of Conclusions by *Baggiolini, Schaffner & Jeger* [3]



to a bicyclo[2.1.0]pentyl isomer at the total expense of the product pattern observed on direct excitation. The photochemical processes under the former conditions were consequently attributed to the excited singlet state.

The continuation of our work in this particular β,γ-enone system included a complementary study of lower methyl homologues and of analogues in which the C=C bond is incorporated into the chromophore of a 1-phenylcyclopentene moiety, and the results are described in this paper. A previous report dealt with another modification in which phenyl ketones had been substituted for the methyl ketones [6].

Synthesis of the β,γ-Unsaturated Ketones 15–18, 30–32, 42, and 43[3]. – The 2-methyl-2-cyclopentenyl and 2,3-dimethyl-2-cyclopentenyl methyl ketones (**15** and **17**) were prepared from the known and readily accessible ethyl 3-cyclopropyl-2-butenoates *(E+Z)*-**1** [7] [8] and *(E)*-**5** [8]. After hydrolysis to the acids **2** and **6** (*(E)*-isomers isolated only) these were converted to *(E)*-**7** and *(E)*-**9** respectively, which were thermally isomerized[4]). The 1,2-dimethyl ketone **16** was equally well synthesized by the same procedure (**3** [8]→**4**→**8**→**16**), and by a route involving a methyl *Grignard* reaction of the keto ester **10** [9], and dehydration of the diastereoisomeric alcohols **11** to the ethyl cyclopentenecarboxylate **12.** This ester was hydrolysed to the acid **13** and methylated to **16.** A similar alkylation of **14** (*rac*-laurolenic acid [9]) furnished the trimethyl homologue **18.**

[3]) All compounds are racemic.

[4]) These pyrolyses were based on a study of the applications of the thermal vinylcyclopropyl→cyclopentene rearrangement of such ketones by *Jorgenson & Gonzenbach.* Communication of their unpublished results is gratefully acknowledged.

Scheme 2. *Synthesis of Ketones* **15–18**[3])

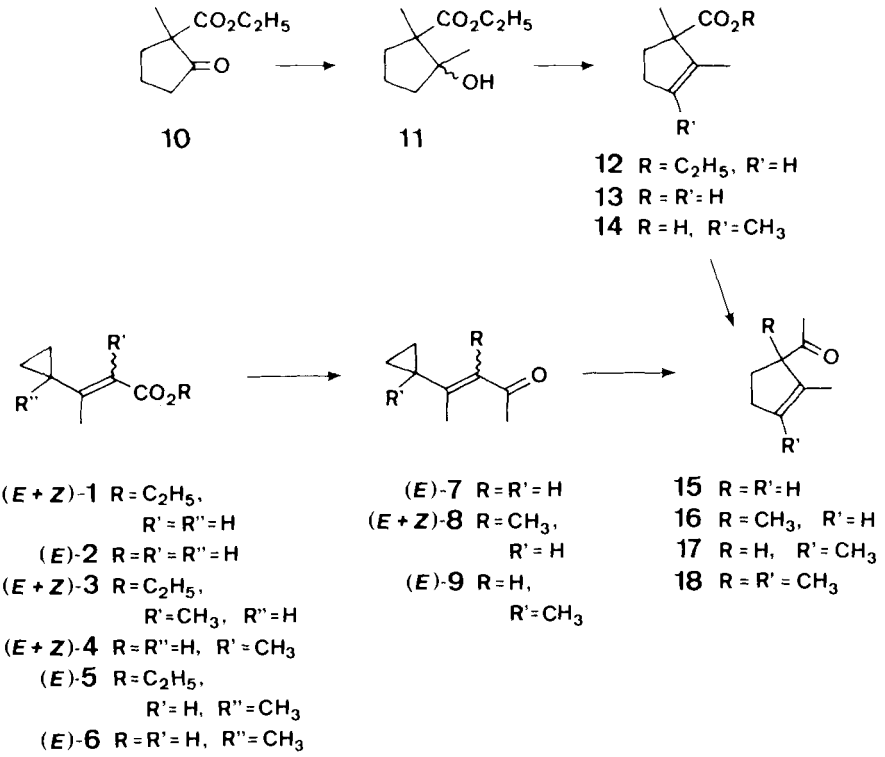
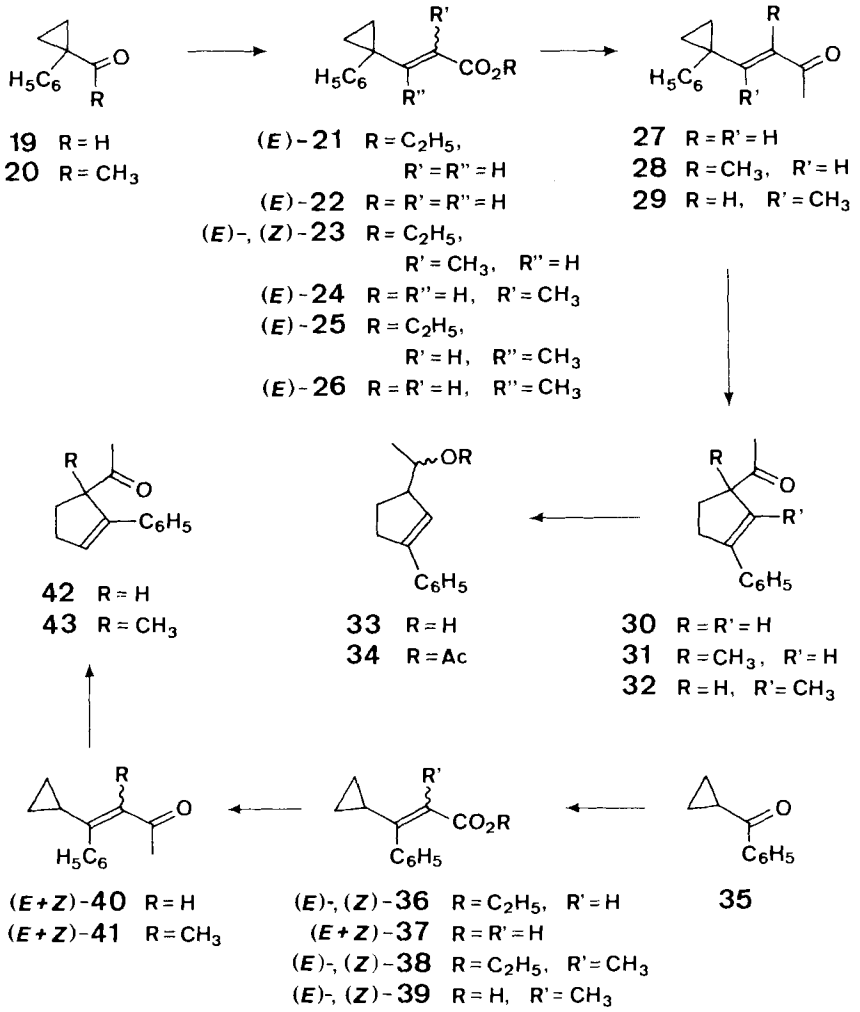


Table 1. *The Configurational Assignment to Esters* **21, 23, 25, 36,** *and* **38:** *NMR. and UV. Data*

Compound	NMR.[δ]				UV.[nm] λ_{max}	$\Delta\lambda$	
	H–C(2)	H_3C–C(2)	H–C(3)	H_3C–C(3)			
(E)-**21**	5.18	–	6.60	–	225	–7[b])	
(E)-**23**	–	1.15	6.85	–	226	+2[b])	
(Z)-**23**	–	1.88	5.95	–	212	+2[b])	
(E)-**25**	5.60	–	–	2.02[a])	235	+4[b])	
	H–C(4)						
(E)-**36**	3.17				241	+3[c])	–36[d])
(Z)-**36**	1.70				209	–27[c])	–61[a])
(E)-**38**	2.66				238	–5[c])	–39[d])
(Z)-**38**	1.82				210	–30[e])	–60[f])

[a]) *Cf.* δ 1.95 *(E)* and 1.50 *(Z)* for **1** [8a], and δ 2.08 for *(E)*-**5**.
[b]) With reference to the corresponding ethyl 4,4-ethano-2-pentenoates [8a] [11].
[c]) With reference to the corresponding ethyl 3-cyclopropyl-2-butenoates [8a].
[d]) With reference to the corresponding ethyl cinnamates [12].

Scheme 3. *Synthesis of Ketones* **30–32, 42,** *and* **43**[3])



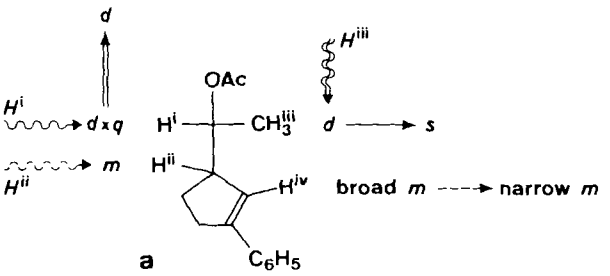
The phenyl-substituted cyclopentenyl methyl ketones **30–32, 42** and **43** were all obtained *via* the vinylcyclopropyl-cyclopentene route. The *Emmons* reaction [10] employing triethyl phosphonoacetate or -propionate and the appropriate cyclopropyl derivative **(19, 20,** or **35),** afforded the unsaturated esters *(E)*-**21** and -**25,** *(E)*- and *(Z)*-**23,** -**36** and -**38.** For acid *(E)*-**22** a *Doebner* condensation of **19** with malonic acid proved to be a superior alternative to the modified *Wittig* procedure and ester hydrolysis.

The configurations of the unsaturated esters **21, 23** and **25** were determined on the basis of their UV. and NMR. data. The vicinal coupling constant of 15 Hz of the olefinic protons of **21** as well as the chemical shifts of olefinic and methyl protons and the UV. data of the esters of this group of compounds are consonant with the assignments (see Table 1). The protons at C(4) (tertiary cyclopropyl-H) of the

pairs **36** and **38** are strongly deshielded by the ethoxycarbonyl group in the *cis* geometry (*ca.* $\Delta\delta$ 3.2 and 2.7, respectively). These shift differences were taken as the diagnostic data for the configurational assignments. The UV. absorptions of *(E* and *Z)*-**36** and -**38** exhibit considerable hypsochromic shifts relative to the parent cinnamic esters, and in the cases of *(E)*-**36** and *(E)*-**38** they closely correspond to those of the 3-cyclopropyl-2-butenoates *(Z)*-**1** and *(Z)*-**3** [8a], respectively (Table 1). These effects may arise from steric crowding between the phenyl and cyclopropyl group preventing optimum conjugative conformation of any one group.

The double-bond position in the phenylcyclopentenyl methyl ketones is apparent from their UV. absorption maxima at 254 nm of $\varepsilon = 10000$–20000 and IR. bands at 1710–1718 cm^{-1} which indicate a styrene-like chromophore and a non-conjugated keto group. Further confirmation on this point in the C(1)-unsubstituted ketone **30** was obtained by NMR. decoupling in the mixture of the diastereoisomeric acetates **34** which were prepared by sodium borohydride reduction and acetylation of the resulting alcohols **33.**

Irradiation (see **a**) at the frequencies of H^i (δ 4.92, $J = 3$ and 6/9 and 6 Hz), H^{ii} (δ 3.04) and H^{iii} (δ 1.21, $J = 6$ Hz) decoupled in respective order the doublet of H^{iii} to a singlet, the multiplet of H^{iv} (δ 6.08) to a signal with allylic fine coupling only, and the two multiplets of H^i to two doublets (one for each diastereoisomer) of $J_{i,ii} = 9$ and 3 Hz. These results establish unequivocally the partial structure including H^{i-iv} in **34**, and in particular the vicinal position of H^{ii} with respect to H^i (in contrast to a 1,4-bisallylic arrangement of these two hydrogen atoms).



The UV. spectra of the cyclopentenyl ketones **16** and **18** exhibit the distinctly separated absorption bands characteristic of the $n \rightarrow \pi^*$ (around 300 nm; Figure 1) and the $\pi \rightarrow \pi^*$/CT transitions of homoconjugated C=O and C=C partial chromophores. The spectra of the other enones in Fig. 1 lack this band separation, and the $n \rightarrow \pi^*$ transitions overlap with the tails of the lower-wavelength bands which extend to over 300 nm. Of course, this lack of band separation may be due in part at least to the presence of undetected trace amounts of α,β-unsaturated ketones where C(1)-unsubstituted ketones are concerned. However, a comparison of the spectra of **30–32, 42,** and **43** shows that this is hardly of great importance in the phenylcyclopentenyl ketones **(30, 32, 42).** The lower intensity of **32** *vs.* **30/31** above 300 nm is possibly due to out-of-double-bond-plane twisting of the phenyl group as a consequence of steric crowding with the methyl group which may lower both the conjugative $\pi \rightarrow \pi^*$ styrene and the homoconjugative transitions[5]). Furthermore, in

[5]) For a similar intensity decrease of UV. absorption upon the introduction of a methyl substituent (at C(4)) see the case of 5-phenylbicyclo[2.2.1]hept-5-en-2-one (a cyclic analog of **30**) [13].

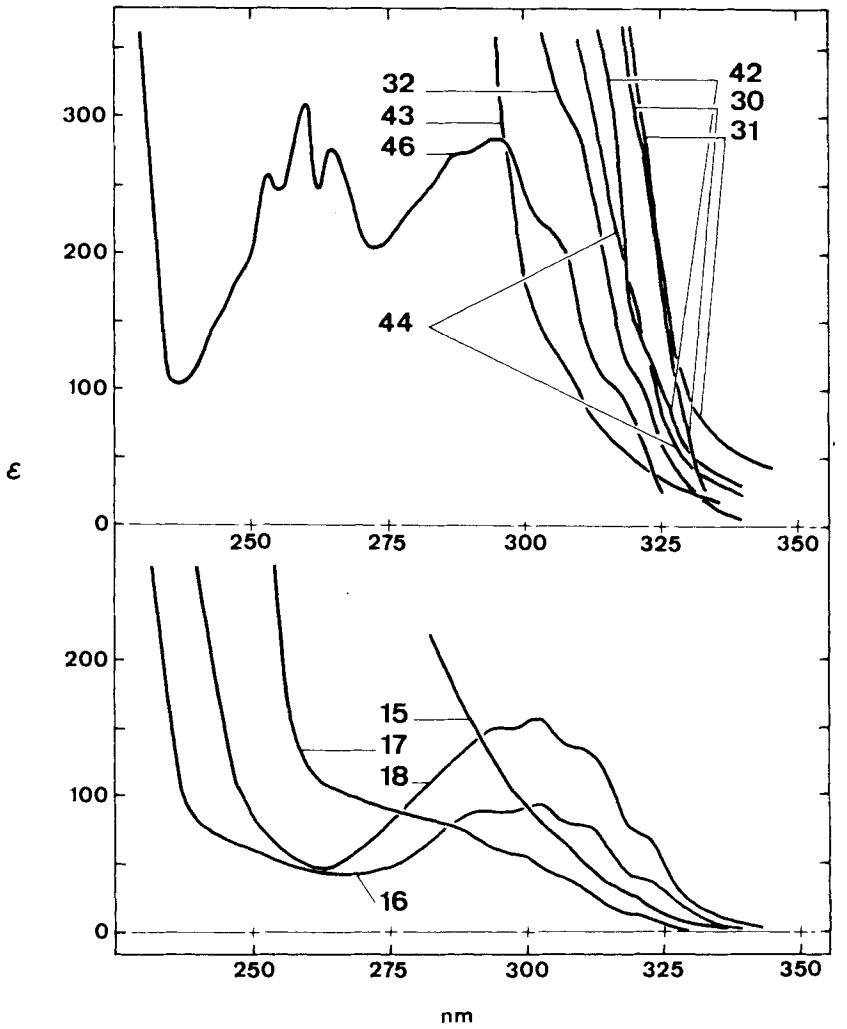
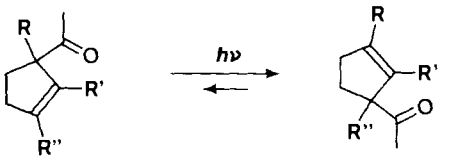


Fig. 1. *UV. Absorption Spectra* (in 2-methylheptane solution)

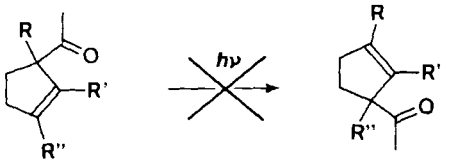
42 and **43** the nonlinear arrangement of ketone and styrene chromophore would be anticipated to be less favorable for homoconjugation (adding to a steric factor in **43** similar to **32**). Finally, a phenyl group (see **46**) is seen to be less important than a double bond **(44)** when both π-systems compete for interaction with the keto group.

Direct Irradiation of Ketones 16, 17, 30–32, 43, and 44-d_3. – Similar to the findings in our initial study of this series *(Scheme 1)*, the direct $n \rightarrow \pi^*$ excitation of the cyclopentenyl ketones **16** and **17** at >300 nm in 2-methylheptane solution at room temperature led to a photostationary equilibrium of the two isomers, with a *ca.* 1:2.3 ratio in favor of the C(1)-unsubstituted ketone **17** *(Scheme 4)*. The phenylcyclopentenyl ketones **30** and **31** on irradiation in benzene disappeared completely,

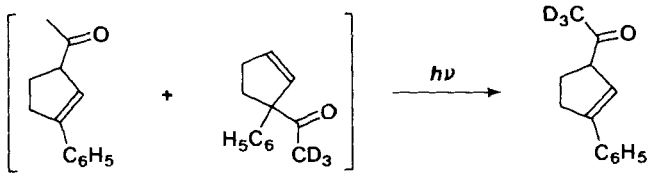
Scheme 4. *Direct Irradiation of Ketones* **16, 17, 30–32, 43,** *and* **44-d$_3$**



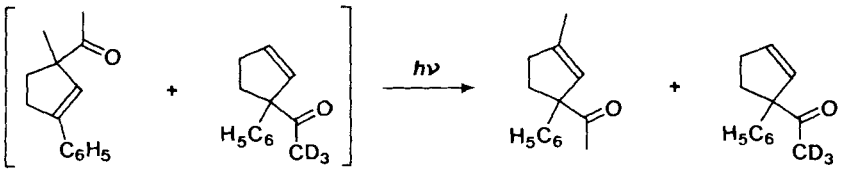
16 . . . . R=R'=CH_3, R''=H . . . **17**
30 . . . R=R'=H, R''=C_6H_5 . . . **44**
31 . R=CH_3, R'=H, R''=C_6H_5 . **45**



32 R=H, R'=CH_3, R''=C_6H_5
43 R=CH_3, R'=C_6H_5, R''=H



30 **44-d$_3$** **30-d$_3$**

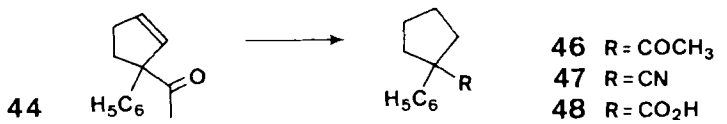


31 **44-d$_3$** **45** **44-d$_3$**

and the 1,3-rearranged products **44** and **45,** respectively, were formed. **32** and **43** gave no detectable products in runs similar to those with **30** and **31.** After irradiation times twice as long as needed for complete isomerization of the latter two, **32** and **43** were still essentially unchanged.

The NMR. spectrum ($CDCl_3$) of **44** shows a singlet at δ 6.1 (in C_6D_6: multiplet at δ 5.8) for the two olefinic protons and multiplets around δ 1.8 (1 H), 2.4 (2 H), and 3.0 (1 H) for the methylene protons. The compound was hydrogenated to the dihydro product **46** which was also obtained by hydrolysis of 1-phenylcyclopentanecarbonitrile **(47)** [14] followed by treatment of the acid **48** with methyl lithium. The structure of **45** was identified by IR. ($\tilde{\nu}_{(CO)}$ = 1715 cm^{-1}) and NMR. data (with an A_3X spectrum at δ 1.80 and 5.60, J = 1 Hz for $H_3C-C=CH$).

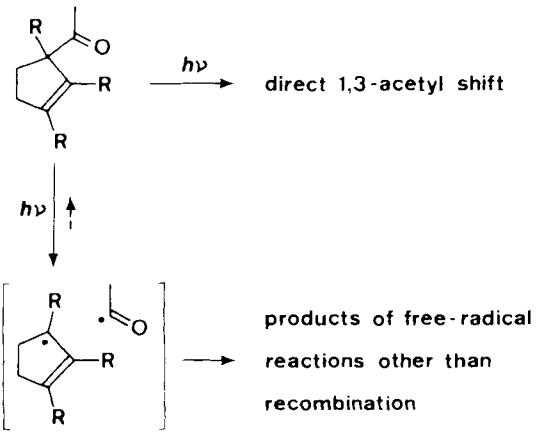
Scheme 5



Upon separate irradiation of **44** under the conditions of its formation no isomerization back to **30** could be observed. The limit for GLC. detection of **30** in this experiment was such that a photostationary equilibrium **30** ⇆ **44** would have to be > 20:1 to remain undetected. The irradiation of a 1:1 mixture of **30** and deuterium-labelled ketone **44**-d_3 at > 300 nm in benzene was designed to uncover the existence of such an equilibrium. After 60% disappearance of **30** the remaining ketone showed admixture of *ca.* 10% **30**-d_3. In the absence of intermolecular acetyl exchange (see below) this result proves the occurrence of the 1,3-acetyl shift **44**-d_3 → **30**-d_3, hence a photostationary equilibrium which is strongly in favor of **44.**

The intramolecular nature of the 1,3-acetyl shift was investigated with another experiment involving a two-component mixture, which now required a label on both the acetyl and the phenylcyclopentene moieties, either combined in one or distributed among both starting materials. The 1,3-acetyl shifts established above for **31** and **44**-d_3 rendered these ketones two such components each being potentially a source of different acetyl and allyl radicals in the mixed photolysis. Irradiation of a 1:1 mixture of **31** and **44**-d_3, isolation by GLC., and MS. analysis of **44**-d_3 and **45** after *ca.* 80% conversion of **31** showed total lack of deuterium scrambling, *i.e.*, **44**-d_3 and **45** had retained the initial isotope distribution, and confirmed the fully intramolecular nature of the 1,3-shift.

It had been shown in the direct photolysis of (+)-methyl 1,2,3-trimethyl-2-cyclopentyl ketone [3] that the intramolecular 1,3-acetyl shift is accompanied by the formation of several low-yield products arising from photolytic α-cleavage (→ **49**) and subsequent free-radical reactions (forming, *e.g.*, trimethylcyclopentenyl dimer), and that acetyl-cyclopentenyl recombination contributes very little at best to



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the 1,3-acetyl rearrangement[6]). The related demethyl compounds **16** and **17** exhibit a similar behavior. The competition of photodecomposition with 1,3-isomerization of these ketones is clearly reflected in the relatively large differences between the quantum yields of consumption and 1,3-rearrangement (Φ(-**16**)–Φ(**17**) and Φ(-**17**)–Φ(**16**); see Table 2, runs 1 and 2)[7]). A similar tendency is also probable in

Table 2. *The Rearrangements of* **16**, **17** *and* **30** *on Direct Irradiation and Triplet Sensitization: Quantum Yields of Disappearance and Product Formation*[a])

Run	Ketone	Sensitizer (E_T, kcal/mol)	Conversion, %	Quantum Yields			
				Φ(-**16**)	Φ(-**17**)	Φ(**16**)	Φ(**17**)
1	**16**[b])[c])	–	6–36	0.52 ± 0.02	–	–	0.14 ± 0.02
2	**17**[b])[c])	–	9–40	–	0.40 ± 0.02	0.06 ± 0.01	–
				Φ(**16**)	Φ(-**17**)	Φ(**51**)[d])	Φ(**57**)
3	**16**[e])	Acetone, neat (*ca.* 78)	16–68	0.28 ± 0.04	–	0.14 ± 0.02	0.04 ± 0.01
4	**16**[b])[e])	0.97M Acetophenone (73.6)	6–24	0.05 ± 0.015	–	0.01 ± 0.002	0.003 ± 0.001
5	**17**[e])	Acetone	13–53	–	0.29 ± 0.03	0.14 ± 0.02	0.04 ± 0.01
6	**17**[b])[e])	0.87M Acetophenone	17–26	–	0.05 ± 0.015	0.01 ± 0.002	0.003 ± 0.001
				Φ(-**30**)	Φ(**44**)	Φ(**53** + **59**)	
7	**30**[c])[f])	–	12–43	0.26 ± 0.03	0.085 ± 0.009	–	
8	**30**[c])	Acetophenone, neat	9–45	0.085 ± 0.009	–	0.020 ± 0.002	
9	**30**[f])[g])	0.10M Benzophenone (68.5)	29–52	0.098 ± 0.01	–	0.035 ± 0.004	
10	**30**[f])[g])	0.01M Thioxanthone (65.5)	7–30	0.084 ± 0.008	–	0.035 ± 0.004	
11	**30**[f])[g])	0.01M *Michler* Ketone (61.0)	17–46	0.083 ± 0.008	–	0.047 ± 0.005	
12	**30**[f])[g])	0.43M β-Acetonaphthone (59.3)	2–13	0.03 ± 0.01	–	–	
13	**30**[f])[g])	0.22M α-Acetonaphthone (56.4)	4–11	0.016 ± 0.005	–	–	

[a]) *Cf.* Exper. Part.
[b]) In 2-methylheptane.
[c]) At 313 nm.
[d]) Lower limit only owing to the photochemical instability of **51**.
[e]) At 254 nm.
[f]) In benzene.
[g]) At 366 nm.

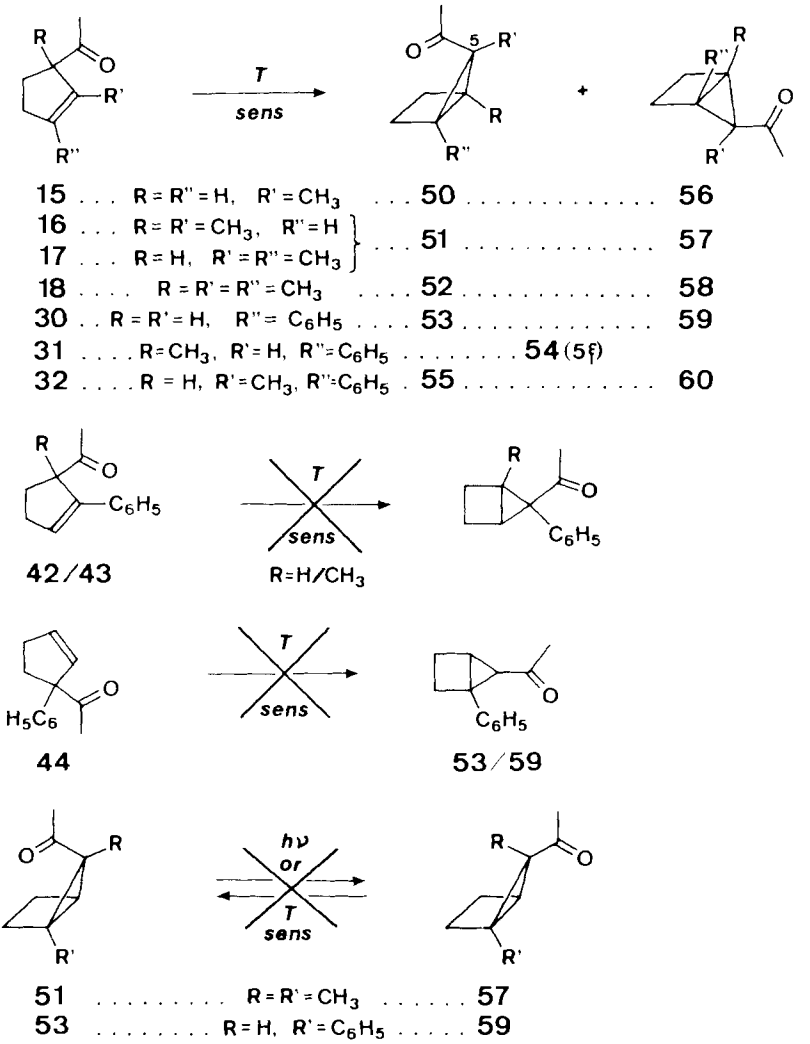
[6]) This is in a marked contrast to the benzoyl-cyclopentenyl radical recombination which accounts for the major reaction path of the photolytic '1,3-benzoyl shift' in the structurally related cyclopentenyl phenyl ketones; *cf.* [6].

[7]) Preliminary results of a photo-CIDNP study indicate that in the photolysis of **16** in benzene acetaldehyde and **17** are formed with enhancement factors V of ≥ 100 and 8 ± 3, respectively (estimated using relaxation times of 30s for CHO and 10s for CH_3). These observations can be attributed to radical pair formation such as **49**. The low value for V of **17** shows, however, that this radical path cannot be very important in the formation of **17** unless the radical pair involved is shorter-lived than 10^{-9} to 10^{-10}s and thus approaches a range of lifetime which renders a distinction between 'radical' and 'nonradical' processes problematic. – We thank Professor *H. Fischer and Dr. B. Blank*, Universität Zürich, for the communication of these unpublished results.

the photolyses of the phenylcyclopentenyl ketones **30** and **31** on the basis of visual observation during irradiation (the solutions slowly turned brown and insoluble material was deposited eventually on the cell walls). The quantum yield difference Φ**(-30)**$-\Phi$**(44)** (Table 2, run 7) indicates that these cleavage reactions are of comparable importance with those in **16** and **17.**

Triplet-sensitized Photolysis of Ketones 15–18, 30–32, and 42–44. – Under triplet-sensitized conditions **15–18** and **30–32** rearranged to 5-bicyclo[2.1.0]pentyl methyl ketones at the expense of the 1,3-acetyl-shifted cyclopentenyl isomers and any other products detectable by GLC. and spectroscopic analysis. When irradiated

Scheme 6. *Triplet-sensitized Photolysis of Ketones* **15–18, 30–32,** *and* **42–44**



in acetone at 254 nm, **15** afforded a mixture of the stereoisomers **50** *(endo)* and **56** *(exo)* in a ratio of *ca.* 3:1 at 5% conversion, and **16** and **17** gave both a *ca.* 7:1 mixture of **51** and **57** under the same conditions. A similar product composition resulted also in an acetophenone-sensitized photolysis of ketone **16.** At prolonged irradiation these products proved somewhat photolabile, with the *endo*-isomers **50** and **51** being destroyed faster although no products of photodecomposition could be isolated so far. In view of this photochemical instability, extrapolation of the observed *endo/exo* ratios to zero conversion should result in an even greater preference for formation of the *endo* isomer in the rearrangement.

The direct formation of both stereosiomeric bicyclopentyl ketones in the triplet ODPM rearrangement of the β,γ-unsaturated precursor was confirmed by various separate irradiations of **51** and **57** which were all carried out at room temperature. They included the conditions of the triplet-sensitized product formation (254 nm in acetone) as well as direct excitations at 208 nm in methanol and pentane solutions, and with the full emission spectrum of a mercury high-pressure lamp in the same solvents and in the gas phase (*cf.* Fig. 2 for the UV. absorption of **51** and **57**). While each ketone underwent slow decomposition to as yet unidentified products, no *endo/exo* isomerization could be observed in any of these experiments and *both endo-* and *exo*-ketones are therefore definitely primary ODPM products.

In the light of this non-stereospecificity a reexamination of this point in our initial study of the cyclopentenyl→bicyclopentyl methyl ketone rearrangement *(Scheme 1)* in which only one stereoisomer of unidentified configuration had been found, appeared desirable. Indeed, repetition of the experiment with *rac* methyl 1,2,3-trimethyl-2-cyclopentyl ketone **(18)** in acetone at 254 nm and GLC. analysis at sufficiently moderate temperature [15] revealed also in this case that *endo-* and *exo*-products (**52** and **58,** respectively) are generated in a $\gtrsim 5:1$ ratio.

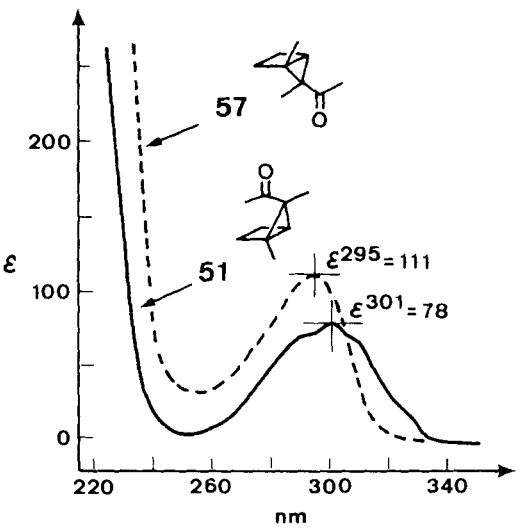


Fig. 2. *UV. Absorption Spectra of* endo **(51)** *and* exo *1,5-Dimethyl-5-bicyclo[2.1.0]pentyl Methyl Ketone* **(57)**

Irradiation of the phenylcyclopentyl methyl ketone **30** in acetone caused disappearance of the compound to an ill-defined mixture of low-yield products. However, upon sensitization with donors in the triplet-energy range of 61–74 kcal/mol (*cf.* Table 2) **30** afforded invariably a *ca.* 3:1 mixture of the *endo*- and *exo*-bicyclopentyl isomers **53** and **59** which again were not interconverted under the conditions of their formation. In acetone and acetophenone **53** and **59** eventually decomposed, and in the presence of benzophenone they remained unchanged. The failure to observe any ODPM product from **30** in acetone appears to be due to sufficiently rapid destruction of **53** and **59** rather than to a lack of rearrangement of **30.**

Sensitization of the methyl homologues **31** and **32** with benzophenone furnished a single 1-methylbicyclopentyl methyl ketone **54** and a 1:1 mixture of the *endo*- and *exo*-5-methyl isomers **55** and **60,** respectively. Attempts to effect acetone-sensitized ODPM rearrangements of **42–44** failed. Even after irradiation times about sevenfold longer than required for complete consumption of **30** in a similar run, these ketones had remained essentially unchanged.

Structure Elucidation of the 5-Bicyclo[2.1.0]pentyl Methyl Ketones **50–60.** The 1,5-dimethyl compounds **51** and **57** have been described previously by *Jorgenson* [16]. The *endo-exo* configuration had been attributed on the basis of an NMR. study of the ethyl ester precursors [8b] [16] [17]. In order to ascertain a definitely unequivocal configurational assignment one of the ethyl 1,5-dimethylbicyclo[2.1.0]-pentane-5-carboxylate isomers **(61)**[8]) was hydrolysed with potassium hydroxide in aqueous methanol to the crystalline acid **62,** m.p. 100°, which on alkylation with methyl lithium afforded in high yield the methyl ketone **57.** An X-ray diffraction analysis of acid **62** established the *exo* orientation of the carboxyl group [18][9]). As a consequence the previous configurational assignment of these esters and methyl ketones [8b] [16] [17] have to be reversed[10]). Inspection of the IR. spectra of **51** and **57** shows that the carbonyl stretching absorptions are at 1708 and 1690 cm^{-1}, respectively (see Table 3). This difference is explicable because in the *endo* orientation the conformation for maximum conjugation between ketone groups and cyclopropane (which is when the C=O plane bisects the three-membered ring [21]) is sterically more hindered as in the *exo* orientation (see formula in *Scheme 6*). The same difference of *ca.* 15 cm^{-1} is exhibited also by the pairs **50/56, 52/58,** and **53/59,** and it is confirmed by a distinct increase in intensity of the UV. 'end absorption' in the *exo*-isomers **56–58** (*e.g.*, $\varepsilon = ca.$ 1600 for **51** and *ca.* 3200 for **57** at 210 nm; *cf.* Fig. 2).

The constitution of the products **53** and **59** was established by synthesis from 1-phenylcyclobutene **(63)** [22]. $CuSO_4$-catalysed reaction with ethyl diazoacetate gave

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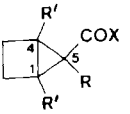
[8]) We thank Professor *Margaret J. Jorgenson* († March 12, 1970) for a sample composed of the ethyl *endo*- and *exo*-1,5-dimethylbicyclo[2.1.0]pentane-5-carboxylates.

[9]) We thank Dr. *D. Hawley,* University of Glasgow, for the communication of the results of the X-ray diffraction analysis.

[10]) The revised configuration is in better accord also with the observations that (i) the sterically less hindered *exo*-ethoxycarbonyl group is more readily hydrolysed with potassium hydroxide (which in fact provides a method to separate the two stereoisomers by selective hydrolysis of the *exo*-ester **61**), and that (ii) in the thermal equilibration of the esters [17] [19] and the ketones [15] [16] the *exo*-isomers (**61** and **57,** respectively) are preferred.

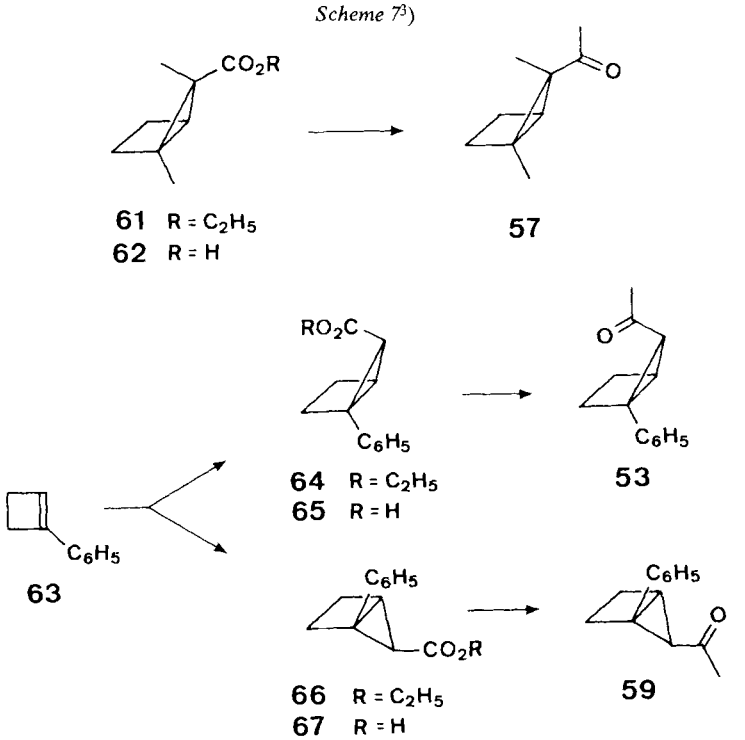
Table 3. *Configurational Assignment of the Methyl 5-Bicyclo[2.1.0]pentyl Ketones* **50–53** *and* **56–59**: *IR. and NMR. Data of These Ketones and of Some Reference Compounds*



Compound	IR. (CCl_4) [cm^{-1}] $\tilde{\nu}$(C=O)	NMR. (CCl_4) [δ] R=CH_3	R'=CH_3
endo/exo	*endo/exo*	*endo/exo*	*endo/exo*
[8b] [17][a])		1.10/1.40	–
[8b] [17]/**61**		1.14/1.30	1.27/1.23
[16] (R=CH_3, R'=H and CD_3, X=OC_2H_5)[b])		1.14/1.30	–
[20] (R=H, R'=H and CH_3, X=CH_3)[c])	1700/–	–	1.30/–
50/56	1705/1690	1.11/1.37	–
51/57	1708/1690	1.17/1.44	1.33/1.14
52/58	1705/1685	[1.09 (3H), 1.13 (6H)]	
53/59	1720/1705	–	–

[a]) Ethyl 5-methylbicyclo[2.1.0]pentane-5-carboxylates.
[b]) Ethyl 1-trideuteriomethyl-5-methylbicyclo[2.1.0]pentane-5-carboxylates.
[c]) Methyl 1-methyl-5-bicyclo[2.1.0]pentyl ketone. – We thank Professor *R. S. Givens*, University of Kansas, for a copy of [20].

Scheme 7[3])



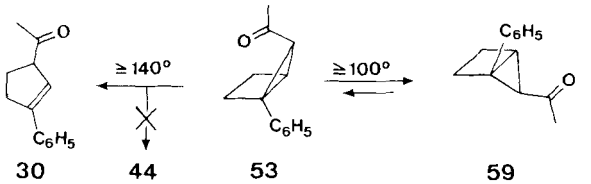
a 2:3 mixture of the *endo*- and *exo*-esters **64** and **66** which could be separated by chromatography. Separate hydrolysis with alkali to the acids **65** and **67** in quantitative yield and alkylation with methyl lithium gave the corresponding methyl ketones **53** and **59** (yields 67% and 48%, respectively). A first contribution to the *endo/exo* assignment gave the NMR. analysis of the two ketones. A shielding effect on the acetyl protons by the *cis*-oriented phenyl group shifts the methyl singlet in the *exo*-compound **59** to δ 1.80 (in contrast to δ 2.18 in the *endo*-isomer **53**). Furthermore, only in **59** the two aromatic *o*-protons were selectively deshielded by the shift reagent $Eu(fod)_3$. This assignment was finally confirmed[11]) in the determination of the molecular structure of the *exo*-acid **67** (m.p. 131°) by an X-ray diffraction analysis by *Bernardinelli et al.* [23].

The constitutions of the methyl homologues **54** and **55/60** have been attributed on the basis of NMR. data only. In particular, the multiplet which appears at δ 3.4 in **32** and is assigned to the proton between the C=O and C=C double bonds, is missing in **55** and **60,** and all three compounds lack any olefinic proton signal.

Dependence of the ODPM Rearrangement on Sensitizer Triplet Energy. Quantum Yields of Reaction. Sensitized irradiations of ketone **16** were carried out using acetone (E_T *ca.* 78 kcal/mol), acetophenone (73.6 kcal/mol), diphenylamine (72 kcal/mol), and benzophenone (68.5 kcal/mol). With the latter two sensitizers, no rearrangement or other products were observed and ketone **16** was recovered unchanged. With acetophenone both the quantum yields of disappearance (Φ**(-16)**) and product formation (Φ**(51)** and Φ**(57)**) were considerably lower than in acetone (Table 2: runs 3–6), and the corresponding quantum yields measured with the isomeric ketone **17** were the same.

The energy range of efficient triplet-sensitizers was considerably wider for the phenylcyclopentenyl methyl ketone **30.** Acetophenone, benzophenone, thioxanthone (E_T 65.5 kcal/mol), and *Michler* ketone (61 kcal/mol) sensitized the ODPM rearrangement to the *ca.* 3:1 mixture of **53** and **59** with all quite similar quantum yields (Φ**(-30)** and Φ**(53+59)**; Table 2: runs 7–11). Only with donor energies of *ca.* 59 kcal/mol and lower (α- and β-acetonaphthones; runs 12 and 13) the product formation vanished completely. Regardless of the failure of the acetonaphthones to sensitize the ODPM rearrangement to **53** and **59,** these compounds persist to destroy **30** although less efficiently than do the sensitizers of higher triplet

[11]) A preliminary investigation showed that also the thermal isomerizations of **53** and **59** are in accord with the expectations based on the configurational assignment. Quite analogously to the results established for **50/56** and **51/57** [15], the *exo* compound **59** predominated in the *endo-exo* equilibrium at 100° in benzene (*cf.* Table 4). The cyclopropyl-allylic rearrangement set in at 140° only and occured at least preferentially from the *endo* isomer **53.** Interestingly, in this case the rearrangement afforded *selectively* the cyclopentenyl ketone **30** only, and no trace of **44** could be detected.



30 44 53 59

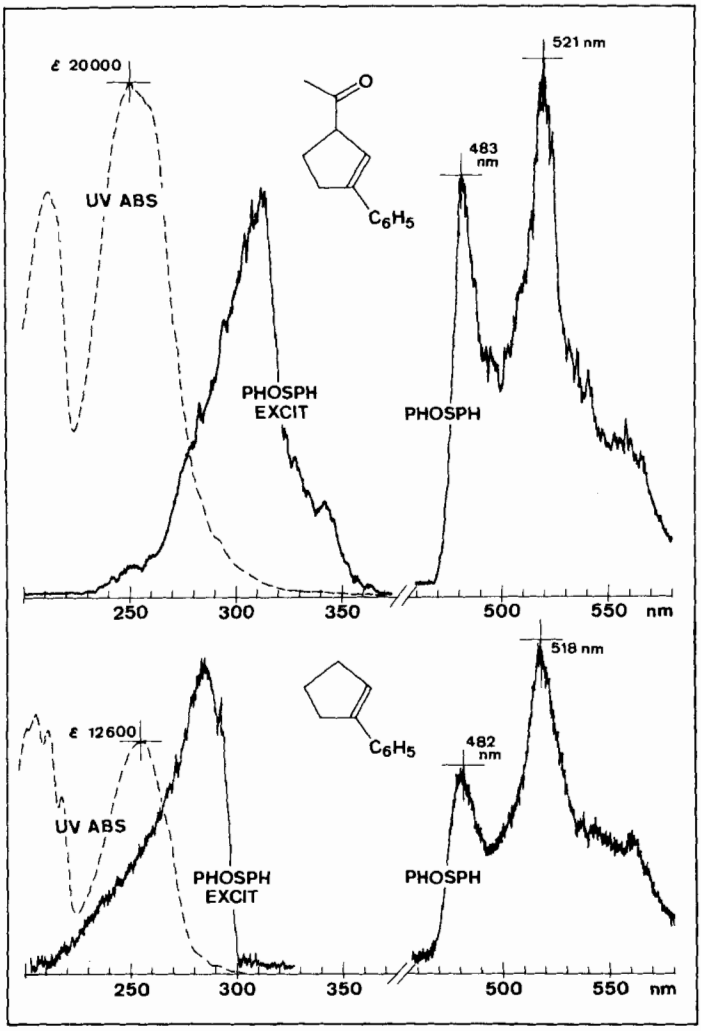


Fig. 3. *Phosphorescence, phosphorescence excitation, and UV. absorption spectra of methyl 3-phenyl-2-cyclopentenyl ketone* **(30)** *and 1-phenylcyclopentene*

energy. This behavior is reminiscent of similar observations by *Engel* [24] with several other β,γ-unsaturated ketones (*cf.* also [25]).

Phosphorescence of Methyl 3-Phenyl-2-cyclopentenyl Ketone **(30).** Ketone **30** exhibited on $n\rightarrow\pi^*$ excitation at 77 K a phosphorescence with a quantum yield $\Phi_p = 0.05 \pm 0.0025$ and a lifetime $\tau_p = 120$ ms. This emission is superimposable in spectral shape and energy (0-0 band at 482–483 nm $\Leftrightarrow$ 59 kcal/mol) with the much weaker phosphorescence of 1-phenylcyclopentene ($\Phi_p = 0.003 \pm 0.0015$, $\tau_p = 625$ ms) (Figure 3)[12]). The excitation spectra of these phosphorescences were in good

[12]) The two compounds were carefully purified by successive column chromatography on silicagel and GLC. prior to the emission study.

agreement with the origins of the UV. absorption of the corresponding compounds. Furthermore, the luminescence of the two substances were measured in both polar and nonpolar glasses, ether/isopentane/ethanol 5:5:2 and 3-methylpentane, and they showed no important difference in the two media.

Discussion. - Both the 1,3-acyl shift and the ODPM rearrangement have been encountered in a large array of β,γ-unsaturated ketones, sometimes competing with other ketone and olefin photoreactions [1] [2]. The structures of these enones range from acyclic to conformationally inflexible compounds in which the bichromophore is rigidly oriented in different arrangements. The characteristic UV. absorption (homoconjugation) is known to provide a sensitive reflection of such geometric differences [26]. These and other structural features can be expected *a priori* to influence any photophysical process, and they may also affect any balance of several mechanistic paths available to a given photochemical β,γ-enone transformation. Such structural dependences appear in fact to contribute to some apparently conflicting findings in this field. *E.g.*, intersystem crossing to the lowest-lying triplet state varies from negligible to unity quantum yields [27]; the 1,3-acyl shift, most frequently occurring on direct irradiation only from an excited state other than the lowest triplet, has occasionally been observed on triplet sensitization [24b] [28], and it proceeds *via* singlet and triplet α-cleavage and free-radical recombination in one extreme [6] and on a strictly intramolecular way in the other (*vide infra* and [28a,b]).

Interpretations of photochemical results with β,γ-unsaturated ketones which resort to analogies must therefore be scrutinized closely - a *caveat* which has only recently been fully recognized [2b,c][13]).

The 1,3-Acetyl Shift on Direct Irradiation. The 1,3-shift observed with **16/17, 30/44,** and **31** occur exclusively on direct irradiation of the ketones, they are intramolecular, and the (albeit preliminary[7])) photo-CIDNP results with **16** indicate that photolytic α-cleavage to a radical pair intermediate (*cf.* **49**) which is at least moderately stabilized is not important. These reactions correspond therefore closely to the process which racemizes the optically active trimethylcyclopentenyl methyl ketone *(Scheme 1).* A unified rationalization within the group of di- and trimethylcyclopentenyl compounds strongly points to a concerted, photochemically symmetry-allowed [30] process (a suprafacial sigmatropic $_{\pi}2+{}_{\sigma}2$ shift; *cf.* transition state **68**) occurring in the lowest singlet excited state[14]). The 'tight-geometry' pericyclic biradical **68** would thus represent a minimum on the S_1 hypersurface - a situation which has been discussed in detail by *Michl* [31]. A stepwise version *via* a ground-state 1,3-bridged biradical (*cf.* intermediate **69**) is a possible alternative. However, steric constraints may prevent that such a species occupies a minimum rather than a non-stabilized geometry point on the S_0 surface[15]), especially so in polycyclic compounds such as **70** and **72** which are related to the cyclopentenyl ketone case insofar as the 1,3-acyl shifts to **71** and **73,** respectively, were found on direct irradiation only and α-cleavage to biradical intermediates has been ruled

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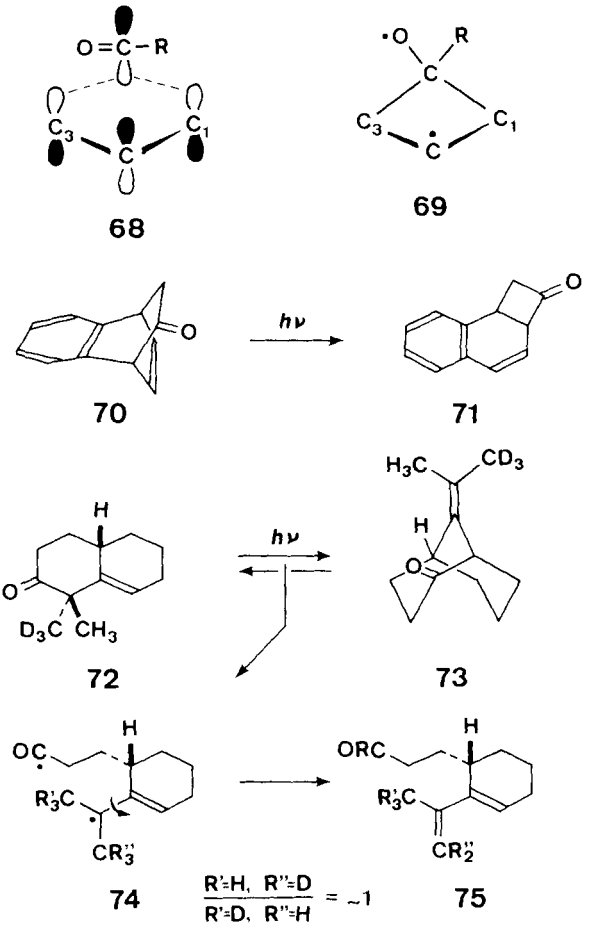
[13]) See also the discussions by *Dalton* and *Schuster & Engel* [29].

[14]) See the Introduction for the arguments in favor of the singlet excited state multiplicity.

[15]) *Cf. Zimmerman* and *Dauben* [32] for the first discussions of the implications of biradical 'intermediates' in terms of ground- and excited-state surfaces.



out in the 1,3-acyl shifts [33] [34][16]). Moreover, formation of an 'open-chain' biradical **(69)** would rather be expected for a triplet process [31] [36].

The *ca.* 2.3:1 preponderance of the less α-substituted ketone **17** in the photostationary equilibrium **16** $\rightleftarrows$ **17** concurs with the tendency of increasing 1,3-acyl shift reactivity of other β,γ-enones with increasing α-methyl substitution [27] [28b] [34a]. When taking **16** $\rightleftarrows$ **17** as the best available reference for the phenylcyclopentenyl system **30** $\rightleftarrows$ **44**, an approximate 1:1 ratio would be expected after correction of the difference in absorptivity ($\varepsilon^{300} \sim 1500$ for **30** and ~ 590 for **44**; *cf.* Fig. 1) and in the absence of any other controlling factors. Furthermore, one

[16]) The latter point is particularly well documented in *Nakanishi*'s example [34a] in which the α-cleavage of the photochemically interconverting enones **72** and **73** to biradical **74** affords aldehyde **75** only. This is shown by the positional scrambling of the deuterium-labelled methyl groups which does not intervene in the equilibrium **72** → **73**[17]).

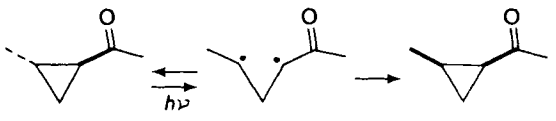
[17]) The stereoequilibration in **74** is interesting in view of the reasonable conformational stability found for other allyl radicals; for literature references see the reviews by *Ingold* and *Kochi* [35].

might naively envisage also an additional increase in reactivity of **44** on the basis of a concerted or α-cleavage mechanism[18]) and the benzylic-allylic attachment of the acetyl group[19]). The strong displacement of the equilibrium toward **44** does not yet satisfy these expectations.

The validity of the universal singlet assignment for the 1,3-acyl shift of β,γ-enones (on direct irradiation) has been reconsidered quite recently in the light of the alternative that reaction may also occur from the $T_2(n,\pi^*)$ state [29] (*cf.* [1b]). The experimental approach employed studies on the structural dependence of rate constants for reaction and decay of singlet excited states [29]. The data show that the $T_2(n,\pi^*)$ route is a possibility but do not discriminate unequivocally from the S_1 mechanism. A similar study with the compounds **16** and **17** would have constituted a valuable additional test. However, we have not detected any fluorescence from these ketones at room temperature[20]).

The Triplet-sensitized ODPM Rearrangement. The sensitized rearrangements of the mono- and dimethylcyclopentyl methyl ketones **15–17** to the bicyclopentyl isomers *(Scheme 5)* conclusively show that the overall structural change involves the 1,2-migration of the acetyl group and bridging of the 5-membered ring rather than a similar endocyclic rearrangement of the cyclopentene skeleton alone. This point had first been established in this series with the sensitized ODPM rearrangement of 1,3-dimethyl-2-ethyl-2-cyclopentenyl methyl ketone to the 5-ethylbicyclopentyl isomer [39], and the finding is of course in accord with all other known examples of ODPM rearrangements including many products with structures which exclude any ambiguity concerning this aspect of the reaction path [1] [2].

The photochemical non-interconvertibility of **51/57** and **53/59,** which establishes the primary nature of the ODPM *endo-exo* product pairs (*cf.* Table 4) has disclosed an unexpected facet of these bicyclopentyl ketones. The result contrasts with the experience that cyclopropyl ketones tend to photoepimerize by cleavage and reclosure of an adjacent cyclopropane bond (*cf.* **76** → **77** [40]). The bicyclopentyl ketones such as, *e.g.*, **51** and **57** would have been anticipated by analogy to interconvert *via* photolytic opening of a lateral cyclopropane bond (*e.g.*, the 1,5-bond to give biradical intermediate **78**), unless rotation around the

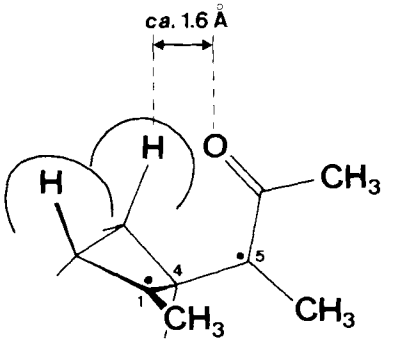


76 **77**

[18]) Note that the tentative elimination of the reaction path *via* an acyl-allyl radical pair[7]) presently lacks any direct experimental foundation for the case **30** ⇄ **44.**

[19]) The carbonyl $^3(n,\pi^*)$ states are generally more reactive toward α-cleavage processes [37]. It is reasonable to assume that the introduction of double bonds and phenyl groups in the β- and β'-positions enhances the reactivity irrespective of the spin multiplicity of the n,π^* state (see, however, the discussion of α-phenyl ketones by *Houk* [2b]).

[20]) Work employing the dioxetane route [38] to study $T_2(n,\pi^*)$ reactivity of β,γ-enones is under way in *Houk*'s and our own laboratories. – We thank Professor *K.N. Houk,* Louisiana State University, for his private communication.



78

remaining lateral bond (C(4)–C(5) in **78**) is sufficiently inhibited to favor reclosure to the starting isomer[21]). Indeed, a *Dreiding* model shows that even the least hindered mode of rotation encounters substantial, and possibly prohibitive steric interactions as indicated in **78**. In the 1-phenyl substituted intermediates from **53** and **59** which lack a methyl group in the α-position to the keto group similarly strong crowding between the acetyl and phenyl group would develop upon rotation around the C(4)–C(5)-bond. An efficient photochemical deactivation of the excited *endo*- and *exo*-bicyclopentyl ketones (accompanied by comparatively low-yield photodecomposition to still unidentified products) at the total expense of a conformational equilibration of the *'endo'* and *'exo'* biradicals may thus account for the failure of these compounds to interconvert.

The more recent mechanistic discussions of the ODPM rearrangements distinguish between concerted paths and a stepwise variation which involves initial bonding between the carbonyl and the β-carbon atoms followed by rearrangement. A concerted mechanism has *a priori* the option of two photochemically allowed stereoisomeric paths, ${}_{\sigma}2_a+{}_{\pi}2_a$ and ${}_{\sigma}2_s+{}_{\pi}2_s$ cycloadditions [30], barring the exclusion of one of these modes for structural reasons. The former path constitutes an *anti*-disrotatory cyclization-migration process, and the latter the *syn*-disrotatory alternative[22]). The *syn*-disrotatory reaction would probably be less favorable than

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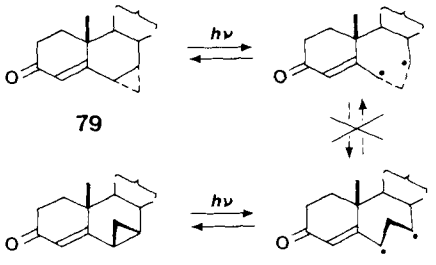
[21]) Another example suspected of such a photostabilization by ring fission-reclosure without epimerization at the centres of cleavage has recently been verified experimentally, namely by the non-interconvertibility of the vinyl-homologous cyclopropyl ketones **79** and **80** [41]. – We thank Dr. *G.R. Lenz*, Searle Laboratories, for the communication of his unpublished results.



79 80

[22]) See [42] for the introduction of the *anti*- and *syn*-disrotatory orbital geometry terminology.

the *anti*-process for geometric reasons in the transition state. Both would be required, however, in order to explain a concerted formation of *endo* and *exo* ODPM products from each of the ketones **15–18** and **30** (Table 4), with a preference for the *anti*-disrotatory path and *endo* formation in all cases.

Table 4. Endo/exo *Ratios of Methyl Bicyclo[2.1.0]pentyl Ketones Obtained by Photorearrangement and by Thermal Stereoequilibration*

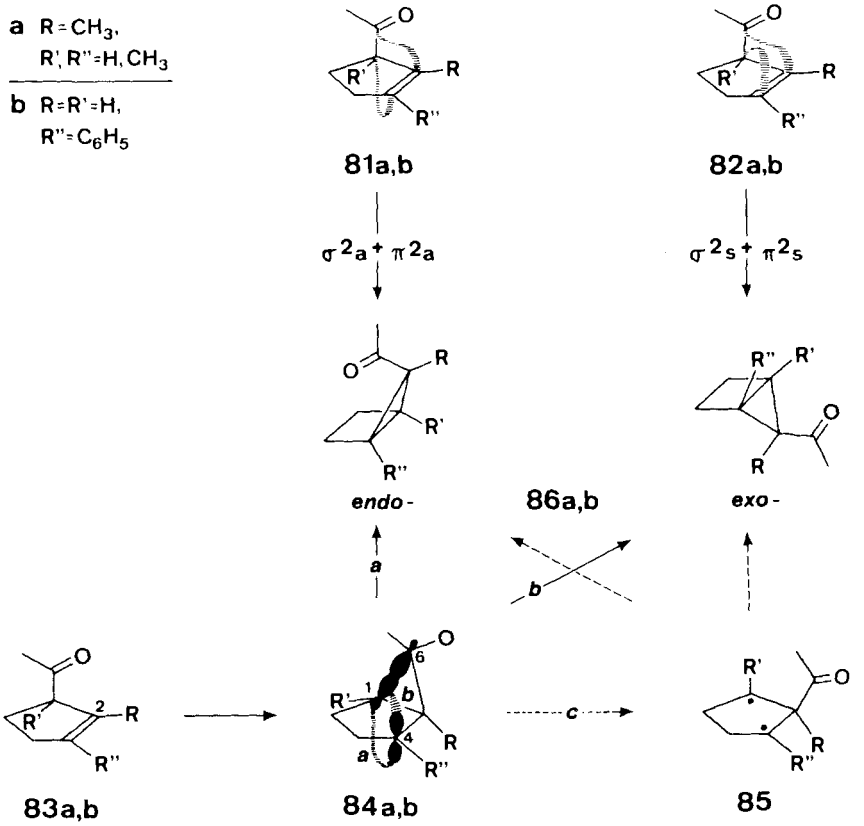
Compounds *(endo/exo)*	*Endo/exo* Ratio	
	by Photorearrangement	by Thermal Equilibrium
50/56	$\gtrsim 3:1$[a])	$1:3.8\pm0.2$[d])
51/57	$\gtrsim 7:1$[a])[b])	$1:1.9\pm0.1$[d])
52/58	$\gtrsim 5:1$[a])	$1:\sim 2.5$[e])
53/59	$\sim 3:1$[c])	$1:\geq 10$[f])
55/60	$\sim 1:1$[c])	not determined

[a]) At 5% conversion in acetone-sensitized photolysis of **15, 16** and **17,** and **18,** respectively.
[b]) Same result also with acetophenone sensitization; *cf.* also Table 2, runs 3–6 and footnote d).
[c]) Estimated by NMR. analysis of the crude mixtures after full photochemical conversion of **30** and **32,** respectively (sensitizers for **30:** acetophenone, benzophenone, thioxanthone, and *Michler* ketone; for **32:** benzophenone).
[d]) Equilibrium calculated from first-order rate constants of stereomutation in benzene at 160–220° (**50**) and 170° (**51**) given in [15], Table 2.
[e]) Pseudoequilibrium estimated from NMR. plots of product composition (**18**+**52**+**58**; *cf.* [3] [15]) *vs.* time using 0.2M solutions of **52** and **58** in hexachlorobutadiene at 120°.
[f]) Estimated by NMR. analysis of the crude mixture after thermal equilibration at 100° in benzene-d_6.

Yet, a mechanistic interpretation in terms of non-concerted processes *via* the intermediate cyclopropyloxy-cycloalkyl biradicals **84** – formal two-step equivalents to the $_\sigma 2 + _\pi 2$ cycloaddition paths – is just as satisfactorily reconciled with the stereochemical results. In this mechanism, bonding between the carbonyl carbon atom and C(2) in **83** occurs in the primary step. The predominant formation of *endo*-**86** from the ketones **83a** would then result from inversion at C(1) by backside radical displacement of C(6) by C(4) in the biradicals **84a** (path *a*), *i.e.*, cleavage of the 3-membered ring by concomitant *anti*-disrotatory cyclization. Alternatively, the minor *exo*-products **86** would be accessible by retention of configuration at C(1) in a *syn*-disrotatory process (path *b*). Furthermore, non-assisted opening of the cyclopropane C(1)–C(6)-bond in **84a** and crossing over to localized biradicals of type **85** (path *c*) should also result in a kinetically controlled *endo-exo* product mixture **86** the composition of which is difficult to anticipate but, barring a coincidence, would differ from the thermodynamically equilibrated ratio (*cf.* Table 4)[23]). A greater preference for path *c* seems a reasonable *a priori* possibility in the case of the phenyl-substituted ketone **30.** Primary bonding **(83a → 84b)** could afford here a cyclopropyloxy-cycloalkyl biradical in which ring opening to 2-acetyl-1-phenyl-

[23]) Work is presently in progress which is designed to generate biradicals of type **85** *via* an independent route, and which may eventually differentiate between paths *a/b* and *c*.

Scheme 8. *Possible Mechanisms of the ODPM Rearrangement of* **15–18** *and* **30**



cyclopentane-1,3-diyl (**85**) would profit from both the restitution of a carbonyl group and the benzyl resonance stabilization of one radical site[24]).

Our results then do not distinguish between concerted and stepwise paths for the ODPM rearrangement to the bicyclopentyl ketone – a question which has been resolved only for the cases of the cyclohexenone **87** [44] and the phenylpentenone **90** [45]. In the former example the configurational outcome (see *Scheme 9* and Table 5) establishes unequivocally a stepwise mechanism for the major product (**89**), and in both cases concerted mechanisms are at best acceptable as less important processes only competing with the stepwise paths[25]).

The Nature of the ODPM-reactive Triplet State. A variety of results suggests that the excited state responsible for the ODPM rearrangement is best described as an alkene $T(\pi,\pi^*)$ state [2]. This conclusion finds theoretical support by *Houk*'s

[24]) For the evidence in favor of this path in the ODPM-type triplet rearrangement of an α,β-unsaturated δ-diketone see [43].

[25]) Retention and inversion of configuration at the α-carbon atom ('methane carbon atom'), either exclusively or concurrently, have been observed previously [43] [46]. For a critical evaluation of apparent preferences [46b] [47] for a concerted $_\sigma2+{}_\pi2$ path see [1b] [2b] [45].

Scheme 9. *ODPM Rearrangements Occurring via a Stepwise Mechanism*

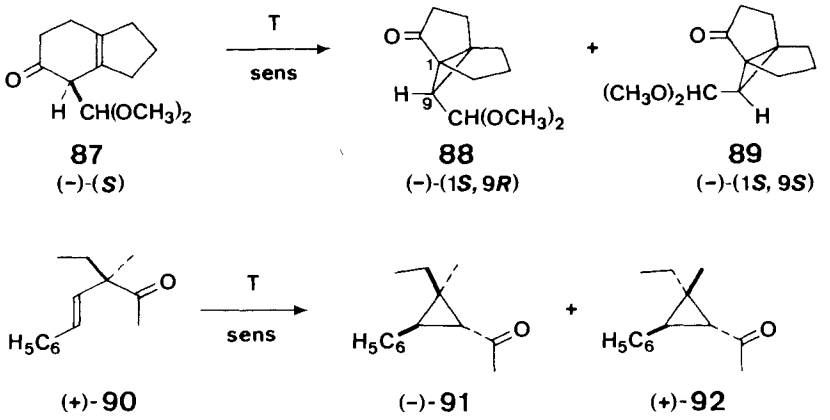


Table 5. *Product Distribution and Enantiomeric Purities in the ODPM Rearrangement of* **87** [44] *and* **9(** [45]

	87	**88**	**89**	**90**	**91**	**9**
Product ratio		1	~ 2		1.2	1
Enantiomeric purity, %						
before rearrangement	54			> 90		
after rearrangement	42	48	48	~ 80	10	

MO approach [48] which complements *Michl*'s 'loose' *vs.* 'tight' biradical geometry generalization [31]. Thus, CNDO/S calculations indicate that a lowest π,π^* triplet of β,γ-enones should strongly increase the C(CO)–C(β)-bond order and decrease the C(β)–C(γ)-bond order. These changes predict precisely the ODPM bonding changes observed[26]). However, the conclusion that the lowest triplet excitation energy of ODPM-rearranging β,γ-enones is indeed localized in the olefinic portion has still been awaiting direct experimental confirmation[27]).

Within the cyclopentenyl ketone class the only previous phosphorescence data have been available from the phenyl and 4-methoxyphenyl 1,2,3-trimethyl-2-cyclopentenyl ketones ($E_T = 74$, $\tau = 5.5$, and $E_T = 70$ kcal/mol, $\tau = 105$ ms, respectively; at 77K in ether/isopentane/ethanol 5:5:2) [6][27]). The spectral shapes, energies and mean lifetimes show that the excitation in both of these lowest-lying

[26]) *Schuster & Underwood*'s model based on spin polarization assumes the n,π^* configuration of the ODPM-reactive triplet state; *cf.* the comprehensive discussion in the review by *Houk* [2b].

[27]) Phosphorescences from several β,γ-enones in rigid glasses at 77K have been reported and they were interpreted in terms of the lowest-lying T(π,π^*) states of these compounds [49]. However, in three cases these have recently been shown [24] to be impurity emissions, and the data of some other of these ketones may warrant reinspection. We have observed luminescences reminiscent of those reported [49] from **16, 18,** 1,3-dimethyl-2-ethyl-2-cyclopentenyl methyl ketone, and they have now also been traced to impurities.

n,π^* triplet states is localized in the aroyl moiety, and these compounds undergo α-cleavage rather than ODPM rearrangement [6].

The absence of sensitization by donors of $E_T = 72$ kcal/mol and lower, and the reduced quantum yield of sensitization by acetophenone (Table 2, runs 4 and 6) place the ODPM-rearranging triplet of the methyl ketones **16** and **17** in the energy range of about 72–73 kcal/mol. This figure corresponds reasonably well with the value of 76 kcal/mol given by *Schexnayder & Engel* for the 'vertical' π,π^* (planar alkene) triplet [24b].

Dauben [50] had made the qualitative observation that the ODPM rearrangement of a β,γ-unsaturated γ-phenyl ketone similar to **90** *(Scheme 9)* proceeds with sensitizers possessing triplet energies as low as 56 kcal/mol, *i.e.*, energies which are definitely below the estimated range of the n,π^* triplet level [24a]. With **30** we have complemented the group of cyclopentenyl ketones with a compound possessing a similar styrene-like chromophore. Twisting around the double bond is prohibited in the five-membered ring of **30**, and its 'pure' styrene π,π^* triplet energy should therefore be only slightly below the spectroscopic $S_0 \rightarrow T_1$ transition energy measured for styrene by absorption under high pressure of oxygen (61.7 kcal/mol [51]). This expectation was met by experiment. The energy range of triplet donors capable of sensitizing the ODPM rearrangement extended down to 61 kcal/mol, with the quantum efficiency for product formation dropping to zero at sensitizer energies of 59 kcal/mol and less (Table 2, runs 8–13).

Confirmation that this energy level coincides with a $T(\pi,\pi^*)$ state of **30** came forth from the 0–0 band at 59 kcal/mol of its phosphorescence at 77 K[28]), and the comparison with the emission of the parent styrene system, 1-phenylcyclopentene, shows that the lowest triplet of **30** is indeed the essentially unperturbed styrene $T(\pi,\pi^*)$ state[29]).

The observation of phosphorescence at 77 K despite the lack of ODPM product formation at room temperature on direct excitation of **30** is unexpected. In fact, the ratio of the phosphorescence quantum yields of 1-phenylcyclopentene and **30** is of the same magnitude as the $S \rightarrow T$ intersystem crossing quantum yield reported for the hydrocarbon ($\Phi_{isc} = 0.1$ [54]). Φ_{isc} of **30** must therefore be close to unity at 77 K[30]). On the other hand, no detectable amount of any photoproduct was formed when **30** was irradiated for prolonged periods at 77–173 K and > 300 nm. This sug-

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[28]) Note that the triplet energy data given here have all been measured in rigid glasses at low temperature. In fluid solution at room temperature these values tend to be lower by a few kcal's (*cf.* [52]). It is possible, therefore, that **30** is marginally higher in triplet energy than β-acetonaphthone under the conditions of sensitized irradiation.

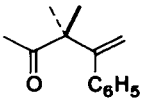
[29]) Relaxation of the double bond in the perpendicular conformation inhibits radiative deactivation of triplet styrene. The lower energy of this twisted geometry accounts presumably for the successful sensitization of acyclic γ-phenyl-β,γ-enones with donors of triplet energies as low as 56 kcal/mol such as reported by *Dauben* [50]. The ring constraints of 1-phenylcyclopentene prevent a similar geometrical change and at the same time facilitate the decay by way of phosphorescence; *cf.* also the emission studies of other ring-constrained styrene-type systems such as indene and related structures [53].

[30]) Intersystem crossing may profit from the predominance of a ground-state conformation of **30** with a pseudoequatorial acetyl group retarding α-cleavage owing to the unfavorable geometry for assistance from allylic resonance.

gests that there are small energy barriers for both the 1,3-acetyl migration and the ODPM rearrangement, and that the competition between the rates of the 1,3-shift and the population of the $T(\pi,\pi^*)$ state turns in favor of the latter at low temperature (irrespective of the spin multiplicity of the 1,3-shift process). A revertible (energy-waisting) initial step towards triplet product formation such as C(CO)–C(β) bonding and relapse to starting material *(cf.* **83** ⇄ **84**, *Scheme 8)* possibly contributes to the reduction of phosphorescence lifetimes of ketone **30** by a factor of *ca.* 5.

The Photochemistry of the Phenylcyclopentenyl Ketones **31**, **32**, *and* **42–44.** The goal for the inclusion of **31** and **32**, which are methyl homologues of the 3-phenylcyclopentenyl portion of **30**, into our investigation was primarily to search for a suitable second component in the mixed experiment with **44**-d_3 *(Scheme 4).* While the 1-methyl compound **31** reacted in the envisaged manner (→ **45**) and thus served to establish the intramolecular nature of the 1,3-shift **30** ⇄ **44**, the 2-methyl isomer **32** failed – as yet unexplicably – to undergo this reaction on direct irradiation. The benzophenone-sensitized ODPM rearrangements of **31** (→ **54**) and **32** (→ **55** + **60**) are again in general accord with expectation. In the absence of further experimentation it appears premature to assess the significance of the stereoisomeric product composition formed in the two reactions.

The altogether negative results with the 2-phenylcyclopentenyl ketones **42** and **43** parallel in part and supplement the observation that the acyclic 'cross-conjugated' analog **93** is unreactive on triplet sensitization[31]). A 1,3-acetyl shift on direct



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irradiation might have been expected to be particularly favored through a bridged biradical (*cf.* **69**) path where the C(2) radical profits from benzylic stabilization. Such is, however, not the case for **43** barring the (unchecked) possibility that the reverse shift process should be strongly predominant. A similar argument with respect to triplet C(CO)–C(β) bonding would disfavor the ODPM reaction (and this time in accordance with the behavior of **42** and **43**) in view of the greater π-conjugative sacrifice in the step **83b** → **84b** than in **83a** → **84a** *(Scheme 8).* Finally, there remains still another problem unresolved with the failure of triplet 1-phenylcyclopentenyl ketone **44** to furnish the ODPM products **53** and **59.**

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[31]) Unpublished results by *Dauben et al.; cf.* [2c].

Experimental Part

Unless specified, *work-up* involved extraction of the crude reaction mixture with ether, washing with H_2O or satd. aqueous NaCl-solution, drying over anhydrous $MgSO_4$, and removal of the solvent in a rotary evaporator. – *Boiling* and *melting point* (b.p., m.p.) data are not corrected. – *Gas liquid chromatography:* on *Perkin-Elmer* 900 and 990 chromatographs. Capillary column (C-GLC.): 0.01″× 150′, carbowax 1540, 2 ml He/min, flame ionization detector. Packed columns (GLC.): 3/8′× 10′ and 1/4× 10′, 2% SE-30 on chromosorb G AW/DMCS (2% SE), 15% SE-30 on chromosorb W HP (15% SE), 15% carbowax 20M on chromosorb P AW/DMCS (CW), 70–150 ml He/min, flame ionization or hot-wire detector. The column temperature is added to the column specification. Electronic peak integration: *Infotronics* CRS-208 integrator with automatic baseline correction. – For *thin-layer chromatograms* (TLC.) *Merck* Fertigplatten F_{254} (silica gel) were used. The spots were located by fluorescence and by treatment with conc. H_2SO_4 and heating. – *Preparative chromatography* was carried out on silica gel *Merck* (0.05–0.2 mm) in columns with decreasing diameter. – *UV. spectra:* in 2-methylheptane unless specified; λ_{max} in nm, ε in parantheses. – *IR. spectra:* in CCl_4 unless specified; λ_{max} in cm^{-1}; *s* = strong, *m* = medium, and *w* = weak band intensity. – *NMR. spectra:* 100 MHz; chemical shifts in δ, coupling constants *(J)* in Hz; br. = broad, *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quadruplet, *m* = other than first-order multiplet. – *Mass spectra* (MS.): base peak in *italics*. – Abbreviations: RT. = room temperature.

Synthesis of the Ketones 15–18, 30–32, 42, 43, 44-d_3, 46, 53, 57, and 59 ***(Schemes 2, 3, 5, and 7)***[3]. – *Methyl 2-methyl-2-cyclopentenyl ketone* **(15).** 35.5 g of a *ca.* 8:1 mixture of ethyl *(E+Z)*-3-cyclopropyl-2-butenoate **(1)** [7] [8] were stirred overnight at RT. in $KOH/CH_3OH/H_2O$ 2:5:5, followed by heating under reflux for 2 h. The mixture was extracted with ether to remove unreacted ester, then acidified with 2N HCl and worked-up. Crystallization from ether/hexane gave 21.5 g (72%) of (E)-*3-cyclopropyl-2-butenoic acid* **(2);** m.p. 101–102°. – IR.: 1620*s*, 1690*s*, 2500–3520 br. – NMR. (CCl_4): 0.6–0.9 (*m*, 2H–C(2′), –C(3′)); 1.5 (*m*, H–C(1′)); 2.00 (*d*, *J*(2,4) = 1.5, 3H–C(4)); 5.6 (br., H–C(2)). – MS.: 126 ($C_7H_{10}O_2^+$), 125, 111, *98*, 81.

18.3 g (0.145 mol) of *(E)*-**2** were methylated with 0.3 mol of CH_3Li in 750 ml of boiling ether for 3 h. The mixture was then poured onto aqueous NH_4Cl solution/ice and worked-up. Distillation of the crude product gave 10 g (56% yield) of (E)-*4-cyclopropyl-3-penten-2-one* **(7),** b.p. 73°/12 Torr. – UV.: 248 (13000), 327 (54). – IR.: 1600*s*, 1680*s*, 3080*w*. – NMR. (CCl_4): 0.6–1.0 (*m*, 2H–C(2′), –C(3′)); 1.5 (*m*, H–C(1′)); 1.90 (*d*, *J*(3,5) = 1.5, 3H–C(5)); 2,05 (*s*, 3H–C(1)); 6.05 (br., H–C(3)). – MS.: 124 ($C_8H_{12}O^+$), 123, 109, *96*, 81, 43.

A *ca.* 3% solution of *(E)*-**7** in benzene (100 ml/h) was passed in a N_2 stream (25 ml/min) through a quartz column filled with quartz *Raschig* tubes and heated to 350–380°. The conversion was complete (C-GLC.: 100°). Distillation of the crude product gave a 70% yield of **15,** b.p. 67°/20 Torr. – UV.: see Fig. 1. – IR.: 1690*m*, 1715*s*, 3050*w*. – NMR. (CCl_4): 1.5–2.4 (*m*, 2H–C(4), –C(5)); 1.70 (*s* with fine structure, H_3C–C(2)); 2.00 (*s*, H_3C–CO); 3.3 (*m*, H–C(1)); 5.5 (br., H–C(3)). – MS.: 124 ($C_8H_{12}O^+$), *81*.

1,2-Dimethyl-2-cyclopentenyl methyl ketone **(16).** a) A *Grignard* reaction of 5 g (29 mmol) of ethyl 1-methyl-2-oxo-cyclopentanecarboxylate **(10)** [9] with CH_3MgI (prepared from 0.7 g (29 mg-atom) of Mg and 4.1 g (29 mmol) of CH_3I) in 120 ml of ether was carried out by heating 1 h under reflux and stirring 4 h at RT. The mixture was then poured into satd. aqueous NH_4Cl-solution and worked up to give 5.2 g of a mixture (GLC.: 2% SE, 150°) of 16% of **10** and 84% (80% yield) of *ethyl 2-hydroxy-1,2-dimethyl-cyclopentanecarboxylate* **(11).** An analytical sample of **11** was collected by GLC., b.p. 48°/0.15 Torr. – IR.: 1720*s*, 3500 br. – NMR. (CCl_4): 1.14, 1.18 (2*s*, H_3C–C(1), –C(2)); 1.25 and 4.10 (*t* and *qa*, *J* = 7, CH_3CH_2O). – MS.: 186 ($C_{10}H_{18}O_3^+$), 171, 141, *112*.

The dehydration of 10 g of the mixture **10** and **11** with 1 g of *p*-toluenesulfonic acid in 350 ml of boiling benzene and with continuous azeotropic removal of H_2O was complete after 14 h (TLC.: benzene/ether 5:1). Aqueous $NHCO_3$-solution was added and the mixture worked up. Distillation of the crude product gave 6.1 g (87%) of *ethyl 1,2-dimethyl-2-cyclopentenecarboxylate* **(12),** b.p. 78–82°/15 Torr. – IR.: 1725*s*, 3020*w*. – NMR. (CCl_4): 1.22 (*s*, H_3C–C(1)); 1.22 and 4.05 (*t* and *qa*, *J* = 7, CH_3CH_2O); 1.65 (*d*, *J* = 1.5, H_3C–C(2)); 5.4 (br., H–C(3)). – MS.: 168 ($C_{10}H_{16}O_2^+$), *95*.

The hydrolysis of **12** (for the procedure see **1** → **2**) gave *1,2-dimethyl-2-cyclopentenecarboxylic acid* **(13),** b.p. 75°/0.1 Torr. – IR.: 1690*s*, 2500–3500 br. – NMR. ($CDCl_3$): 1.30 (*s*, H_3C–C(1)); 1.72 (*d*, *J* = 1.5, H_3C–C(2)); 5.5 (br., H–C(3)). – MS.: 140 ($C_8H_{12}O_2^+$), 125, *95*.

The methylation of **13** with CH_3Li (for the procedure see **2**→**7**) afforded **16** in 75% yield, b.p. 56°/12 Torr. – UV.: 202 (4000), 300 (101; see Figure 1); in C_2H_5OH: 295 (102). – IR.: 1655*w*, 1705*s*, 3040*w*. – NMR. ($CDCl_3$): 1.18 (*s*, $H_3C-C(1)$); 1.58 (*d*, *J*=2, $H_3C-C(2)$); 2.08 (*s*, H_3C-CO); 5.52 (br., H–C(3)). – MS.: 138 ($C_9H_{14}O^+$), 123, *95*.

b) Compound **16** was also prepared using the reaction sequence described for **1**→**15** and starting with an *(E+Z)* mixture of ethyl 3-cyclopropyl-2-methyl-2-butenoate (**3**) [8]. The overall yields of the two syntheses were similar (*ca.* 25%). Method b) involved the following intermediates:

(E+Z)-*3-Cyclopropyl-2-methyl-2-butenoic acids* (**4**), m.p. 65–68°. – IR.: 1600*m*, 1675*s*, 2500–3500 br. – NMR. (CCl_4): 0.5–0.9 (*m*, 2H–C(2′), –C(3′)); 1.46 (*s*, $H_3C-C(2)$ of *(Z)*); 1.76 (*s* with fine structure, $H_3C-C(2)$ of *(E)*); 1.93 (*s*, 3H–C(4) of *(Z)*); 2.03 (*qa*, *J*=2, 3H–C(4) of *(E)*). – MS.: 140 ($C_8H_{12}O_2^+$), 135, *112*, 95.

(E+Z)-*4-Cyclopropyl-3-methyl-3-penten-2-ones* (**8**), b.p. 95–100°/18 Torr. – UV.: 250 (21000), 314 (238). – IR.: 1600*w*, 1685*s*, 3080*w*. – NMR. (CCl_4): 0.3–1.0 (*m*, 2H–C(2′), –C(3′)); 1.40 (*s*, $H_3C-C(3)$ of *(Z)*); 1.46 (*s* with fine structure, $H_3C-C(3)$ of *(E)*); 1.76 (*s*, 3H–C(5) of *(Z)*); 1.93 (*qa*, *J*=2, 3H–C(5) of *(E)*); 2.13, 2.23 (2*s*, 3H–C(1)). – MS.: 137 ($C_9H_{14}O^+ - 1$), 123, *110*, 95, 81.

2,3-Dimethyl-2-cyclopentenyl methyl ketone (**17**). The hydrolysis (for the procedure see **1**→**2**) of ethyl *(E)*-3-(1-methylcyclopropyl)-2-butenoate (**5**) [8] furnished after crystallization from hexane and sublimation at 60°/760 Torr (E)-*3-(1-methylcyclopropyl)-2-butenoic acid* (**6**) in 95% yield, m.p. 88–89°. – IR. ($CHCl_3$): 1620*s*, 1640*s*, 1685*s*, 2400–3520 br. – NMR. (CCl_4): 0.5–0.9 (*m*, 2H–C(2′), –C(3′)); 1.25 (*s*, $H_3C-C(1')$); 2.08 (*d*, *J*(2,4)=1.5, 3H–C(4); 5.73 (*qa*, H–C(2)). – MS.: 140 ($C_8H_{12}O_2^+$), 125, *112*.

(E)-**6** was methylated with 2.2 mol.-equ. of CH_3Li at RT. overnight, followed by heating under reflux for 1 h. Addition of satd. aqueous NH_4Cl-solution, work-up and distillation of the crude product gave (E)-*4-(1-methylcyclopropyl)-3-penten-2-one* (**9**) in 88% yield, b.p. 68°/12 Torr. – NMR. (CCl_4): 0.45–0.85 (*m*, 2H–C(2′), –C(3′)); 1.20 (*s*, $H_3C-C(1')$); 1.96 (*d*, *J*(3,5)=1.5, 3H–C(5)); 2.08 (*s*, 3H–C(1)); 6.05 (*q*, H–C(3)). – MS.: 138 ($C_9H_{14}O^+$), *110*.

The pyrolysis (for the procedure see **7**→**15**) of *(E)*-**9** gave **17** in 60% yield. – UV.: see Fig. 1. – IR.: 1705*s*. – NMR. (CCl_4): 1.5, 1.8 (2*s*, $H_3C-C(2)$, –C(3)); 2.00 (*s*, H_3C-CO); 3.4 (*m*, H–C(1)). – MS.: 138 ($C_9H_{14}O^+$), *95*.

Methyl 1,2,3-trimethyl-2-cyclopentenyl ketone (**18**). The methylation of 1,2,3-trimethyl-2-cyclopentenecarboxylic acid (**14**) [9] (for the procedure see **6**→**9**) afforded **18** in 80% yield, b.p. 68–70°/12 Torr. – UV. (see Fig. 1): 300 (151). – Identification by comparison with *(R)*–(+)-**18** [9] by IR. and NMR.

Methyl 3-phenyl-2-cyclopentenyl ketone (**30**). 61.0 g (0.23 mol) of triethyl phosphonoacetate were added dropwise to a suspension of 5.5 g (0.23 mol) of NaH in glyme at RT. When the evolution of H_2 had stopped 25.0 g (0.12 mol) of (1-phenylcyclopropyl)methanal (**19**) [55] were added dropwise. The mixture was heated under reflux for 2 days. Work-up and distillation of the crude product gave 18.1 g (50%) of *ethyl* (E)-*3-(1-phenylcyclopropyl)-2-propenoate* (**21**), b.p. 85°/0.08 Torr. – UV.: 225 (6500); see Figure 1. – IR.: 1720*s*. – NMR. (CCl_4): 1.05 (*m*, 2H–C(2′), –C(3′)); 1.23 and 4.35 (*t* and *q*, *J*=7, CH_3CH_2O); 5.18, 6.60 (2 *d*, *J*=15, H–C(2) and –C(3), resp.); 7.18 (*s*, 5 arom. H). – MS.: 216 ($C_{14}H_{16}O_2^+$), 188, *143*.

3.0 g of *(E)*-**21** were stirred in a 1:1 mixture of 20% methanolic KOH solution and H_2O at RT. until a homogeneous solution was formed. After acidification with 10% H_2SO_4 solution and work-up, crystallization of the crude product from CH_2Cl_2/hexane gave 1.9 g (73%) of (E)-*3-(1-phenylcyclopropyl)-2-propenoic acid* (**22**), m.p. 134°. – IR. ($CHCl_3$): 1638*m*, 1695*s*, 2500–3500 br. – NMR. ($CDCl_3$): 1.26 (*m*, 2H–C(2′), –C(3′)); 5.27, 5.75 (2 *d*, *J*=15, H–C(2) and –C(3), resp.); 7.28 (*s*, 5 arom. H). – MS.: 188 ($C_{12}H_{12}O^+$), *143*, 128.

A higher yield of *(E)*-**22** was obtained in a *Doebner* condensation: 4.3 g (42.3 mmol) of malonic acid in 50 ml of pyridine were treated with 4.0 g (27.4 mmol) of **19** in 2 ml of piperidine. The mixture was heated to 100° for 2 h until the evolution of CO_2 had stopped, then poured into 2N H_2SO_4 and worked up. After crystallization of the crude product from ether/hexane 3.5 g (68%) of *(E)*-**22** were obtained.

The methylation of 1.5 g of *(E)*-**22** (for the procedure see **6**→**9**) gave, after column chromatography with toluene/ethyl acetate 4:1 and crystallization from hexane, 1.3 g (88%) of (E)-*4-(1-phenylcyclopropyl)-3-buten-2-one* (**27**), m.p. 47°. – UV.: 240 (14000), 313 (100). – IR.: 1620*s*, 1675*s*, (*s-anti*), 1700*s* (*s-syn*). – NMR. (CCl_4): 1.5 (*m*, 2H–C(2′)), –C(3′)); 2.00 (*s*, 3H–C(1)); 5.45, 6.45 (2 *d*, *J*=15, H–C(3) and –C(4), resp.); 7.24 (*m*, 5 arom. H). – MS.: 186 ($C_{13}H_{14}O^+$), 171, *158*, 143, 43.

The pyrolysis of 1.0 g of *(E)*-**27** (for the procedure see **7**→**15**) was carried out at 400° and recycled until the conversion was complete. Chromatography with toluene/ethyl acetate 4:1 gave 0.9 g (90%) of **30**. – UV.: 254 (20000); see Figure 1. – IR.: 1605*m*, 1717*s*. – NMR. ($CDCl_3$): 2.10 (*s*, H_3C–CO); 3.6 (*m*, H–C(1)); 6.1 (*m*, H–C(2)); 7.2 (*m*, 5 arom. H). – MS.: 186 ($C_{13}H_{14}O^+$), *143*.

Structure proof for **30**. 0.25 g (1.34 mmol) of **30** were reduced with 1.5 mmol of $NaBH_4$ in CH_3OH/H_2O 1:1 at 0°. The mixture was warmed up to RT. until the evolution of H_2 had stopped and then added to satd. aqueous NH_4Cl solution. The work-up gave a mixture of the diastereoisomeric *1-(3-phenyl-2-cyclopentenyl)ethanols* **(33)**. – IR. ($CHCl_3$): 3620*m*. – NMR. (CCl_4): 1.12 (*d*, *J*=6, 3H–C(2)); 1.6–3.0 (*m*, H–C(1'), 2H–C(4'), –C(5')); 3.7 (*m*, H–C(1)); 6.1 (*m*, H–C(2')); 7.35 (*m*, 5 arom. H).

The acetylation of this mixture in acetic anhydride/pyridine 1:1 at RT. overnight afforded after chromatography with toluene/ethyl acetate 4:1 0.15 g (50% yield based on **33**) of a mixture of diastereoisomeric *1-(3-phenyl-2-cyclopentenyl)ethyl acetates* **(34)**. – IR.: 1740*s*. – NMR. ($CDCl_3$): 1.21 (*d*, *J*=6, 3H–C(2); 2.24 (*m*, 2H–C(4'), –C(5')); 1.97, 2.02 (2*s*, H_3C–CO); 3.04 (*m*, H–C(1')); 4.94 (2 *d*×*qa*, *J*(1,1')=3 and 9, resp., *J*(1,2)=6, H–C(1)); 6.08 (*m*, H–C(2')); 7.3 (*m*, 5 arom. H). Decoupling experiment: see text.

Methyl 1-methyl-3-phenyl-2-cyclopentenyl ketone **(31)**. The *Emmons* reaction of 3.65 g (25 mmol) of **19** with 10.0 g (40 mmol) of triethyl phosphonopropionate (for the procedure see **19**→**21**) gave 2.6 g (50%) of a 6:1 mixture of *ethyl* (E+Z)-*2-methyl-3-(1-phenylcyclopropyl)-2-propenoate* **(23)**, b.p. 99°/0.17 Torr, which were separated by chromatography with toluene/ethyl acetate 4:1. *(E)*-**23**: UV.: 226 (7500). – IR.: 1710*s*. – NMR. (CCl_4): 1.2 (*m*, 2H–C(2'), –C(3')); 1.15 (*d*, *J*=1.5, H_3C–C(2)); 1.25 and 4.17 (*t* and *q*, *J*=7, CH_3CH_2O); 6.85 (*qa*, *J*=1.5, H–C(3)); 7.20 (*s*, 5 arom. H). – MS.: 230 ($C_{15}H_{18}O_2^+$), 202, *173*, 157.

(Z)-**23**: UV.: 212 (5800). – IR.: 1728*s*. – NMR. (CCl_4): 1.0 (*m*, 2H–C(2'), –C(3')); 1.10 and 3.95 (*t* and *qa*, *J*=7, CH_3CH_2O); 1.88 (*d*, *J*=1.5, H_3C–C(2)); 5.93 (*qa*, *J*=1.5, H–C(3)); 7.10 (*s*, 5 arom. H). – MS.: same as MS. of *(E)*-isomer.

The hydrolysis (for the procedure see **21**→**22**) of 2.0 g of *(E)*-**23** gave 1.4 g (80%) of (E)-*2-methyl-3-(1-phenylcyclopropyl)-2-propenoic acid* **(24)**, m.p. 90°. – IR. ($CHCl_3$): 1692*s*, 2700–3600 br. – NMR. ($CDCl_3$): 1.15 (*m*, 2H–C(2'), –C(3')); 1.60 (*d*, *J*=1, H_3C–C(2)); 6.95 (*qa*, *J*=1, H–C(3)); 7.15 (*s*, 5 arom. H). – MS.: 202 ($C_{13}H_{14}O_2^+$), *174*, 157.

The methylation (for the procedure see **6**→**9**) of 3.7 g of *(E)*-**24** gave after chromatography with toluene/ethyl acetate 4:1 3.5 g (95%) of (E)-*3-methyl-4-(1-phenylcyclopropyl)-3-buten-2-one* **(28)**. – UV.: 240 (15580), 313 (120). – IR.: 1610*m*, 1640*m*, 1680*s*. – NMR. (CCl_4): 1.12 (*m*, 2H–C(2'), –C(3')); 1.64 (*d*, *J*=1, H_3C–C(3)); 2.20 (*s*, 3H–C(1)); 6.70 (*qa*, *J*=1, H–C(4)); 7.10 (*s*, 5 arom. H). – MS.: 200 ($C_{14}H_{16}O^+$), 185, 172, *157*, 43.

Repeated pyrolyses (total time 6 h; for the procedure see 7→**15**) of *(E)*-**28** at 350° resulted in a 70% conversion and, after chromatography with toluene/ethyl acetate 4:1, a 50% yield of **31**. – UV.: 254 (18000); see Figure 1. – IR.: 1600*m*, 1710*s*. – NMR. (CCl_4): 1.25 (*s*, H_3C–C(1)); 2.05 (*s*, H_3C–CO); 5.9 (*m*, H–C(2)); 7.25 (*m*, 5 arom. H). – MS.: 200 ($C_{14}H_{16}O^+$), *157*, 43.

Methyl 2-methyl-3-phenyl-2-cyclopentenyl ketone **(32)**. The *Emmons* reaction of 5.1 g (30 mmol) of 1-phenylcyclopropylmethyl ketone **(20)** [56] with 11.2 g (50 mmol) of triethyl phosphonoacetate (for the procedure see **19**→**21**) afforded after 4 days in boiling diglyme 3.5 g (48%) of *ethyl* (E)-*3-(1-phenylcyclopropyl-2-butenoate* **(25)**, b.p. 125°/1 Torr. – UV.: 235 (9100). – IR.: 1650*m*, 1722*s*. – NMR. (CCl_4): 1.1 (*m*, 2H–C(2'), –C(3')); 1.21 and 4.05 (*t* and *qa*, *J*=7, CH_3CH_2O); 2.02 (*d*, *J*=2, 3H–C(4)); 5.60 (*qa*, *J*=2, H–C(2)); 7.1 (*s*, 5 arom. H). – MS.: 230 ($C_{15}H_{18}O_2^+$), 202, 173, *157*.

The hydrolysis (for the procedure see **21**→**22**) of 3.0 g of *(E)*-**25** furnished 2.0 g (75%) of (E)-*3-(1-phenylcyclopropyl)-2-butenoic acid* **(26)**, m.p. 99°. – IR. ($CHCl_3$): 1645*m*, 1695*s*, 2800–3600 br. – NMR. ($CDCl_3$): 1.2 (*m*, 2H–C(2'), –C(3')); 2.10 (*d*, *J*=1.5, 3H–C(4)); 5.78 (*qa*, *J*=1.5, H–C(2)); 7.3 (*s*, 5 arom. H). – MS.: 202 ($C_{13}H_{14}O_2^+$), *174*, 157.

The methylation (for the procedure see **6**→**9**) of 2.0 g of *(E)*-**26** gave 1.8 g (80%) of (E)-*4-(1-phenylcyclopropyl)-3-penten-2-one* **(29)**. – UV.: 242 (17500), 313 (120). – IR.: 1618*s*, 1698*s*. – NMR. (CCl_4): 1.05 (*m*, 2H–C(2'), –C(3')); 2.00 (*d*, *J*=1, 3H–C(5)); 2.03 (*s*, 3H–C(1)); 6.00 (*qa*, *J*=1, H–C(3)); 7.15 (*s*, 5 arom. H). – MS.: 200 ($C_{14}H_{16}O^+$), 185, 172, 157, *43*.

Two pyrolytic runs (for the procedure see 7→**15**) of *(E)*-**29** at 400° gave almost quantitatively **32**. – UV.: 254 (15000); see Fig. 1. – IR.: 1605*m*, 1710*s*. – NMR. (CCl_4): 1.68 (br., H_3C–C(2)); 1.96 (*s*, H_3C–CO); 3.41 (*m*, H–C(1)); 7.15 (*s*, 5 arom. H). – MS.: 200 ($C_{14}H_{16}O^+$), *157*, 43.

Methyl 2-phenyl-2-cyclopentenyl ketone **(42).** The *Emmons* reaction (for the procedure see **19→21**) of 10.0 g (70 mmol) of cyclopropyl phenyl ketone **(35)** and 27.7 g (120 mmol) of triethyl phosphonoacetate gave 8.9 g (60%) of a 1:1 mixture of *ethyl* (E+Z)-*3-cyclopropyl-3-phenyl-2-propenoate* **(36),** b.p. 90°/0.1 Torr. An analytical sample was separated by GLC. (15% SE). *(E)*-**36:** UV.: 241 (4700). - IR.: 1635*m*, 1720*s*. - NMR. (CCl_4): 0.7 (*m*, 2H−C(2′), −C(3′)); 1.26 and 4.12 (*t* and *qa*, *J*=6, CH_3CH_2O); 3.17 (*m*, H−C(1′)); 5.68 (*s*, H−C(2)); 7.2 (*m*, 5 arom. H). - MS.: 216 ($C_{14}H_{16}O_2^+$), *188*, 143.

(Z)-**36:** UV.: 209 (5800). - IR.: 1635*m*, 1735*s*. - NMR. (CCl_4): 0.65 (*m*, 2H−C(2′), −C(3′)); 0.98 and 3.85 (*t* and *qa*, *J*=6, CH_3CH_2O); 1.70 (*m*, H−C(1′)); 5.71 (*s*, H−C(2)); 7.2 (*m*, 5 arom. H). - MS.: same as *(E)*-isomer.

The hydrolysis (for the procedure see **21→22**) of 1.5 g of *(E+Z)*-**36** gave 1.0 g (80%) of (E+Z)-*3-cyclopropyl-3-phenyl-2-propenoic acid* **(37),** m.p. 110°. - IR. ($CHCl_3$): 1632*m*, 1692*s*, 2800-3500 br. - NMR. ($CDCl_3$): 0.5-0.7 (*m*, 2H−C(2′), −C(3′)); 1.75 and 3.10 (2*m*, H−C(1′) of *(Z)* and *(E)*, resp.); 5.77 and 5.70 (2*s*, H−C(2) of *(Z)* and *(E)*, resp.); 7.15 (*m*, 5 arom. H). - MS.: 188 ($C_{12}O_{12}O_2^+$), *160*, 143.

7.7 g of *(E+Z)*-**37** were methylated to 7.4 g (96%) of (E+Z)-*4-cyclopropyl-4-phenyl-3-buten-2-one* **(40)** (for the procedure see **6→9**). - UV.: 254 (11000), 313 (170). - IR.: 1590*s*, 1665*s (E)*, 1685*s (Z)*. - NMR. (CCl_4): 0.65 (*m*, 2H−C(2′), −C(3′)); 1.60 and 2.14 (2*s*, 3H−C(1) of *(Z)* and *(E)*, resp.); 1.78 and 3.20 (2*m*, H−C(1′) of *(Z)* and *(E)*, resp.); 5.96 and 6.02 (2*s*, H−C(3) of *(Z)* and *(E)*, resp.); 7.2 (*m*, 5 arom. H). - MS.: 186 ($C_{13}H_{14}O^+$), 171, *158*, 143, 43.

One pyrolysis of *(E+Z)*-**40** at 400° (for the procedure see **7→15**) gave a quantitative yield of **42.** - UV.: 254 (10000); see Fig. 1. - IR.: 1590*m*, 1715*s*. - NMR. (CCl_4): 1.88 (*s*, H_3C−CO); 3.83 (*m*, H−C(1)); 6.28 (*m*, H−C(3)); 7.25 (*s*, 5 arom. H). - MS.: 186 ($C_{13}H_{14}O^+$), *143*, 43.

Methyl 1-methyl-2-phenyl-2-cyclopentenyl ketone **(43). 35** and triethyl phosphonopropionate gave a 1:2 mixture of *ethyl* (E+Z)-*3-cyclopropyl-2-methyl-3-phenyl-2-propenoate* **(38),** b.p. 100-105°/0.2 Torr), (for the procedure see **19→21**), which was separated by GLC. (15% SE). *(E)*-**38:** UV.: 238 (5400). - IR.: 1720*s*. - NMR. (CCl_4): 1.22 and 4.20 (*t* and *qa*, *J*=7, CH_3CH_2O); 1.3 (*m*, 2H−C(2′), −C(3′)); 1.58 (*s*, H_3C−C(2)); 2.66 (*m*, H−C(1′)); 7.1 (*m*, 5 arom. H). - MS.: 230 ($C_{15}H_{18}O_2^+$), *202*, 157.

(Z)-**38:** UV.: 210 (9300). - IR.: 1735*s*. - NMR. (CCl_4): 0.3 (*m*, 2H−C(2′), −C(3′)); 0.68 and 3.68 (*t* and *qa*, *J*=7, CH_3CH_2O); 1.82 (*m*, H−C(1′)); 2.16 (*s*, H_3C−C(2)); 7.1 (*m*, 5 arom. H). - MS.: same as MS. of *(E)*-isomer.

(E)- and *(Z)*-**38** were separately hydrolysed (for the procedure see **21→22**) to the *(E)*- (m.p. 138°) and *(Z)*-isomers (m.p. 134°), respectively, of *3-cyclopropyl-2-methyl-3-phenyl-2-propenoic acid* **(39).** *(E)*-**39:** IR. ($CHCl_3$): 1600*m*, 1685*s*, 2700-3500 br. - NMR. ($CDCl_3$): 0.55 (*m*, 2H−C(2′), −C(3′)); 1.68 (*s*, H_3C−C(2)); 3.01 (*m*, H−C(1′)); 7.3 (*m*, 5 arom. H). - MS.: 202 ($C_{13}H_{14}O_2^+$), *174*, 157.

(Z)-**39:** NMR. ($CDCl_3$): 0.6 (*m*, 2H−C(2′), −C(3′)); 1.86 (*m*, H−C(1′)); 2.15 (*s*, H_3C−C(2)); 7.25 (*m*, 5 arom. H).

The methylation (for the procedure see **6→9**) of an *(E+Z)*-mixture of **39** (3.7 g) afforded 3.3 g (90%) of (E+Z)-*4-cyclopropyl-3-methyl-4-phenyl-3-buten-2-one* **(41).** - UV.: 252 (17000), 313 (150). - IR.: 1600*m*, 1670*s (E)*, 1680*s (Z)*. - NMR. (CCl_4): 0.5 (*m*, 2H−C(2′), −C(3′)); 1.46 and 1.58 (2*s*, H_3C−C(3) of *(Z)* and *(E)*, resp.); 2.05 and 2.32 (2*s*, 3H−C(1) of *(Z)* and *(E)*, resp.); 7.2 (*m*, 5 arom. H). - MS.: 200 ($C_{14}H_{16}O^+$), 185, *172*, 157, 43.

Pyrolysis of *(E+Z)*-**41** (for the procedure see **7→15**) for 8 h at 350° gave a 75% conversion and a 45% yield of **43.** - UV.: 254 (10000); see Fig. 1. - IR.: 1605*w*, 1710*s*. - NMR. (CCl_4): 1.30 (*s*, H_3C−C(1)); 2.02 (*s*, H_3C−CO); 6.22 (*m*, H−C(3)); 7.2 (*s*, 5 arom. H). - MS.: 200 ($C_{14}H_{16}O^+$), *157*, 43.

1-Phenyl-2-cyclopentenyl trideuteriomethyl ketone **(44-d_3).** A mixture of 300 mg of **44** (see below) and 250 mg of K_2CO_3 in 12 ml of dioxan and 12 ml of D_2O was stirred overnight at 75° and then extracted with ether. The organic phase was washed with D_2O, dried and concentrated to give quantitatively **44-d_3**. - NMR. ($CDCl_3$): the signal at 2.01 is missing. - MS.: 189 ($C_{13}H_{11}D_3O^+$), *143*, 46.

Methyl 1-phenylcyclopentyl ketone **(46).** a) 1.0 g of 1-Phenylcyclopentanecarbonitrile **(47)** [14] and a 1:1 mixture of H_2O and 20% methanolic KOH-solution were heated under reflux until a homogeneous solution was formed. Acidification with 10% H_2SO_4 and work-up gave a 50% yield of *1-phenylcyclopentanecarboxylic acid* **(48),** m.p. 150°. - IR.: 1702*s*, 2500-3500 br. - NMR. ($CDCl_3$): 1.9 (*m*, 6H); 2.65 (*m*, 2H); 7.2 (*m*, 5 arom. H). - MS.: 190 ($C_{12}H_{14}O_2^+$), *145*.

2.2 Mol.-equiv. of a 2M etheral CH_3Li solution were added under N_2 to 0.9 g of **48** in 40 ml of ether. After 5 h heating under reflux, hydrolysis and work-up 0.8 g (88%) of **46** were obtained, m.p. 140°. - UV.: 254 (290), 300 (250), 313 (80). - IR.: 1710*s*. - NMR. ($CDCl_3$): 1.7 (*m*, 6H); 1.86 (*s*, H_3C−CO); 2.5 (*m*, 2H); 7.1 (*s*, 5 arom. H). - MS.: 188 ($C_{13}H_{16}O^+$), *145*, 43.

b) Hydrogenation of 100 mg of methyl 1-phenyl-2-cyclopentenyl ketone (**44**; see below) with Pd/C catalyst in 15 ml of ethyl acetate gave quantitatively **46** (identification by mixed m.p., IR., and NMR.).

Preparation of exo-*1,5-dimethylbicyclo[2.1.0]pentane-5-carboxylic acid* (**62**) *and its correlation with* **57.** Ethyl *exo*-1,5-dimethylbicyclo[2.1.0]pentane-5-carboxylate (**61**) [NMR. (CCl_4): 1.23 and 1.30 (2*s*, $H_3C-C(1)$ and $-C(5)$, resp.)] [8b] was separated by GLC. (CW, 160°) from a mixture of the *endo*- and *exo*-isomers[8]) and hydrolysed by stirring in a solution of 20% KOH in CH_3OH/H_2O 1:1 at RT. until a homogeneous phase was obtained. Crystallization of the crude acid from CH_3OH/H_2O gave quantitatively **62**, m.p. 100°. – NMR. (CCl_4): 1.36 (br. *s*, $H_3C-C(1)$, $-C(5)$).

A sample of this acid was analysed by X-ray diffraction [18][9]. The remaining part was methylated with CH_3Li (for the procedure see **6**→**9**) to give *exo 1,5-dimethyl-5-bicyclo[2.1.0]pentyl methyl ketone* (**57**). – UV.: see Fig. 2. – IR.: 1690*s*, 3050*w*. – NMR. (CCl_4): 1.14 and 1.44 (2*s*, $H_3C-C(1)$ and $-C(5)$, resp.); 2.16 (*s*, H_3C-CO). – MS.: 138 ($C_8H_{14}O^+$), 123, *95*, 67, 55, 43.

Endo (**53**) *and* exo *methyl 1-phenyl-5-bicyclo[2.1.0]pentyl ketone* (**59**). Three portions of 70 mg of dry $CuSO_4$, each followed by 0.5 Mol.-equiv. of ethyl diazoacetate, were added to 1.2 g of 1-phenylcyclobutene (**63**) [22]. The mixture was maintained at −40° and the reaction was followed by TLC. (toluene/ethyl acetate 4:1). Filtration of the mixture and chromatography of the filtrate with toluene/ethyl acetate 4:1 gave the *ethyl* endo- (**64**; 0.4 g) *and* exo-*1-phenylbicyclo[2.1.0]pentane-5-carboxylates* (**66**; 0.6 g) in a total yield of 63%. **64:** UV.: 220 (4100), 248 (850), 253 (600), 260 (440), 267 (260), 276 (120), 313 (9). – IR.: 1610*m*, 1735*s*. – NMR. (CCl_4): 1.25 and 4.10 (*t* and *qa*, $J=7$, CH_3CH_2O); 1.9–2.5 (*m*, H–C(4), $-C(5)$, 2H–C(2), $-C(3)$); 7.0–7.3 (*m*, 5 arom. H). – MS.: 216 ($C_{14}H_{16}O_2^+$), *143*.

66: UV. and MS. same as **48.** – IR.: 1610*m*, 1730*s*. – NMR. (CCl_4): 0.9 and 3.8 (*t* and *qa*, $J=7$, CH_3CH_2O); 1.4–1.5 and 1.8–2.6 (2*m*, 1H and 5H, resp., H–C(4), $-C(5)$, 2H–C(2), $-C(3)$); 7.0–7.3 (*m*, 5 arom. H).

The hydrolysis of **64** and **66** (for the procedure see **21**→**22**) gave quantitatively endo- (**65**) and exo-*1-phenylbicyclo[2.1.0]pentane-5-carboxylic acids* (**67**). **65:** m.p. 110° (crystals from CH_2Cl_2/hexane). – IR.: 1608*m*, 1705*s*, 2500–3500 br. – NMR. (CCl_4): 2.0–2.8 (*m*, H–C(4), $-C(5)$, 2H–C(2), $-C(3)$); 7.1–7.4 (*m*, 5 arom. H). – MS.: 188 ($C_{12}H_{12}O_2^+$), *143*.

67: m.p. 131° (crystals from CH_2Cl_2/hexane). – IR.: 1608*m*, 1698*s*, 2500–3500 br. – NMR. ($CDCl_3$): 1.5–2.8 (*m*, H–C(4), $-C(5)$, 2H–C(2), $-C(3)$); 7.2 (*s*, 5 arom. H). – MS.: same as MS. of **65.** – A sample of **67** was analysed by X-ray diffraction [23].

The methylation of **65** and **67** with CH_3Li (for the procedure see **6**→**9**) afforded **53** (67% yield) and **59** (48% yield), respectively. **53:** UV.: 210 (11000), 220 (9400), 252 (4000), 262 (3000), 292 (500), 300 (400), 313 (250), 323 (150), 348 (53). – IR.: 1608*m*, 1710*s*. – NMR. ($CDCl_3$): 2.18 (*s*, H_3C-CO); 6.9–7.3 (*m*, 5 arom. H). – MS.: 181 ($C_{13}H_{14}O^+$), *143*.

59: UV. and MS. same as **53.** – IR.: 1608*m*, 1705*s*. – NMR. ($CDCl_3$): 1.80 (*s*, H_3C-CO); 7.1 (*s*, 5 arom. H). In the presence of Eu(fod)$_3$ the signal of the two *o*-protons of the phenyl group of **59** is selectively shifted to lower field.

Irradiations. – Prior to irradiation the solutions were thoroughly flushed with argon or nitrogen. All experiments were carried out at RT. – *Light sources for 254 nm:* A low-pressure Hg lamp (*Quarzlampen GmbH.*, Hanau) was placed in a water-cooled quartz jacket and immersed into the magnetically stirred solution of reactant. Analytical runs were carried out in quartz tubes of 1–2 ml content, equipped with magnetic stirrer and serum cap, and placed in the center of 4–8 circular low-pressure Hg lamps (Minerallight PCQXl, *Ultraviolet Products Inc.*, San Gabriel,Calif.). *For > 300 nm and > 340 nm:* 125 and 250 W medium-pressure Hg lamps placed in a water-cooled pyrex jacket. For > 340 nm a jacket equipped with an additional mantel of 1 cm width filled with a filter solution of 750 g of NaBr and 7 g of Pb $(NO_3)_2$ per l H_2O [opt. density: 1.5 (340 nm), 0.6 (345), 0.03 (360)] was used. These jackets were immersed into the magnetically stirred solution of reactant in preparative runs. Pyrex tubes (1–2 ml content, magnetic stirrer, serum cap) attached to the jackets served for analytical irradiations. *For 208 nm:* A microwave-excited I_2 resonance lamp was used, with the window facing a rectangular quartz cell holding the solution of the reactant.

Direct irradiation of **16.** A solution of 1 g of **16** in 150 ml of 2-methylheptane was photolysed at > 300 nm until the photostationary pseudoequilibrium was approximately reached. According to GLC. (CW, 150°) the two isomeric ketones **16** and **17** were the major components of the mixture. The solution was concentrated and 120 mg of **17** were separated by GLC. (identification by IR., NMR., MS., and GLC. coinjection with synthetic **17**).

Photostationary pseudoequilibrium **16⇄17.** 1 ml each of 0.2M solutions of **16** and **17** in 2-methy heptane were irradiated at > 300 nm. Plots of concentration *vs.* time (GLC.: CW, 150°) gave a pseud equilibrium **16:17** of *ca.* 1:3.

Direct irradiation of **30.** a) In a GLC.-monitored (15% SE, 175°) analytical irradiation of a 0.2 solution of **30** in benzene at > 300 nm the starting ketone had disappeared after 80 h. A brow insoluble deposit had formed and **44** was the only soluble product detectable by GLC. and NMR.

b) 1.0 g of **30** in 150 ml of ether was irradiated at 254 nm. After 3 h the starting material had bee consumed completely, and the soluble crude product was chromatographed with toluene/ethyl acetat 4:1 furnishing *methyl 1-phenyl-2-cyclopentenyl ketone* **(44)** in 52% yield. – UV.: 258 (1400); see Fig. 1. IR.: 1603*m*, 1712*s*. – NMR. ($CDCl_3$): 1.8, 2.4 and 3.0 (3*m*, 1H, 2H and 1H, resp., 2H–C(4), –C(5)); 2.01 (*s*, H_3C–CO); 6.10 (*s*, H–C(2), –C(3)) (in C_6D_6: 5.80 (*m*)); 7.35 (*m*, 5 arom. H). – MS.: 18 ($C_{13}H_{14}O^+$), *143*, 43.

Direct irradiation of **30** *and* **44**-d_3. A solution of 50 mg each of **30** and **44**-d_3 in 1 ml of benzene wa irradiated at > 300 nm until 60% of **30** had disappeared. The remaining **30** was collected by GLC. (15% SE). – MS.: 189 ($C_{13}H_{11}D_3O^+$), 186 ($C_{13}H_{14}O^+$), *143*, 46, 43 (ratio 189/186 = 1:9).

Direct irradiation of **31.** After 75 h irradiation of a 0.04M solution of **31** in benzene at > 300 nm th starting ketone had disappeared. A brown insoluble deposit had formed and **45** was the only solubl product detectable by GLC. and NMR. *Methyl 3-methyl-1-phenyl-2-cyclopentenyl ketone* **(45)** wa isolated in 30% yield by GLC. (15% SE, 175°). – IR.: 1610*m*, 1715*s*. – NMR. (CCl_4): 1.80 (*d*, *J* = 1 H_3C–C(3)); 1.86 (*s*, H_3C–CO); 1.9–2.7 (*m*, 2H–C(4), –C(5)); 5.60 (*qa*, *J* = 1, H–C(2)); 7.1 (*m*, 5 arom H). – MS.: 200 ($C_{14}H_{16}O^+$), *157*, 43.

Direct irradiation of **31** *and* **44**-d_3. A solution of 40 mg each of **31** and **44**-d_3 in 1 ml of benzene wa photolysed at > 300 nm until 80% of **31** had disappeared. **44**-d_3 and **45** were isolated by GLC. (15% SE 175°). MS. analysis showed that both ketones were isotopically uniform.

Direct irradiation of **32** *and* **43.** 0.2M solutions of **32** and **43** in benzene were irradiated at > 300 nm for 160 h. GLC. (15% SE, 175°) and NMR. showed that both samples had remained quantitatively unchanged (parallel runs with **30** and **31** showed complete conversion after 80 h).

Sensitized irradiation of **15.** The irradiation of a 0.2M solution of **15** in acetone at 254 nm wa monitored with C-GLC. (100°). Only two photoproducts, *endo* and *exo methyl 5-methyl-5-bicyclo[2.1.0]pentyl ketones* **(50** and **56,** respectively), were formed in the initial ratio of ≳3:1 (at 5% conversion). They were isolated by GLC. (15% SE, 90°). **50:** IR.: 1705*s*, 3030*w*. – NMR. (CCl_4): 1.11 (*s*, H_3C–C(5)); 2.18 (*s*, H_3C–CO). – MS.: 124 ($C_8H_{12}O^+$), 109, *81*, 53.

56: IR.: 1690*s*, 3060*w*. – NMR. (CCl_4): 1.37 (*s*, H_3C–C(5)); 1.88 (*s*, H_3C–CO). – MS.: same as MS. of **50.**

Sensitized irradiation of **16.** a) The irradiation of a 0.2M solution of **16** in acetone at 254 nm gave endo- *and* exo-*1,5-dimethyl-5-bicyclo[2.10]pentyl methyl ketones* **(51** and **57,** respectively). The initial ratio was ≳7:1 (at 5% conversion; C-GLC., 100°). The products were isolated by GLC. (CW, 140°). **51:** UV.: see Fig. 2. – IR.: 1708*s*, 3020*w*. – NMR. (CCl_4): 1.17, 1.33 (2*s*, H_3C–C(5) and –C(1), resp.); 2.16 (*s*, H_3C–CO). – MS.: 138 ($C_9H_{14}O^+$), 123, *95*, 67, 55, 43.

57: identification by IR., NMR. and GLC. (CW, 140°) coinjection with synthetic **57.**

b) In parallel analytical runs 0.2M solutions of **16** in benzene were irradiated at > 340 nm in the presence of 0.5M each of acetophenone, diphenylamine, and benzophenone. When **16** had completely rearranged to **51** and **57** (ratio ≳7:1 at 5% conversion) in the acetophenone-sensitized run, the starting material was still fully unchanged in the runs with diphenylamine and benzophenone.

Sensitized irradiation of **17.** The procedure described for **16→51+57** (experiment a)) was followed. The results were identical in all respects.

Direct irradiation of **51** *and* **57.** a) *In solution.* Analytical runs with 0.2M solutions of **51** and **57,** each in pentane and CH_3OH, were carried out with 208 nm and > 300 nm radiations. The experiments were monitored with C-GLC. (100°). No *endo-exo* interconversion was detectable in any run, and both ketones were very slowly converted to several unidentified products of shorter retention times.

b) *In the gas phase.* A quartz spiral tube was used which is connected with a high-vacuum pump, has a spherical bulb attached at each end through a ground joint, and encircles a water-cooled quartz jacket with a medium-pressure Hg lamp. 150 mg of **51** were placed in one bulb and cooled in liquid N_2. The system was evacuated to 10^{-5} Torr and the cooling transferred to the second empty bulb in order to slowly distil the ketone through the spiral tube. After 5 repetitions of this molecular distillation **51** was

still unchanged and no *endo-exo* isomerization was detectable (C-GLC., 100°). A similar experiment with **57** gave the same result.

Sensitized irradiation of **51** *and* **57.** 0.2M solutions of **51** and **57** in acetone were photolysed at 254 nm. *Ca.* 50% of the starting material had disappeared after 75 and 115 min, respectively, without detection of *endo-exo* interconversion or formation of other identifiable products (C-GLC., 100°).

Sensitized irradiation of **18.** A 0.2M solution of **18** in acetone gave with 254 nm *endo* and *exo methyl 1,4,5-trimethyl-5-bicyclo[2.1.0]pentyl ketones* (**52** and **58,** respectively) in the initial ratio $\gtrsim$5:1 (at 5% conversion; C-GLC., 100°). The products were isolated by GLC. (15% SE, 90°). **52:** IR.: 1705*s*. – NMR. (CCl_4): 1.09 (*s*, H_3C–C(5)); 1.13 (*s*, H_3C–C(1), –C(4)); 2.08 (*s*, H_3C–CO). – MS.: 152 ($C_{10}H_{16}O^+$), 137, *109*, 81.

58. IR.: 1685*s*. – NMR. (CCl_4): 1.16 (*s*, H_3C–C(1), –C(4)); 1.42 (*s*, H_3C–C(5)); 2.16 (*s*, H_3C–CO). – MS.: same as MS. of *endo*-isomer.

Sensitized irradiation of **30.** a) 0.2M solutions of **30** in acetone (at > 300 nm), in neat acetophenone (> 300 nm), and in benzene with 0.2M benzophenone (> 340 nm), 0.02M thioxanthone (> 340 nm), 0.02M *Michler* ketone (> 340 nm), 0.4M *α*- and 0.4M *β*-acetonaphthone (> 340 nm) were irradiated. The reactions were monitored by GLC. (15% SE, 175°). When **30** had completely disappeared in acetone, no identifiable photoproduct was detected by GLC. and NMR. With the acetonaphthones the concentration of **30** decreased much more slowly, and again, no new products could be observed by GLC. and NMR. In all the other runs, **30** was converted into a ~3:1 mixture (by NMR.; stereoisomers not separable by GLC.) of **53** and **59.**

b) In preparatively scaled-up sensitizations as described in a), chromatography with toluene/ethyl acetate 4:1 gave *ca.* 65% yields of *endo* and *exo methyl 1-phenyl-5-bicyclo[2.1.0]pentyl ketones* (**53** and **59,** respectively). Identification with synthetic material by GLC. coinjection, IR., and NMR.

Sensitized irradiation of **53** *and* **59.** 0.2M solutions of **53** and **59,** each in acetone (at > 300 nm), in neat acetophenone (> 300 nm), and with 0.2M benzophenone in benzene (> 340 nm), were irradiated. In neither run an *endo-exo* interconversion was observed by NMR. In acetone and acetophenone the ketones were slowly consumed without appearance of detectable products, and in the presence of benzophenone both compounds remained unchanged.

Sensitized irradiation of **31** *and* **32.** 0.2M benzene solutions of **31** and **32,** each with 0.2M benzophenone, were irradiated at > 340 nm. In both cases GLC. analysis (15% SE, 175°) showed the appearance of one product peak. The NMR. spectra of the mixtures indicated the formation of **54** only from **31** and of **55** and **60** (ratio 1:1) from **32.** *Endo methyl 1-methyl-4-phenyl-5-bicyclo[2.1.0]pentyl ketone* (**54**): NMR. ($CDCl_3$): 1.30 (*s*, H_3C–C(1)); 1.7–2.5 (*m*, 2H–C(2), –C(3), H–C(5)); 2.17 (*s*, H_3C–CO); 7.0 (*m*, 5 arom. H).

Endo and *exo methyl 1-phenyl-5-methyl-5-bicyclo[2.1.0]pentyl ketones* (**55** and **60,** respectively): NMR. ($CDCl_3$): 1.47 and 1.53 (2*s*, H_3C–C(5) of *exo* and *endo*, resp.); 1.6–2.3 (*m*, 2H–C(2), –C(3), H–C(5)); 2.02 (*s*, H_3C–CO); 7.05 (*m*, 5 arom. H).

Sensitized irradiation of **42, 43** *and* **44.** 0.2M solutions of **42, 43** and **44** in acetone and with 0.2M benzophenone in benzene were irradiated at > 300 nm and > 340 nm, respectively. In all runs the ketones had remained unchanged when in parallel experiments with **30** complete conversion was obtained (GLC. and NMR.).

Quantum yields of reaction. The quantum yields were determined at 20° in degassed solutions (3 freeze-pump(10^{-5} Torr)-thaw cycles) using an electronically integrating actinometer [57]. The results are summarized in Table 2. The product compositions were analysed by C-GLC. at 75–90° using hexadecane (runs 1–3 and 5) and octadecane (runs 4 and 6) as an internal standard, and by GLC. (15% SE, 175°) using dodecane or tridecane (runs 7–13). Under these conditions the thermal reactions **51** $\rightleftarrows$ **57**, **51** → **16** + **17** (*cf.* [15]) and **53** → **30** (*cf.* footnote 11)) are negligible. The Φ values given in the Table are averaged from multiple measurements at each of several conversions within the ranges indicated in one or two runs of different concentrations of starting ketone. These concentrations were: run 1, 0.0286M and 0.0290M **16;** run 2, 0.0266M and 0.0312M **17;** run 3, 0.0302M and 0.0713M **16;** run 4, 0.028M **16;** run 5, 0.0275M and 0.0370M **17;** run 6, 0.0386M **17;** runs 7–9 and 13, 0.10M **30;** run 10, 0.11M **30;** runs 11 and 12, 0.12M **30.**

Emission spectroscopy and phosphorescence quantum yields. A detailed description of the instrume and techniques employed for phosphorescence measurements has been given in [58]. The phosphore cence quantum yields of **30** and 1-phenylcyclopentene are based on β-acetonaphthone, $\Phi_p = 0.05$. For tl results see text and Fig. 3.

The mass spectra were run by Professor *A. Buchs*, University of Geneva.

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