Photochemistry of Ketones in Solution. 53. Stereospecific Triplet-State Photorearrangements of Chiral 2-Cyclohexenones: Type A Lumiketone Rearrangement and Phenyl Migrations[1,2]

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Abstract: The photochemical behavior of two chiral monocyclic enones, 4-methyl-4-phenyl- and 4-methyl-4-propyl-2-cyclohexenone, has been investigated. In both systems, it was found that the rearrangement to bicyclo[3.1.0]hexan-2-ones (lumiketones) proceeds stereospecifically, with no loss in optical purity. The same conclusion is reached for the products of aryl migration in the former case, while the rearrangement to a 3-substituted 2-cyclopentenone in the latter case is at least 64% stereospecific. The results are consistent with synchronous mechanisms for these rearrangements describable in terms of orbital symmetry formalisms as $[_\sigma 2_a + _\pi 2_a]$ and $[_\sigma 2_a + _\sigma 2_a]$ cycloadditions, originating from triplet excited states of the reactants. Open diradical intermediates are clearly not involved in these reactants. This supports the contention of Woodward and Hoffmann that considerations of orbital symmetry can be used to predict the stereochemical course of reactions proceeding from excited states with unpaired electrons. The inefficiency in these reactions is found not to be due to reversion to starting material from diradical intermediates, but rather is a consequence of the shape of the T_1 and S_0 potential surfaces in the region corresponding to twisting of the enone around the C=C bond.

The photochemical rearrangements of substituted 2-cyclohexenones continue to be an enigma.[4] A major unresolved question is the source of the extremely high inefficiency ($\geq 99\%$) observed in these photorearrangements.[4] This contrasts with the photorearrangements of cyclohexadienones, e.g., **1** to **2**, $\phi = 0.85$.[5] Substituents on the olefinic moiety often wipe out reactivity altogether.[6] Using stereochemistry as a probe, we have explored the possibilities of reversible diradical formation as the source of this energy wastage.[2,3]

Prior stereochemical studies of the type A[7] photorearrangement to lumiketones were confined to polycyclic enones. Thus, Chapman et al. showed that the photorearrangement of **3** to **4** proceeded with $\geq 95\%$ retention of optical activity.[8] Schaffner and co-workers showed that the configuration of C_1 in **5** was retained on photorearrangement to **6**.[9] Because of the

1   **2**

3   **4**

5   **6**
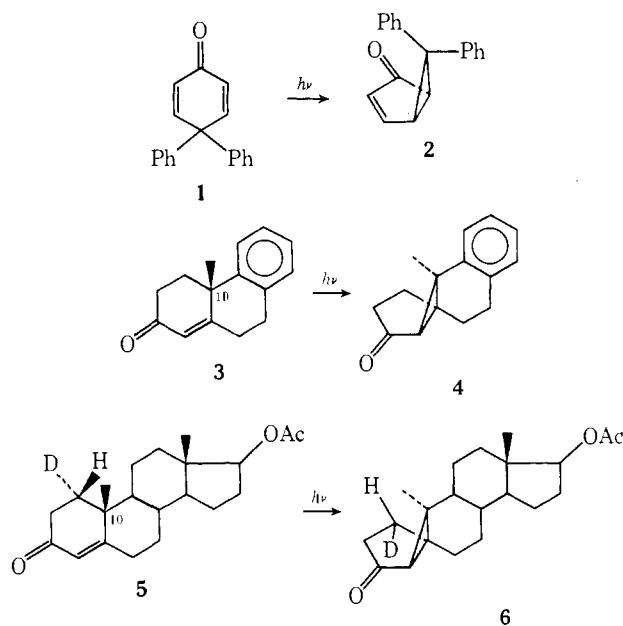
necessary cis fusion of the cyclopropane to the five- and six-membered rings in **4** and **6**, the lumiketone rearrangement in both these systems[8,9] must proceed with inversion of configuration at C_{10}. While these results rule out the intermediacy of

planar chiral radicals, and are inconsistent with the mechanism as depicted in Scheme Ia, they do not require that the rearrangement is a concerted process, as noted by Chapman and co-workers[4] and by us.[10] However, in these polycyclic systems, steric constraints operate such that a diradical **7** formed by cleavage of the C_1-C_{10} bond would probably not be planar in any event, according to molecular models, since C_1 must lie either above or below the trigonal center at C_{10}. The angular methyl as well as the conformation of ring B make it likely that C_1-C_5 bond formation would occur preferentially from the rear face of the molecule, as in **7**.[11] The formation of racemic
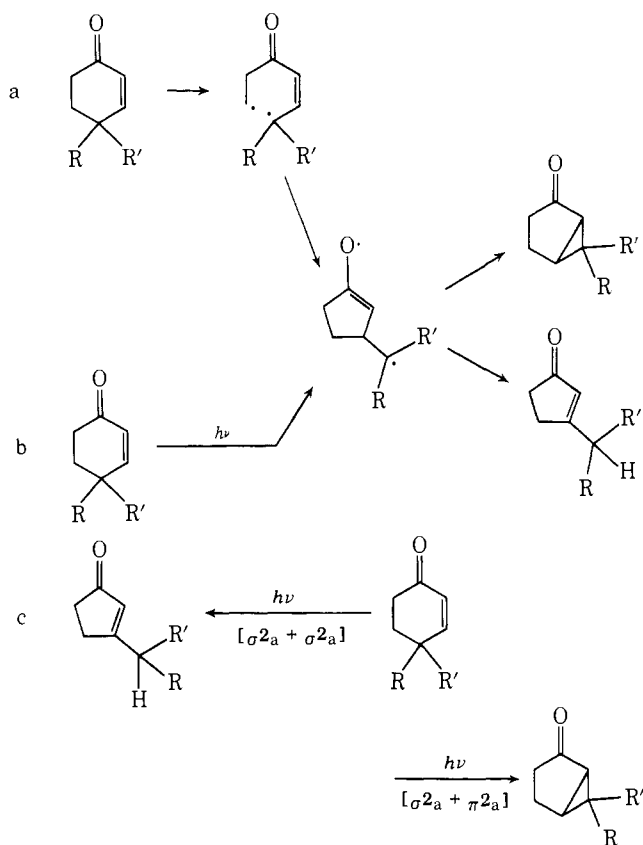

7   **8**
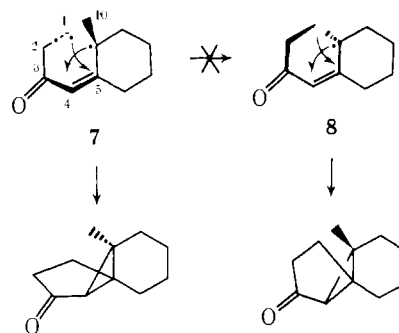
products from **3** and steroidal enones would therefore require rotation of the C_1-C_5 chain around to the top face of the diradical as in **8** before bonding between C_1 and C_5, and models of **7** suggest that this is energetically prohibitive compared with ring closure.

Zimmerman and co-workers[12] showed that, when aryl substituents are present on the cyclohexenone, 1,2-aryl shifts occur instead of the type A rearrangement. Extensive studies of the stereoselectivity, migration aptitudes, and other mechanistic features of these reactions have been made by these workers.[12,13] A diradical mechanism was proposed for these rearrangements (vide infra).

To avoid the ambiguities inherent in the polycyclic enones and to gain further insight into the mechanism of the type A rearrangement and 1,2-aryl shifts, we have examined the absolute stereochemistry of photochemical rearrangements of the unconstrained chiral cyclohexenones **9** and **10**. In such systems, the lumiketone rearrangement can occur a priori with either retention or inversion at C_4, the only controlling factor

Scheme I. Possible Pathways for the Type A Rearrangement

Scheme II

the known absolute configuration of a number of α-cyclopropyl ketones. In the case of **11**, the circular dichroism curve shows a positive Cotton effect centered at 288 nm.

Photolysis of (+)-**9** ([α]$_D$ +53.83°, OP 41.73%) in 95% ethanol through Pyrex with a Hanovia immersion well apparatus for 24 h gave several products, which were collected with residual starting material by preparative GLC. The compounds and their rotations were as follows: **9**, [α]$_D$ +51.25°; **11**, [α]$_D$ −1.76°; **12**, [α]$_D$ +80.52°; **13**, [α]$_D$ −4.41°. Two additional products, noted by analytical GLC, could not be isolated in sufficient purity to permit reliable structural assignments. These presumably correspond to **14** and **15**, which were reported as products of the photolysis of racemic **9**.[14] Product **13** was identified by comparison of the ^{1}H NMR data with those reported for the racemic compound.[14] A positive Cotton effect for (−)-**13** centered at 292 nm was observed, corresponding to the configuration shown in Scheme II.[16] Experiments to determine the absolute configuration of (+)-**12** are still in progress, although a tentative assignment of *R* can be made (see Discussion).

Because the amount of recovered **9** from the 24-h ethanol photolysis was very small, a large experimental error was associated with the reading of its optical rotation, which could account for the apparent racemization. An additional quantity of **9**, [α]$_D$ +51.16°, was irradiated in methanol for 7 h through Corex with the apparatus mentioned above. The residual starting material recovered by preparative GLC, and rechromatographed twice, had [α]$_D$ +50.39 ± 0.77°,[17] which was experimentally indistinguishable from the starting value.

Optical purities of **11** and **13** were determined using the chiral ^{1}H NMR shift reagent tris(3-heptafluoropropylhydroxymethylene-*d*-camphorato)europium(III). The ratio of the resonances of the enantiomeric phenyl groups, separated in the presence of this shift reagent, was measured up to 10 times, at each of two or three concentrations of the shift reagent.[3b,17] The optical purities calculated for **11** and **13** from these data are given in Table I, which summarizes all the stereochemical results.

B. Photolysis of (*R*)-(+)-10. Optically active **10**, [α]$_D$ +11.93°, was prepared by the asymmetric induction route of Yamada.[15] Attempts to determine the optical purity of **10** using the chiral ^{1}H NMR shift reagent by monitoring the 4-methyl resonance were unsuccessful. Treatment of **10** with KMnO$_4$ gave a diacid which was cyclized to anhydride **16**,

being the reaction mechanism. In addition, since **9** also gives aryl migration products, the stereochemistry of both rearrangement pathways could be investigated in the same system. We find that the photochemical rearrangements of (*R*)-(+)-**9** and (*R*)-(+)-**10** are totally stereospecific within experimental error, and appear to proceed via completely concerted pathways.
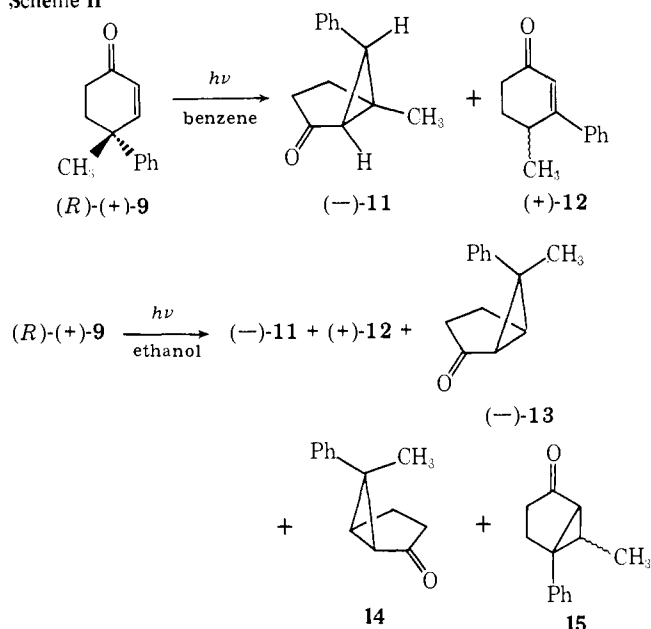

9, R = Ph
10, R = CH$_2$CH$_2$CH$_3$
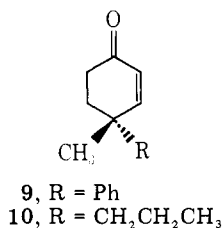
Results

A. Photolysis of (*R*)-(+)-9.[14] Optically active **9**, [α]$_D$ +62.88°, was prepared by the asymmetric induction route of Yamada,[15] and the optical purity (OP) was determined directly from the observed optical rotation, since the rotation of optically pure material has been established.[15] The absolute configuration of (+)-**9** had been previously assigned as *R* by chemical correlation with compounds of known configuration.[15]

Photolysis of (+)-**9** ([α]$_D$ + 62.88°, OP 48.75%) in benzene through Pyrex with a Hanovia immersion well apparatus for 24 h gave two products. These were collected with residual starting material by preparative glc, with the following results: **9**, [α]$_D$ +62.32°; **11**, [α]$_D$ −3.24°; **12**, [α]$_D$ +85.92°.

Products **11** and **12** were identified from spectral data and comparison with literature data in the case of **11**.[14] The absolute configuration of **11**, **13**, and other bicyclo[3.1.0]-hexan-2-ones was assigned using the "inverse octant rule",[16] in which the sign of the Cotton effect has been correlated with

Table I. Summary of Data Correlating Optical Purities of Enones **9** and **10** and Products of Photolysis

| Reaction	Compd	$[\alpha]^{25}_D$, deg	Optical purity, %
Photolysis of **10** in *t*-BuOH at 350 nm for 325 h	**10** (starting)	+4.60	10 ± 1
	10 (recovered)	+4.96	10 ± 1
	18	−8.35	10 ± 1
	17	+7.76	10 ± 1
	19	+3.01	≥6.5[a]
Photolysis of **10** in *t*-BuOH at 254 nm for 12 h	**10** (starting)	+11.93 ± 0.01	26.8 ± 1.3
	10 (recovered)	+11.89 ± 0.03	26.4 ± 0.1
	18	−13.13 ± 0.36	27.2 ± 1.0
	17	+9.96 ± 0.50	27.5 ± 0.9
	19	+7.81 ± 0.07	≥16.9[a]
Photolysis of **9** in benzene for 20 h through Pyrex	**9** (starting)	+62.88 ± 0.03	48.75 ± 0.02
	9 (recovered)	+62.32 ± 0.29	48.31 ± 0.22
	11	−3.24 ± 1.04[b]	47.4 ± 1.7
	12	+85.92 ± 2.82[b]	Not determined
Photolysis of **9** in 95% EtOH for 24 h through Pyrex	**9** (starting)	+53.83 ± 0.02	41.73 ± 0.02
	9 (recovered)	+51.25 ± 2.38[b]	39.73 ± 1.84
	13	−4.41 ± 0.98	41.9 ± 1.5
	11	−1.76 ± 0.42[b]	41.2 ± 1.3
	12	+80.52 ± 0.78	Not determined
Photolysis of **9** in MeOH for 7 h through Corex[c]	**9** (starting)	+51.16 ± 0.04	39.66 ± 0.02
	9 (recovered)	+50.39 ± 0.78	39.06 ± 0.61

[a] This represents a minimal optical purity based on the α-methylvaleric acid obtained by Kuhn–Roth oxidation. [b] Optical rotation measurements in these cases were subject to a particularly large error because of the small amount of sample available after repeated purification by GLC. [c] This run was made specifically to look at recovered starting material. Conversion was 35%; nevertheless, only 12 mg of pure recovered **9** was isolated after four GLC purification cycles.

Table II. Effect of NMR Shift Reagent on C_6 Methyl Resonances of Ketones **17** and **18**

| Shift reagent,[a] µL	δ_{CH_3}		$\Delta\delta_{CH_3}$	
	17	**18**	**17**	**18**
0	1.10	1.08	0.0	0.0
90	1.40	1.30	0.30	0.22
140	1.58	1.41[b]	0.48	0.33
200	1.71	1.63	0.61	0.55
260	2.10[b]	1.80	1.00	0.72
300	2.21	1.95	1.11	0.87
375	2.41	2.10	1.31	1.02

[a] Tris(3-heptafluoropropylhydroxymethylene-*d*-camphorato)europium(III). [b] Splitting of the methyl resonance seen at this and higher concentrations of the optishift reagent.

$[\alpha]_D$ −9.1°, whose 2-methyl resonance was split in the presence of the optishift reagent. Using different optishift con-

(R)-(+)-**10**   (R)-(−)-**16**
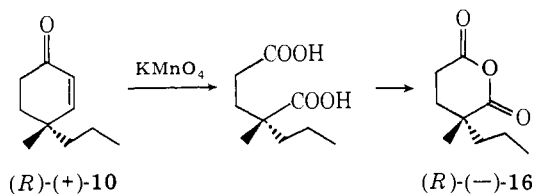
centrations the optical purity of **16**, and hence of **10**, was determined to be 26.9 ± 1.2%.[17] The *R* configuration was assigned to (+)-**10** on the basis of the identical sign of its long wavelength Cotton effect with that of other chiral cyclohexenones prepared by the same asymmetric induction route, two of which have absolute configurations assigned independently and unambiguously.[15]

Photolysis of **10** in *tert*-butyl alcohol at 350 nm through Pyrex gave three primary products, isolated by preparative gas–liquid partition chromatography, assigned structures **17**, **18**, and **19**.[18] The relative stereochemistry of **17** and **18** (i.e., exo–endo position of substituents at C_6) was assigned during our photochemical studies of racemic **10** based principally on the clear difference in the shifts of the nuclear resonances of
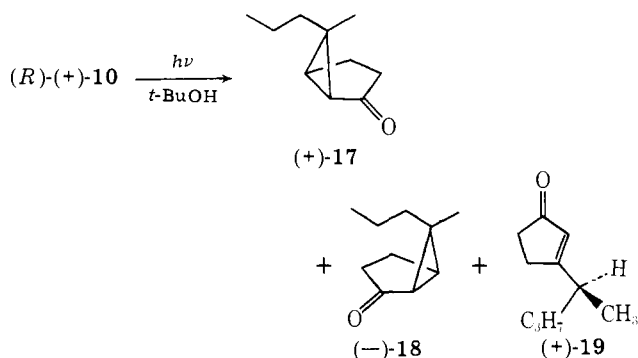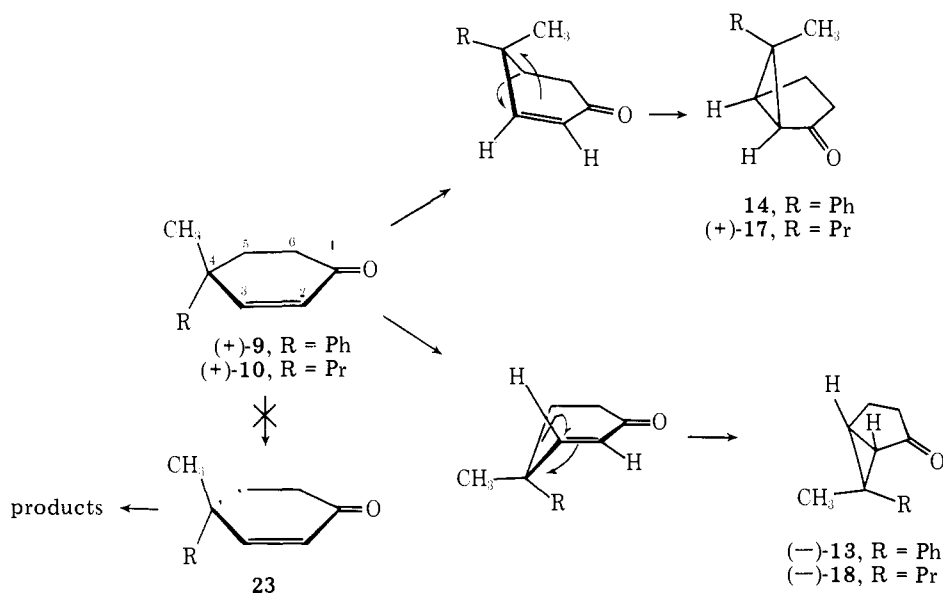

the diastereomeric 6-methyls in **17** and **18** in the presence of the ¹H NMR shift reagent (Table II).[3a,20]

Photolysis of (+)-**10** ($[\alpha]_D$ +4.60°, OP 10,4%) in *tert*-butyl alcohol at 350 nm for 325 h led to 72% conversion to products, which were collected along with residual starting material by preparative GLC. These materials were all optically active: **10**, $[\alpha]^{25}_D$ +4.96°; **17**, $[\alpha]^{25}_D$ +7.76°; **18**, $[\alpha]^{25}_D$ −8.35°; **19**, $[\alpha]^{25}_D$ +3.01°. The OP of **17** and **18** was found to be 10 ± 1% from splitting of the C_6 methyl resonances with the chiral ¹H NMR shift reagent at several different concentrations. The absolute configurations of (+)-**17** and (−)-**18** were determined by circular dichroism, again making use of the "inverse octant rule".[16] Since these compounds show, respectively, negative and positive Cotton effects centered at 292 nm, they must have the absolute configurations as shown above.

In another run using material of greater optical purity, photolysis of (+)-**10** ($[\alpha]_D$ +11.93°, OP 26.8 ± 1.2%) in *tert*-butyl alcohol at 254 nm for 12 h led to 50% conversion to products. These were collected as before, along with residual starting material with the following results: **10**, $[\alpha]^{25}_D$ +11.89°; **17**, $[\alpha]^{25}_D$ +9.96°; **18**, $[\alpha]^{25}_D$ −13.13°; **19**, $[\alpha]^{25}_D$ +7.81°. The OP of **17** and **18**, determined as above, was 27.5 ± 0.9% and 27.2 ± 1.0%, respectively.

The absolute configuration of **19** was determined by a Kuhn–Roth type oxidative degradation to **20**,[21] of known configuration.[22] Optically pure **20** has been reported as having a specific rotation of 18.5°.[23] Cyclopentenone **19** with $[\alpha]^{25}_D$ +6.06°, gave **20** with $[\alpha]_D$ +2.42 ± 0.50°. Since there is no

Scheme III

14, R = Ph
(+)-17, R = Pr

(+)-9, R = Ph
(+)-10, R = Pr

products ←

23

(−)-13, R = Ph
(−)-18, R = Pr

reason a priori to assume that the degradation is totally stereospecific, these data afford only a minimal OP for **19**. We found that **10** (OP 10%) gave **19** (OP ≥6.5%), and **10** (OP 27%) gave **19** (OP ≥16.9%).


(S)-(+)-**19** $\xrightarrow{CrO_3/H_2SO_4}$ (S)-(+)-**20**
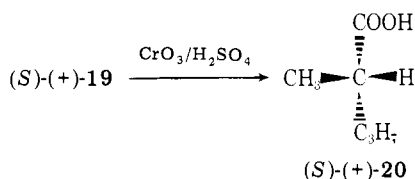
The stereochemical data for these photochemical transformations is summarized in Table I.

Other Results. Photolysis of lumiketone (−)-**18** at 300 nm in *tert*-butyl alcohol gave (−)-**17** as well as racemic **19**. Similarly, photolysis of racemic **13** gives **14**, but no **21**. Photolysis

14 ⇄ **13** ↛

21
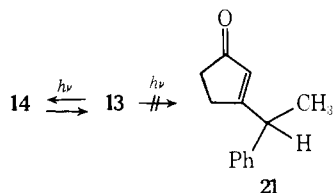
of **11** at 254 nm in ethanol gave no photoproducts detectable by GLC, which indicated there was little if any consumption of **11**. Photolysis of **12** at 254 nm in ethyl alcohol gave a single unisolated product whose retention time on analytical GLC is the same as the fraction ascribed to **15** from photolysis of **9**.

12   15
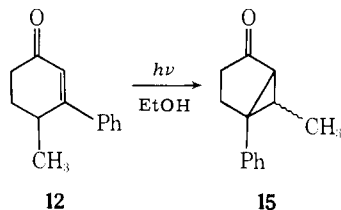
To check on the accuracy of using a chiral pseudocontact ^{1}H NMR shift reagent to determine the OP in these systems, **9** of known OP (39.66% based on $[\alpha]_D$ +51.16°) was converted to **22** by the same method used in the conversion of **10** to **16**. The ^{1}H NMR data for **22** corresponded to those reported previously,[15] and the product had $[\alpha]_D$ −60.25°. The results from addition of the optishift reagent corresponded to an op-


(+)-9   (−)-22
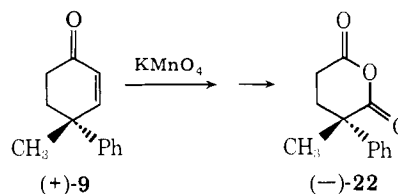
tical purity for **22** of 39.5 ± 0.8%. Thus, the measurements of OP using the NMR method can be safely assumed to be accurate within experimental error.[17]

Discussion

Cyclohexenone **10** is apparently the first optically active monocyclic 4,4-disubstituted cyclohexenone whose photolysis was reported.[2a,3a] Photolysis in *tert*-butyl alcohol gives the three photoproducts shown above, in approximately the same ratio upon irradiation at either 350 or 254 nm. The rearrangements to the lumiketones are at least 99% stereospecific. As postulated previously,[2] the rearrangement is stereospecific on each face of the ring, giving diastereomeric lumiketones with inversion of configuration at the migrating carbon (C_4) in each instance (see Scheme III). Thus, ring opened achiral· diradicals such as **23**[8-19] can no longer be viewed as plausible intermediates in this reaction.

In early discussions of the mechanism of the type A rearrangement, Zimmerman and co-workers[24] suggested that the methylene radical center might be stabilized by bonding to the 2,3 π bond, to give a species represented as in **24**. Here the

3 →   ≡   → products

24
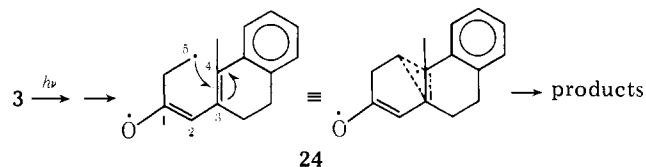
methylene radical is not completely dissociated from the rest of the molecule, such that a stereospecific course of reaction was considered likely. The intermediacy of such an achiral species, which could be a true reaction intermediate or perhaps just a shallow minimum along the potential surface, is not ruled out by our results. In **23**, the tertiary radical center is not allylic since the p orbital at C_4 is orthogonal to the 2,3 π bond such that rotation around the C_3-C_4 bond in either direction in an open structure ought to be relatively free. Complexation with

the π bond, however, would probably result in some stereochemical control in product formation, although as shown below it would be unlikely that stereospecificity would be observed unless formation of the bond between C_2 and C_4 followed very closely behind, or synchronous with, formation of the bond between C_3 and C_5.

The finding that irradiation of (−)-**18** in *t*-BuOH affords (−)-**17** indicates that photochemical epimerization of the lu-

(−)-**18**   **25**   (−)-**17**
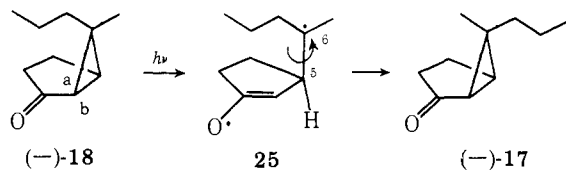
miketones involves predominantly (if not exclusively) breaking of bond a of the electronically excited lumiketone rather than bond b, to give diradical **25** which then closes to **17** after rotation around the C_5-C_6 bond; i.e., configuration is preserved at C_5. This was the same pathway established by Zimmerman et al.[25] in their studies of photochemical epimerization of *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones, where they were able to show that trans* → cis involved complete retention of configuration at C_5, while cis* → trans involved 28% racemization, implying 85% reaction via cleavage of bond a and 15% by cleavage of bond b. In our study, the amount of racemization in **18*** → **17** was not determined. Nonetheless, the fact that *no* racemization is observed in the formation of **17** and **18** from enone **10** requires that **25** cannot be an intermediate in the pathway from enone to lumiketones. Such a conclusion could not be reached in the earlier studies of enone photorearrangements[8,9,24] because the constraints of ring fusion prohibited rotation around the C_5-C_6 bond of intermediates analogous to **25**. Similar reasoning leads to the conclusion that **25** must also be excluded from the pathway leading from excited enone to optically active cyclopentenone **19**, which was formed with a minimum of 64% retention of optical activity. Assuming that some racemization of **19** might be associated with its formation and not entirely with the Kuhn–Roth degradation (vide supra), such racemization would most likely arise during formation of **19** via **25** on secondary photolysis of lumiketones **17** and **18**.

The observed stereochemistry of the type A rearrangement of excited enones is seen to be in precise accord with its depiction as a $[_\sigma2_a + _\pi2_a]$ cycloaddition involving antarafacial addition to the 2,3 π bond and inversion of configuration at C_4, consistent with considerations of orbital symmetry.[26] Similarly, the direct pathway from excited enones to cyclopentenones such as **19** can be viewed in effect as a $[_\sigma2_a + _\sigma2_a]$ cycloaddition, in which the hydrogen shift from C_3 to C_4 of the enone is synchronous with ring contraction, as shown in Scheme IV. The specific geometry of **10** depicted in Scheme IV is irrelevant, since, regardless of the conformation of the system, only the (*S*)-cyclopentenone can be formed from the (*R*)-cyclohexenone by this type of mechanism, again with inversion of configuration at C_4. Although these designations using Woodward–Hoffmann terminology obscure the details of the reaction mechanism to some extent, there is no evidence at present which requires or even suggests that these are not in fact concerted molecular rearrangements.

The same seems to be true of the photorearrangements of the 4-phenyl enone **9**. The type A rearrangement to **13** in alcohols, as well as the phenyl shift to give **11** in benzene and in alcohols, proceeds without loss of optical purity and without racemization of the starting material. The stereochemistry of the type A rearrangement again corresponds to a $[_\pi2_a + _\sigma2_a]$ cycloaddition with inversion at C_4. The arguments given above with respect to the exclusion of achiral diradicals as intermediates holds in these reactions as well. Although the lumiketone

Scheme IV

(*R*)-(+)-**10**   (*S*)-(+)-**19**
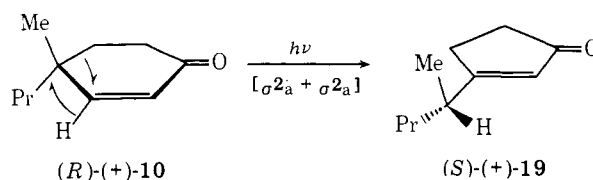
Scheme V
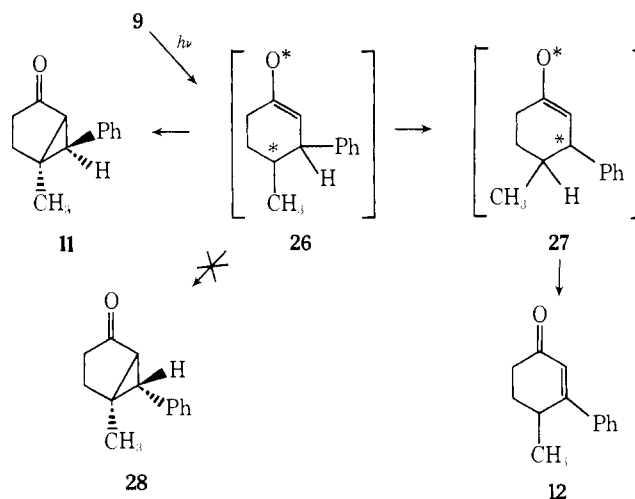
diastereomer **14** could not be isolated in sufficient quantity to allow purification and determination of its absolute configuration, we expect that it too is formed stereospecifically in accord with the $[_\sigma2_a + _\pi2_a]$ formalism.[26]

An intermediate **26** was proposed in the formation of **11** from **9**, and the additional conversion **26** to **27** by a hydrogen shift was suggested to account for the formation of **12** (Scheme V).[14] Both the phenyl and hydrogen shifts must occur stereospecifically, presumably on opposite faces of the ring system, in order to account for the formation of optically active **12**. The absence of compound **28** among the photolysis products is difficult to understand, however, if **26** is indeed a discrete intermediate. Scheme VI presents an alternative mechanism for the formation of both **11** and **12** which explicitly bypasses **26** and **27**. A similar mechanism has been considered by Zimmerman et al.[13] to account for the stereochemistry of aryl migrations in 4-aryl enones. The absolute configuration of **12** is predicted to be *R* as shown in Scheme VI. The bridged structure **29** need not be a discrete intermediate, but may[12,13] merely represent an intermediate molecular geometry (not necessarily at an energy minimum) along the reaction coordinate.

The formation of **15** from **9** has previously been attributed to a methyl shift.[14] However, **15** could arise from a type A photorearrangement of **12**. While we cannot at this time exclude direct formation of **15** from excited states of **9**, it seems to us more likely that **15** is a secondary photoproduct. One might note that Hahn and co-workers did not report an analogous photoproduct in their studies of **30**.[27] The formation of

30
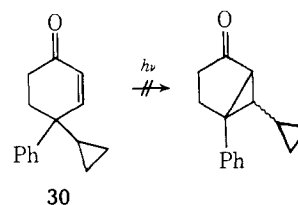
15 exclusively in polar solvents[14] could then be understood on the basis of the solvent effects which are known to influence the efficiency of the type A photorearrangement.[4,14,28]

Scheme VI

29
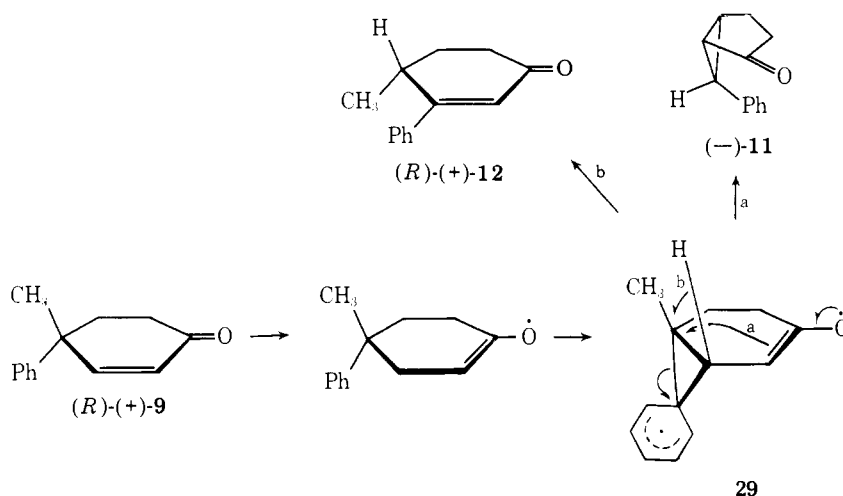
The photorearrangements of **9** and **10** have been found to occur exclusively from triplet excited states.[3a,14,20] Although Zimmerman suggested that these photorearrangements proceed from $^3n,\pi^*$ states,[24] Dauben,[14] Chapman,[4] and Schaffner[28] have suggested, on the basis of quenching studies, that the type A rearrangement proceeds from the lowest $^3\pi,\pi^*$ state and aryl migration from a $^3n,\pi^*$ state. This complicated problem will be discussed by us in a future paper,[20] in which the mechanism of photoreduction in these systems will also be tackled. Within the context of the present paper, it is sufficient only to note that these molecular rearrangements proceeding from triplet excited states have all the characteristics of concerted processes. If any intermediates are involved in these reactions, they must represent shallow minima along the reaction coordinate and they must be chiral.

Conclusions

The results of our work indicate that inefficiency in enone photorearrangements is not due to biradical reversion to starting material by either a competing process of α cleavage[3a,20] or from a biradical intermediate formed along the rearrangement pathway. The data are consistent with rapid relaxation of the spectroscopic enone triplet (i.e., having a geometry corresponding to the energy minimum in the S_0 potential surface[29]) by twisting around the carbon–carbon double bond to form a "twisted π-bond radicaloid",[29,30] which may well represent a potential minimum.

Joussot-Dubien and co-workers have recently provided experimental evidence from flash studies for the transient intermediacy of *trans*-cyclohexenes in the photochemistry of 1-phenylcyclohexene,[31a] and more recently for acetylcyclohexene.[31b] They also have evidence for twisted cyclohexene and cyclohexenone triplets with lifetimes on the order of nanoseconds.[31b]

In any event, the twisted triplet serves as an ideal geometry ("funnel")[29] for crossing from T_1 to S_0 in the region of the T_1 surface corresponding to an S_0 energy maximum. The biradicaloid (or *trans*-cyclohexene, if actually formed) partitions between decay to the ground-state potential surfaces of starting material (major pathway) and products (minor pathway) (Figure 1). The presumption that the partitioning ratio, and hence the quantum efficiency, should depend critically on the exact shapes of the S_0 and T_1 surfaces in this region is consistent with the finding of Dauben et al.[6] that the quantum efficiency is highly sensitive to structural changes and substituent effects in 2-cyclohexenones.

Despite the fact that the rearrangements emanate from triplet excited states, our results suggest the following: (1) a mechanism for the type A rearrangement that is stereospecific and apparently concerted, and is consistent with the orbital

symmetry-allowed $[_\pi2_a + _\sigma2_a]$ cycloaddition formalism proposed by Woodward and Hoffmann;[26] (2) a mechanism that at least formally can be considered a $[_\sigma2_a + _\sigma2_a]$ cycloaddition for the formation of cyclopentenones from excited 2-cyclohexenones; (3) a mechanism for formation of aryl shift products that is stereospecific and perhaps also synchronous with respect to bond breaking and bond making.
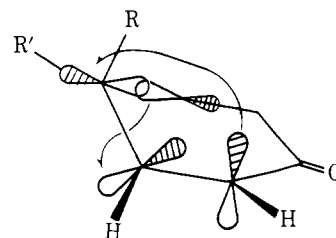
These results support the original contention of Woodward and Hoffmann[26] that electronically concerted pathways which follow the dictates of orbital symmetry can originate from triplet excited states. That is, it appears that the contour of the triplet surfaces, insofar as maxima and minima resulting from orbital symmetry and electronic correlations are concerned, resemble those predicted for the corresponding singlet excited states to a large extent, indicating that the effect of electron spin correlations is relatively weak, at least in these Systems. In the present case, the twisting motions which characterize the energy surface followed by the triplet state in effect determine the nature of the products as well as the quantum efficiency. It also appears that radiationless decay occurs directly from the excited triplet surface to the ground-state surface without a prior spin flip and intervention of a singlet diradical or some other spin-paired intermediate. There is no need whatsoever to invoke any such additional species to accommodate the experimental evidence available at this time.

Experimental Section

Melting points were obtained using a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer Models 137 and 735 spectrophotometers with a polystyrene film used for calibration. Proton magnetic resonance spectra were measured with Hitachi Perkin-Elmer Models R-20B and R-24 and Varian Associates Models A-60 and XL-100 spectrometers, with tetramethylsilane as internal reference. Time averaging or Fourier transform techniques were used in several cases. The mass spectra were obtained at 70 eV on a Varian Model M-66 double-focusing cycloidal path mass spectrometer. Optical rotations were measured on a Perkin-Elmer Model 141 digital polarimeter at the sodium D line. A 10-cm cell with a volume of 5 mL was used to contain the solution. Circular dichroism spectra were obtained using a Cary Model 60 spectropolarimeter. Unless specified
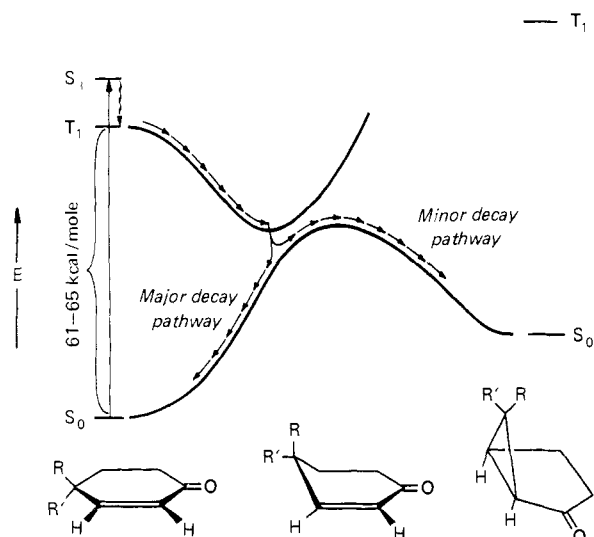
Figure 1. Proposed topology of the T_1 and S_0 potential surfaces along the reaction coordinate cooresponding to the conversion of conjugated enones to bicyclo[3.1.0]hexan-2-ones (lumiketones).

otherwise, solvents and reagents were of commercial reagent grade and were used without further purification.

The optically active shift reagent used in the ^{1}H NMR studies was tris(3-heptafluoropropylhydroxymethylene-*d*-camphorato)europium(III), which was purchased from Willowbrook Laboratory, Inc., or Stohler Isotope Chemicals, Inc. A solution of 0.2 g of shift reagent in 2 mL of carbon tetrachloride (Baker Spectrophotometric) was used as the reagent in the shift experiments and was added with the use of a 100-μL syringe to the solution to be analyzed by ^{1}H NMR.

Gas–Liquid Partition Chromatography. Analyses were made using a Hewlett-Packard F&M Model 5750 gas chromatograph, equipped with dual column flame ionization detection. The column used was 8 ft × $^1/_8$ in. 20% GEXE-60 on Chromosorb W/AW/DMCS, column temperature 180 °C, injection port 300 °C. A Varian Model 920 chromatograph was used for all preparative GLC work. Collections were made using a "U" tube cooled in a Dewar flask containing dry ice-acetone. The columns used follow: A, 10 ft × $^1/_4$ in. 25% PDEAS on Chromosorb P/AW/DMCS (column temperature 190 °C, injection port temperature 260 °C), A' (column temperature 150 °C, injection port temperature 280 °C); B, 10 ft × $^1/_4$ in. 20% GEXE-60 on Chromosorb P (column temperature 225 °C, injection port temperature 290 °C); C, 12 ft × $^1/_4$ in. 15% Apiezon L on Chromosorb W (column temperature 190 °C, injection port temperature 260 °C).

Photolytic Apparatus. A. Immersion Well Apparatus. This consists of a water-jacketed immersion well containing a 450-W Hanovia medium-pressure mercury arc lamp. The immersion well fits into a Pyrex vessel which has a gas inlet and an outlet at the bottom for removing samples for analysis during the photolysis.

B. Rayonet Reactor. This apparatus, supplied by the Southern New England Ultraviolet Co., Inc., consists of a circular array of 16 lamps inside a reflecting surface. Lamps with output concentrated around 2537, 3000, or 3500 Å were used. A cyclindrical vessel containing the solution to be photolyzed was placed in the center of the apparatus.

Synthesis of *dl*-4-Methyl-4-propyl-2-cyclohexenone (10). A solution of freshly distilled 2-methylpentanal (20.0 g, 0.20 mol) and pyrrolidine (14.2 g, 0.20 mol) in 1 L of benzene was heated to reflux, and the water produced was removed using a Dean-Stark separator. After 4 h, 4.3 mL of water had collected, indicating the reaction had gone to completion. The benzene solution was then evaporated to yield a residue that was redissolved in 300 mL of methanol. Freshly distilled methyl vinyl ketone (16.8 g, 0.24 mol) was then added to the ice-cooled methanol solution, which was then allowed to stand at this temperature for 5 h. Aqueous acetic acid (30%, 75 mL) was subsequently added and the solution was heated to reflux for 1 h and then evaporated under reduced pressure. The residue was dissolved in benzene and washed with 10% HCl and water and then dried over Na_2SO_4. The benzene was then removed under vacuum and the remaining residue was distilled to yield 7.3 g (24%), bp 81-83 °C (4 mm) (lit.[15] 101-103 °C (14 mm)). Spectral data: IR ν_{max} 1680 (s), 1120 (m) cm^{-1}; UV λ_{max} 227 nm (ϵ 8460), 322 (25); ^{1}H NMR (CDCl$_3$) δ 6.65 (1.0 H, d, J =

10 Hz), 5.85 (1.0 H, d, J = 10 Hz), 2.42 (2.0 H, t, J = 6 Hz), 0.90–1.98 (9.5 H, m), 1.10 (3.0 H, s).

Synthesis of *N*-Carbobenzoxy-L-proline. A mixture of 40.0 g (0.23 mol) of benzyl chloroformate and 150 mL of 2.0 N NaOH were added simultaneously during a 2.5-h period with vigorous agitation to an ice-cooled solution of 23.0 g (0.20 mol) of L-proline (Aldrich Gold Label, $[\alpha]^{20}_D$ −84° (*c* 4.0, H$_2$O)) in 100 mL of 2.0 N NaOH. After the addition was completed, the reaction mixture was extracted twice with 250 mL of ethyl ether and these extracts were discarded. The aqueous layer was acidified to Congo Red (color change to blue at approximately pH 4) with 6.0 N HCl. The oil that separated was then taken up in 1.0 L of ethyl acetate. This solution was washed with water and dried over Na_2SO_4. After the solvent was evaporated, the remaining oil was placed in 300 mL of hot petroleum ether and hot carbon tetrachloride was added until the cloudpoint was obtained. The mixture was allowed to stand for 3 days during which time crystallization occurred. The crystals which were isolated by suction filtration weighed 41.6 g (84%) and had $[\alpha]^{23}_D$ −61.7°, mp 76–77 °C (lit.[32] α_D −61.7°, mp 76–77 °C).

Synthesis of *N*-Carbobenzoxy-L-proline Pyrrolidide. A solution of *N*-carbobenzoxy-L-proline (41.6 g, 0.168 mol) and triethylamine (17.0 g, 0.170 mol) in 100 mL of dried tetrahydrofuran was cooled in ice. Ethyl chloroformate (18.5 g, 0.170 mol) was then added to this solution at 5–10 °C for 20 min. Homogeneity was maintained with the use of mechanical stirring. After the addition was completed, stirring was maintained for an additional 45 min with cooling. A solution of pyrrolidine (16.4 g, 0.238 mol in 100 mL of dried tetrahydrofuran) was then added in drops to the stirred mixture over 15 min at a temperature below 10 °C. After being stirred for an additional hour with cooling, the solution was filtered and the crystals were washed with ethyl acetate. The filtrate and washings were combined and evaporated under reduced pressure. The residue was dissolved in ethyl acetate and washed with water and aqueous sodium bicarbonate solution. The organic layer was dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crystals that were obtained were triturated with cold acetone. After being dried, these crystals weighed 28.5 g (57%) and had mp 132-133 °C and $[\alpha]^{25}_D$ −13.3° (lit.[15] $[\alpha]^{25}_D$ −14.1°, mp 130-133 °C).

The basic and aqueous layers from above were acidified with 6.0 N HCl. An oil separated, which crystallized after standing for 2 days, to yield 40% of recovered starting material.

Synthesis of L-Proline Pyrrolidide. A mixture of 28.4 g (0.10 mol) of carbobenzoxy proline pyrrolidide and 2.0 g of 10% Pd/C was added to 150 mL of absolute ethanol. Hydrogen gas was bubbled through the well-stirred suspension. The reaction was followed by thin layer chromatography. Baker silica gel plates were spotted with the reaction mixture and then eluted with acetone. The plates were developed in an iodine chamber. The R_f of the reactant was 0.65-0.70 while the R_f of the product was 0.10-0.20. The reaction was complete after 2 days. The reaction mixture was then filtered and evaporated under reduced pressure to leave an oil. This oil was distilled to yield 14.5 g (95%) of pure L-proline pyrrolidide, bp 133-135 °C (4 mm), $[\alpha]^{25}_D$ −104.6° (*c* 0.040, EtOH) (lit.[15] bp 134-136 °C (4 mm), $[\alpha]_D$ −112.5° (*c* 0.91, EtOH)). The ^{1}H NMR spectrum (CDCl$_3$) indicated peaks at δ 3.2-3.8 (7 H, m), 2.75 (1 H, s), 1.6-2.1 (8 H, m) [lit.[15] δ 3.0-3.8 (m), 2.80 (s), 1.4-2.2 (m)).

Synthesis of (+)-4-Methyl-4-*n*-propyl-2-cyclohexenone (10). Method 1. A solution of freshly distilled 2-methylpentanal (7.3 g, 73 mmol) and L-proline pyrrolidide (12.3 g, 73 mmol) in 300 mL of benzene was heated to reflux, and the water produced was removed using a Dean-Stark separator. The reaction produced 1.3 mL of water after 2 h. The benzene solution was then evaporated under reduced pressure. The residue was redissolved in 300 mL of methanol. Freshly distilled methyl vinyl ketone (7.8 mL, 12 mmol) was then added to the ice-cooled solution which was then allowed to remain at this temperature for 5 h. Aqueous acetic acid (30%, 25 mL) was then added and the solution was heated to reflux for 1 h and then evaporated under reduced pressure. The residue was dissolved in benzene and washed with 10% HCl and then water. The organic layer was separated and dried over Na_2SO_4. The benzene was evaporated and the residue was distilled to yield 2.5 g (18%) of **10**, bp 81-83 °C (4 mm), $[\alpha]^{20}_D$ +4.60° (*c* 0.08, CH$_3$OH) (lit.[15] bp 101-103 °C (14 mm), $[\alpha]_D$ +4.96° (*c* 2.26, MeOH)).

Method 2. By substituting 9:1 benzene-methanol for the methanol above and stirring for 27 h instead of 5, we eventually obtained a 10% yield of (+)-**10**, $[\alpha]^{25}_D$ +11.9°.

(+)-4-Methyl-4-phenyl-2-cyclohexenone (9). A solution of 12.5 g (0.077 mol) of L-proline pyrrolidide and 10.3 g (0.077 mol) of 2-phenylpropanal in 300 mL of benzene was heated to reflux and the water produced was removed with a modified Dean-Stark trap. After several hours, the reaction had produced the theoretical amount of water. The benzene solution was evaporated in vacuo and the residue redissolved in a solution that was 9:1 benzene-methanol. The solution was ice cooled and 5.6 g (0.080 mol) of methyl vinyl ketone was added. Stirring was continued for 27 h with the temperature maintained at 7 °C. To this was added 30 mL of 30% aqueous acetic acid and the solution was heated to reflux for 2 h. The solution was then evaporated in vacuo and redissolved in benzene. The solution was washed with 10% HCl and then water, dried (Na_2SO_4), and evaporated in vacuo. The residual oil was distilled to give 1.1 g (8%) of 9, bp 80 °C (0.5 mm), $[\alpha]^{25}_D$ +59.1° (c 0.17, EtOH) (lit.[16] 125-128 °C (3 mm), $[\alpha]^{25}_D$ +54.3° (c 1.05, MeOH)).

The ^1H NMR, mass spectral, IR, and refractive index data were in agreement with those in the literature.[14,15]

(−)-2-Methyl-2-phenylglutaric Anhydride (22). A solution of 1.38 g (7.4 mmol) of 9, $[\alpha]^{25}_D$ +51.2°, in 30 mL of acetone was treated with 2.9 g (19 mmol) of $KMnO_4$, added a small portion at a time over a period of 30 min. After the color of $KMnO_4$ was gone, the solution was filtered and the precipitate was washed with acetone and then with water. The combined filtrate and washings were acidified with dilute H_2SO_4 to pH 1 and extracted with ether. The extracts were dried (Na_2SO_4) and evaporated in vacuo to give an oil. The oil was dissolved in 30 mL of acetic anhydride and the solution was stirred overnight and then heated at reflux for 1 h. The acetic acid was removed in vacuo and the resulting oil was purified by preparative GLC using column C. A white solid, 44.4 mg (3%), was obtained, mp 77-80 °C (lit.[15] mp 75-78 °C), $[\alpha]^{25}_D$ −60.2°.

(−)-2-Methyl-2-n-propylglutaric Anhydride (16). In an exactly analogous manner, 10 ($[\alpha]^{25}_D$ +12.1°) afforded 0.18 g (7.6%) of (−)-2-methyl-2-n-propylglutaric anhydride, $[\alpha]^{25}_D$ −9.1°.

Kuhn–Roth Oxidation of (+)-3-(2-pentyl)cyclopent-2-en-1-one (19). A solution of 8.4 g (85 mmol) of CrO_3 in 50 mL of H_2O was left standing overnight and then filtered through a sintered-glass funnel. To the filtrate was then added 12.5 mL of concentrated H_2SO_4. To a flask containing 122.7 mg (0.66 mmol) of 19 was added 20 mL of the solution prepared above and 20 mL of water. Steam distillation was begun immediately. After 250 mL of distillate had been collected, the residue was acidified (pH <0) and extracted (5 × 150 mL) with ether. The combined extracts were dried (Na_2SO_4) and evaporated in vacuo to yield an oil which smelled like 2-methylpentanoic acid and rotated light positively at 589 nm.

Purification by preparative GLC using preparative column A' gave 20.1 mg (26%) of 2-methylpentanoic acid (20), $[\alpha]^{25}_D$ +2.4 ± 0.50°. The ^1H NMR spectrum showed δ ($CDCl_3$) 0.8-1.1 (m, 3 H), 1.2 (d, 3 H, J = 7 Hz), 1.3-1.7 (m, 4 H), 2.2-2.7 (m, 1 H), 11.0 (brs, 1 H) which compares well with the ^1H NMR of authentic material.

Photolysis of (+)-4-methyl-4-n-propyl-2-cyclohexenone ((+)-10). Run 1. A solution of 0.990 g of 10, $[\alpha]^{25}_D$ +4.60° (c 0.512, t-BuOH), in 6.5 mL of t-BuOH was irradiated in a Pyrex well suspended in a Srinivasan Rayonet photochemical reactor equipped with 16 3500-Å lamps. The progress of the reaction was followed by optical polarimetry and analytical GLC (Table III).

After 72% of the reaction was completed, the products were isolated by preparative GLC using preparative column A.

Substance	Wt collected, mg	α_{exp},[a] deg	$[\alpha]^{25}_D$, deg
Recovered 10	73.5	+0.073	+4.96
Lumi I (18)	49.3	−0.082	−8.35
Lumi II (17)	38.0	+0.059	+7.76
Cyclopentenone 19	84.5	+0.051	+3.01

[a] The material was dissolved in 5.0 mL of t-BuOH.

Run 2. A solution of 8 g of 10, $[\alpha]^{25}_D$ +11.9°, in 160 mL of tert-butyl alcohol was irradiated in a quartz well suspended in a Srinivasan Rayonet photochemical reactor equipped with 16 2537-Å lamps for 12 h. Progress was followed by analytical GLC. The products were isolated by preparative GLC using column A. All fractions except the last were rechromatographed to ensure purity.

Table III

Time, h	α_{exp}, deg	% disappearance of 10
0	+0.701	
6.5	+0.690	~4
24.0	+0.650	~10
50.0	+0.598	~18
72.0	+0.551	~24
100.0	+0.501	~30
157.0	+0.384	~42
325.0	+0.192	~72

Substance	Wt collected, mg	α_{exp},[a] deg	$[\alpha]^{25}_D$, deg
Recovered 10	292.8	+0.696	+11.9
Lumi 1 (18)	27.6	−0.073	−13.13
Lumi 2 (17)	30.2	+0.040	+9.96
Cyclopentenone 19	141.2	+0.221	+7.81

[a] Material dissolved in 5.0 mL of EtOH.

Photolysis of (+)-4-Methyl-4-phenylcyclohexenone (9) in Benzene. A solution of 0.7 g of 9, $[\alpha]^{25}_D$ +62.88°, in 320 mL of benzene was irradiated through Pyrex, in an immersion well apparatus for 24 h. The products were separated by GLC using preparative column B. All fractions were rechromatographed to ensure purity.

Substance	Wt collected, mg	α_{exp},[a] deg	$[\alpha]^{25}_D$, deg
Recovered 9	69.2	+0.43	+62.32
11	19.3	−0.006	−3.24
12	7.1	+0.061	+85.92

[a] Material dissolved in 5 mL of EtOH.

Photolysis of 9 in Ethanol and Methanol. A solution of 1.1 g of 9, $[\alpha]^{25}_D$ +53.85°, in 320 mL of absolute ethanol was irradiated for 24 h in the apparatus described above. The products were separated as described above.

Substance	Wt collected, mg	α_{exp},[a] deg	$[\alpha]^{25}_D$, deg
Recovered 9[b]	0.5	+0.005	+51.25
11	24.1	−0.0085	−1.76
12	12.9	+0.207	+80.52
13	10.2	−0.009	−4.41

[a] Material dissolved in 5 mL of EtOH. [b] Rechromatographed twice.

Similarly, after irradiating a solution of 0.4 g of 9, $[\alpha]_D$ +51.16°, in 320 mL of 90% aqueous methanol for 7 h, 12 mg of 9 was recovered, $[\alpha]^{25}_D$ +50.39°.

Irradiation of (−)-6-exo-Methyl-6-endo-propylbicyclo[3.1.0]-hexan-2-one (18). A solution of 32.3 mg of 18 dissolved in 5 mL of t-BuOH was irradiated through Pyrex using a Srinivasan Rayonet photochemical reactor equipped with 16 3000-Å lamps. After 5 h the reaction mixture was shown to be approximately a 1:1:2 ratio of 17, 18, and 19. The reaction mixture was separated by preparative GLC using preparative column A. An observed optical rotation of −0.002 to −0.003° was obtained for 17 while zero rotation was observed for 19.

Photolysis of 6-exo-Methyl-6-endo-phenylbicyclo[3.1.0]hexan-2-one (13). A solution of 13.1 mg of 13 in 15 mL of absolute ethanol was irradiated in a quartz well suspended in a Srinivasan Rayonet photochemical reactor equipped with 16 2537-Å lamps for 30 min. Analytical GLC indicated about 60% conversion. The product was isolated by preparative GLC using column B. The ^1H NMR spectrum ($CDCl_3$) showed δ 1.45 (s, 3 H), 1.0-2.5 (m, 6 H), and 7.3 ppm (s, 5 H), which corresponds to the data reported[15] for 14.

Photolysis of 5-Methyl-6-endo-phenylbicyclo[3.1.0]hexan-2-one

(11). A solution of 2 mg of **11** in 15 mL of absolute ethanol was irradiated in a quartz well suspended in a Srinivasan Rayonet photochemical reactor equipped with 16 2537-Å lamps for 30 min. The reaction was monitored by analytical GLC which showed little or no loss of starting material. No volatile products could be detected.

Photolysis of 4-Methyl-3-phenylcyclohex-2-en-1-one (12). A solution of 5.1 mg of **12** in 15 mL of absolute ethanol was irradiated in a quartz well in a Srinivasan Rayonet photochemical reactor equipped with 16 2537-Å lamps for 1 h. Analytical GLC showed a peak with retention time the same as one of the two unrecovered products of photolysis of **9**. The peak differed from that attributed to **14** (vide supra) and is tentatively attributed by us to compound **15**. There was insufficient quantity of material for further characterization.

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Differentiation of Excited-State and Biradical Processes. Photochemistry of Phenyl Alkyl Ketones in the Presence of Oxygen

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Abstract: The photochemistry of butyrophenone, valerophenone, γ-methylvalerophenone, and γ-phenylbutyrophenone has been examined in the presence of oxygen. The use of triplet quenchers to tune the triplet lifetime to a conveniently short value allows the differentiation of triplet state and biradical reactions. Typically oxygen quenches the triplet state with rate constants of $\sim 4 \times 10^9$ M^{-1} s^{-1} and interacts with the biradicals with $k_8 \sim 7 \times 10^9$ M^{-1} s^{-1}. The interaction results in the formation of an intermediate which has as its main decay path the fragmentation to acetophenone, olefin and the regeneration of oxygen. About 75% of these intermediates decay giving type II products, while the other 25% yields a hydroperoxide. The ratio of products is probably controlled by spin statistical factors. Previous reports indicating that oxygen has no effect on the Norrish type II reaction are incorrect.

The behavior of the biradicals generated in the Norrish type II reaction has received considerable attention during the last few years. Several substrates have been shown to trap these biradicals in reactions involving hydrogen abstraction,[2,3] addition to double bonds,[4] and electron transfer.[5,6] Far from being unique, the examples which have been examined represent a few cases where the reactions of the biradical can be easily differentiated from those of the precursor excited states.

Photochemical processes involving the intermediacy of more