Systematic Structural Modifications in the Photochemistry of β,γ-Unsaturated Ketones. I. Cyclic Olefins

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Abstract: The photochemical behavior of six β,γ-unsaturated ketones (**5a–e, 19**), whose double bond is incorporated into rings of four to eight members, has been studied under acetone sensitization and direct irradiation. In the triplet manifold, the four and five-membered rings undergo the oxadi-π-methane (ODPM) rearrangement, but the larger rings do not. Only the four-membered compound (**5a**) shows α cleavage upon direct irradiation, but all of the others give cyclobutanols. The seven- and eight-membered compounds yield oxetanes, a reaction which is favored by high olefin π electron density and the ability of the olefin to twist in the excited state. Several thermal rearrangements of the products to starting ketone and to one another have been noted.

In view of the rich photochemistry exhibited by ketones and olefins, it might be expected that incorporation of both groups into the same molecule would lead to a variety of fascinating reactions. Indeed, recent work on β,γ-unsaturated ketones[1] has uncovered at least five distinct photochemical pathways, but the factors which influence the competition between them are not yet understood.

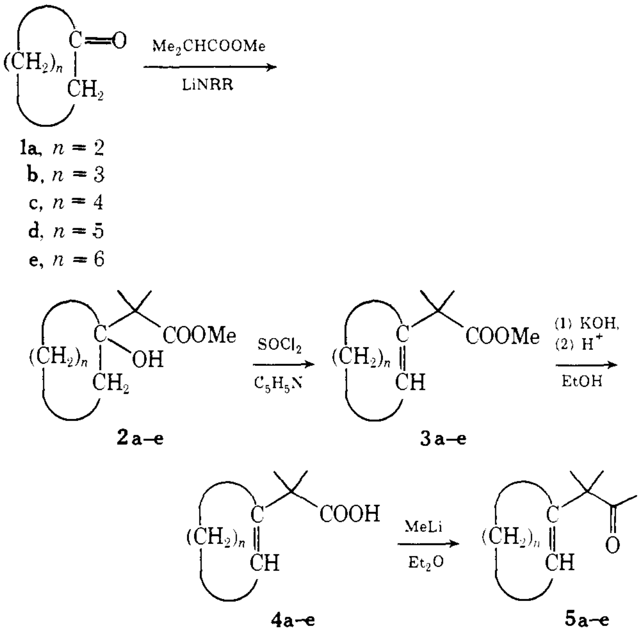
The study to be described here was undertaken with the aim of isolating one structural parameter, flexibility of the double bond. We prepared a series of β,γ-unsaturated ketones in which the olefinic moiety was incorporated into a ring of four to eight members while the carbon separating the two π systems generally carried two methyl groups to prevent olefin migration. It was found that the triplet state photochemistry depended entirely on the rigidity of the double bond, the oxadi-π-methane (ODPM) rearrangement occurring only in the smaller rings. The singlet photochemistry was controlled additionally by the electron-donating ability of the double bond, as evidenced by a correlation of both the yield of oxetane and the quantum yield for ketone disappearance with the olefin π ionization potential. A second example of the α-methyl effect[2] was discovered in the five-membered olefin; that is, intersystem crossing was observed only when the methyl groups at the central carbon were omitted.

Synthesis of Ketones and Selected Products

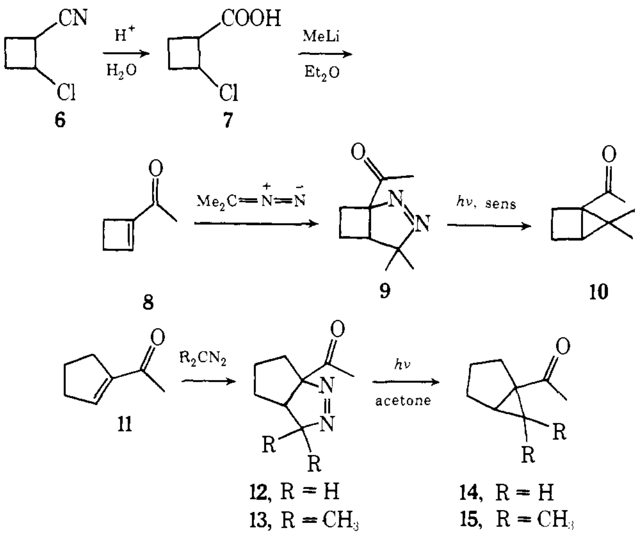
The β,γ-unsaturated ketones used in this study were prepared by first reacting the appropriate cycloalkanone with the enolate of methyl isobutyrate, an elegant procedure developed by Rathke[3,4] and in most cases a distinct improvement over the Reformatsky reaction (*cf.* Scheme I). The resulting hydroxy esters were dehydrated with phosphorus pentoxide or with thionyl chloride in pyridine. Saponification of the olefinic esters and treatment of the resulting carboxylic acids with methyllithium[5] provided ketones **5a–e** in high yield (*cf.* Table IV). The same sequence was followed in preparing normethyl compound **19** except that the enolate of ethyl acetate[3] was employed.

Authentic samples of the ODPM rearrangement products **10, 14,** and **15** were prepared by 1,3-dipolar cycloaddition of 2-diazopropane[6,7] or diazomethane to 1-acetylcyclopentene and 1-acetylcyclobutene (*cf.* Scheme II). Triplet sensitized loss of nitrogen from the pyrazolines led to the desired products.[8] 1-Acetylcyclobutene was obtained about 90% pure by hydrolysis of 1-cyano-2-chlorocyclobutane[11] (**6**) and treatment of the β-chloro acid **7** with methyllithium. Similar attempts to prepare **22** were unsuccessful.

Scheme I



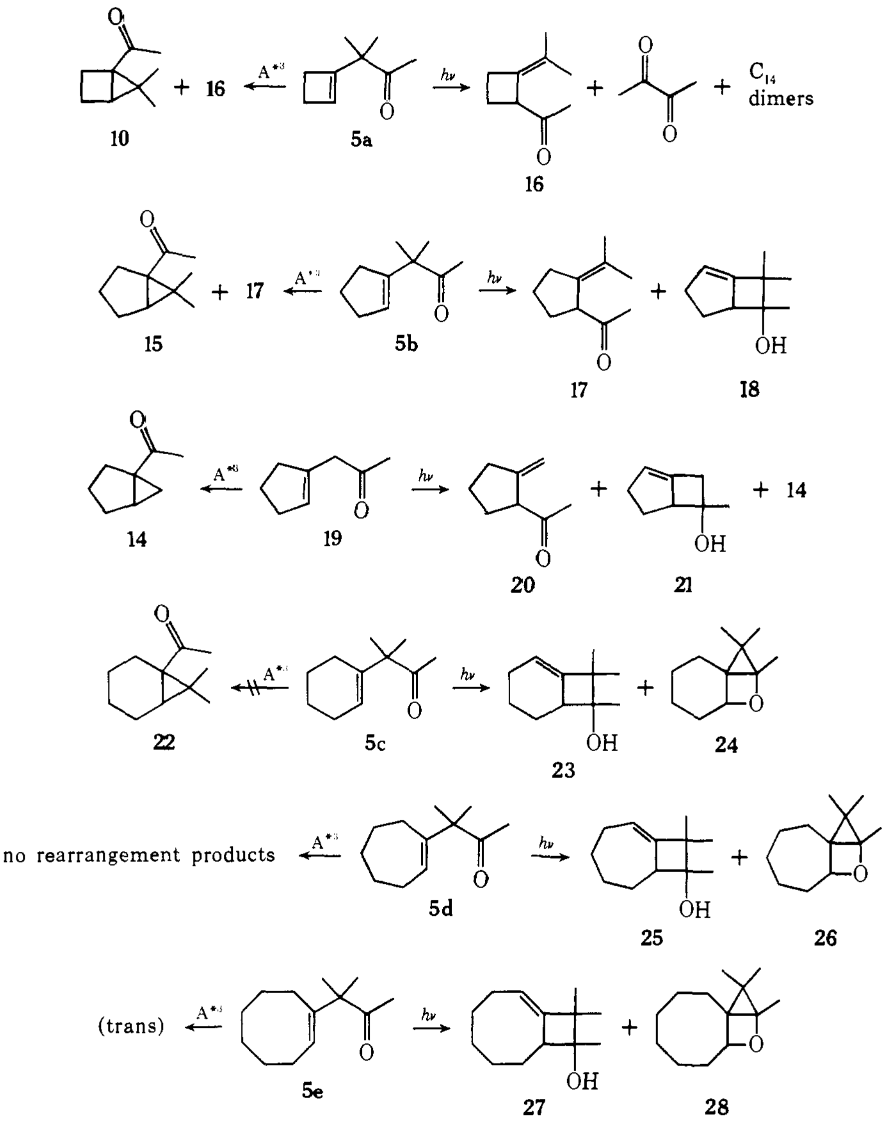
Scheme II



Results

Acetone Sensitization. The photochemical pathways followed by ketones **5a–e** and **19** are depicted in Scheme III. Cyclopropyl ketones **10, 14,** and **15** isolated from irradia-

Scheme III. Direct and Acetone (A) Sensitized Irradiation of β,γ-Unsaturated Ketones

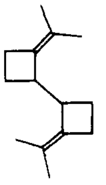


tion of **5a**, **5b**, and **19** in acetone exhibited identical spectral properties to the authentic compounds described above. Sensitized irradiation of **5c** gave only very inefficient destruction of starting material and no products aside from those due to acetone photolysis could be detected by nmr of the concentrated photolysate. Thus there is a clear trend toward triplet sensitized ODPM rearrangement only in the smaller rings.

Irradiation of **5d** in acetone again resulted in slow disappearance of starting material without formation of isomeric products. Column chromatography of the complex mixture, followed by preparative vpc, allowed isolation of two compounds whose nmr and mass spectra suggested that one hydrogen atom in **5d** had been replaced by an acetyl and an acetonyl group. It appears, therefore, that when rearrangement is slow, the β,γ-unsaturated ketone is attacked by excited acetone or its primary photolysis products.

Since triplet sensitized olefin cis-trans isomerization had been observed previously in several systems,[12-14] it seemed possible that this reaction might also be occurring in **5e**. In fact a new vpc peak of similar retention time to **5e** was observed during the course of irradiation in acetone and its mass spectrum, obtained on an LKB vpc-mass spectrometer, was identical with that of **5e** except for some minor differences in peak intensities. Unfortunately, attempts to isolate this material or to synthesize authentic trans **5e** were unsuccessful.

Direct Irradiation. The structures of the acyl shift products **16**, **17**, and **20** were apparent from their spectral data, given in the Experimental Section. That biacetyl was formed during irradiation of **5a** was proven by observation of its characteristic uv-visible absorption spectrum and comparison of vpc retention time with that of authentic material. None of the other ketones produced detectable amounts of biacetyl on direct irradiation. The formation of acetyl radicals from **5a** suggested that products from recombination of hydrocarbon radicals (referred to in Scheme III as C_{14} dimers) should also be present. In fact three vpc peaks were observed at reasonable retention times for such hydrocarbons. The two major products were isolated and assigned structures **29** and **30** on the basis of spectral data. Although the third peak was so minor as to discourage isolation, it is presumed to be the other possible dimer **31** (see Experimental Section).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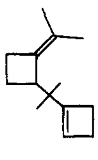
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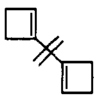
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Direct irradiation of the ketones with five-membered and

Table I. Quantum Yields for β,γ-Unsaturated Ketones

Compd	Direct[a] Φ_{-k}[c]	Direct[a] Φ_p[d]	Sensitized[b] Φ_{-k}[c]	Sensitized[b] Φ_p[d]
5a	0.58	**16**, 0.28	0.45	**10**, 0.09; **16**, 0.22
5b[e]	0.31	**17**, 0.04; **18**, 0.02	0.25	**17**, 0.15; **15**, 0.03
19	0.22	**20**, 0.01; **21**, 0.06; **14**, 0.02	0.35	**14**, 0.12
5c	0.24	**23**, 0.10; **24**, 0.02	0.009	
5d	0.18	**25**, 0.03; **26**, 0.02	0.05	
5e	0.15	**27**, 0.007; **28**, 0.05	0.05	**28**, 0.005[f]

[a] In benzene. [b] In acetone. [c] Ketone disappearance. [d] Appearance of specified product; estimated reliability ±15%. [e] The figures for **5b** are more reliable than the ones given in ref 14. [f] Attributable to direct light absorption by **5e**.

larger rings gave cyclobutanols in varying amounts. Formation of **18** was not noticed at the time of our preliminary report[14] on account of its tendency to rearrange; in fact, its presence was suspected only when cyclobutanol **21** was discovered among the products from ketone **19** (see below). Oxetanes **26** and **28** were isolated by column chromatography and preparative vpc, respectively. These materials were characterized on the basis of spectral data and their immediate reversion to ketones **5d** and **5e** on treatment with acid.[15] In order to search for oxetane **24**, a solution of **5c** in benzene was irradiated until no ketone remained. The nmr spectrum of the material remaining after removal of solvent showed alcohol **23** plus a smaller set of peaks which closely matched those from oxetane **26** (*cf.* Table V). Addition of acid caused immediate disappearance of these peaks and formation of ketone **5c**. Although isolation of this oxetane was not possible, the nmr spectrum indicates its amount to be about 17% that of alcohol **23**.

Mechanistic Studies. Quantum yields for disappearance of starting material and for product formation were measured for each ketone by vpc using internal standards. As shown in Table I, formation of volatile products generally accounted for less than half of the ketone which reacted. Tlc of irradiated mixtures always left a spot at the base line, which is presumably due to polymers. Two important features of Table I are the steadily decreasing value of Φ_{-k} under direct irradiation as one proceeds toward larger rings and the sharp break in efficiency of the sensitized reaction between the five- and six-membered rings.

Table II summarizes the uv spectra of the ketones studied and shows that they are all very similar. As indicated in the fourth column of Table II, the quantum yield for ketone disappearance is hardly affected by addition of 0.1 *M* 2,2,6,6-tetramethylpiperidine-1-oxyl (nitroxyl), a powerful quencher of singlets and triplets.[17] Clearly, the lifetime of the photochemically reactive excited state is very short and it decreases with increasing ring size in the dimethyl series **5a–e**. Attempts to monitor formation of ketone triplets employing cyclohexadiene dimerization gave a positive result only in the case of **19**, which lacks the α-methyl groups.

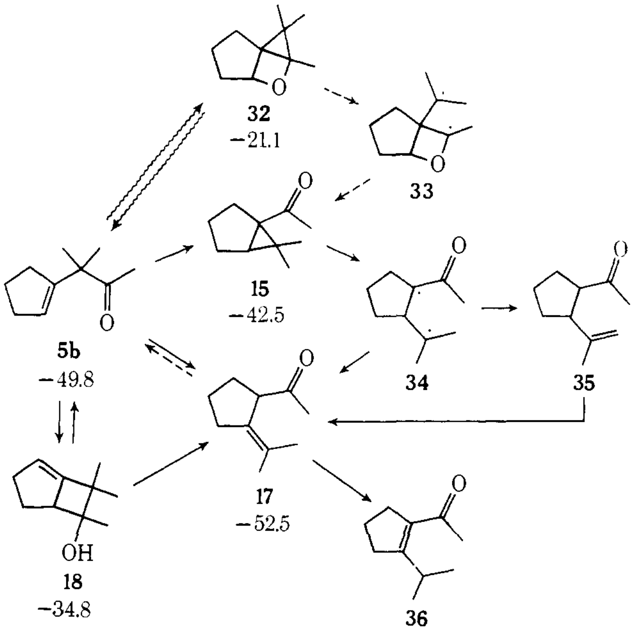
Table II. Uv and Mechanistic Data for β,γ-Unsaturated Ketones

Compd	λ_{max},[a] nm	ϵ_{max}[a]	Φ_0/Φ[b]	$IP_n(\pi)$[c]	Φ_{dimers}[d]	Biacetyl[e] yield, %
5a	288, 296	106	1.53	9.69	0	1.2
5b	300	118	1.40	9.51	0	0.1
19	290	75	1.85	9.65	0.014	0
5c	299	100	1.32	9.45	0	<0.9
5d	298	106	1.06	9.39	0	<0.6
5e	300	119	1.03	9.40	0	<0.7

[a] In hexane. [b] Ketone disappearance in the absence and presence of 0.1 *M* 2,2,6,6-tetramethylpiperidine-1-oxyl. [c] Vertical ionization potential (eV) of the π orbital. See ref 16. [d] Dimerization of 0.1 *M* 1,3-cyclohexadiene in benzene. [e] Measured by visible spectroscopy on irradiated solutions in benzene.

Interconversion of Products. A difficulty in the study of β,γ-unsaturated ketones is that many of the products are photochemically or thermally unstable. Furthermore, as shown in Scheme IV, all of the products can rearrange to starting material or to other products by chemically reasonably pathways. Compound **5b** was picked for illustration because it actually undergoes many of these rearrangements.

Scheme IV. Possible Pathways for Interconversion of a β,γ-Unsaturated Ketone and Its Photoproducts[a]



[a] Solid arrows indicate reactions observed in **5b**; wavy arrows are those observed with the seven- and eight-membered rings; dashed arrows represent reactions shown not to occur. Heats of formation calculated by group additivity[18] are shown below each compound.

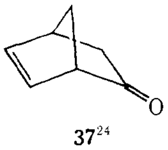
Three of the four products are thermodynamically unstable with respect to starting material[18] and two of these have been found to revert even under mild conditions. Thus, the oxetanes go back to starting ketone on treatment with acid while cyclobutanol **18** rearranges to ketones **5b** and **17** on attempted preparative vpc or silica gel tlc. Analytical vpc on QF-1 of the product mixture from direct irradiation of **5b** gave well-separated, symmetrical peaks, indicating that no rearrangement was taking place under these conditions. This conclusion is supported by the good agreement between the composition of the mixture obtained by vpc with that determined by nmr. The instability of **18** must be due in part to its high ring strain energy. Although the parent hydrocarbon bicyclo[3.2.0]hept-1-ene is known,[19] the isomeric bicyclo[3.2.0]hept-1(7)-ene is extremely unstable.[20] Rearrangement of a cyclobutanol to β,γ-unsaturated ketones is much slower in **21**, which lacks the gem dimethyl group. This compound was easily isolable by preparative vpc, although treatment with acid eventually rearranged it to **19** and the α,β-unsaturated ketone derived from **20**. The acyl shift product **17** did not revert to starting ketone upon uv irradiation; however, the double bond tended to go into conjugation if a pure sample was stored at ambient temperature.

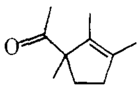
Cyclopropyl ketone **15** was a very unpleasant material indeed; on attempted preparative vpc or treatment with acid, it produced a mixture of **17**, **35**, and **36**. Fortunately, it survived analytical vpc on certain columns and could be isolated by fluorisil column chromatography. Direct irradiation of **15** produces **35** by the expected photochemical γ-hydrogen abstraction.[21] Compound **10** was stable to vpc only on a ⅛ in. SP-1000 column; with all others it underwent extensive rearrangement to **16**. In contrast to these cyclopropyl ketones, **14** proved to be so stable that it would survive preparative vpc. The difference between **14** and **15**, coupled with the fact that 1,1-dimethyl-2-acetylcyclopropane undergoes a facile thermal 1,5-hydrogen shift,[22] suggests that the lability of **15** may be due to the presence of an accessible γ-hydrogen.

Discussion

Acetone Sensitization. The effect of ring size on the triplet ODPM reaction is clear: the four-membered olefin is more efficient than the five-membered one while the larger rings do not undergo this reaction. These results complement the work of Hancock,[13] who showed that cis-trans isomerization[12-14,23] supersedes ODPM rearrangement when the olefin can rotate freely in the excited triplet state. The decreasing quantum efficiency of rearrangement in the series **5a–c** suggests an increasing rate of radiationless decay due to torsional motion about the double bond.

In agreement with the above conclusion, a survey of the literature reveals that triplet sensitized ODPM rearrangements of simple β,γ-unsaturated ketones are most common when the olefin is rigid, as shown by the examples below.[24-28] At the other end of the spectrum are the ketones[13-15,29-34] which do not produce ODPM products under triplet sensitization and in most cases the double bond is part of a ring larger than five or is acyclic. The exceptional ketones can be divided into three categories: (a) nonrigid systems which give ODPM products, (b) rigid systems which do not give ODPM products, and (c) compounds in which the olefin is part of a six-membered ring. The latter category contains many steroids in which rigidity depends on the particular structure and in which conformational effects may become important. Attempts to observe ODPM products in such systems have given both positive[32-34] and negative[32,33,35] results.


37[24]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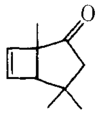
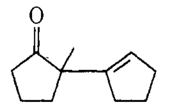

39[26]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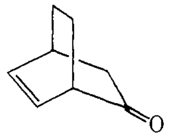
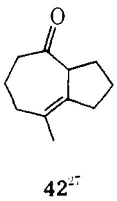
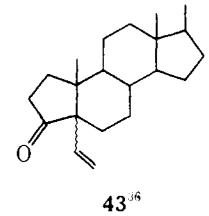
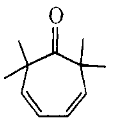
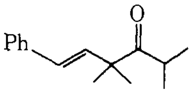

41[28]

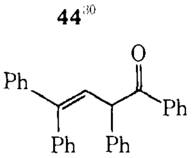
Of the simple nonrigid ketones, only **42** and **43** have been found[27,36] to undergo ODPM rearrangements, but with lower efficiency than the rigid systems. Although quantum yields in these cases would be helpful, it may be that observation of the rearrangement in a flexible olefin depends simply on how long one is willing to irradiate and on the rate at which polymeric materials are formed. Cyclopropyl ketones have also been obtained from the nonrigid compounds **44–46** but the fact that triplet **47** does not rearrange disallows any generalization regarding the effect of conjugation.


42[27]


43[36]


44[30]


45[37]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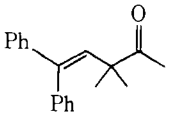
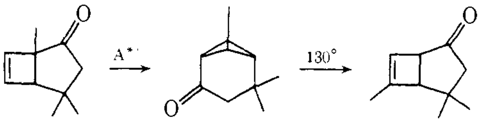

47[34]

Aside from the steroids, no case has been reported of a rigid β,γ-unsaturated ketone whose triplet fails to produce a cyclopropyl ketone. In one apparent exception,[39] it has since been shown[26] that the ODPM product **48** escaped detection on account of its facile rearrangement to **49**. An insidious aspect of this thermal reorganization is that **49** is indistinguishable from the 1,3-acyl shift product of **39**.



39 **48** **49**

The presence of 1,3-acyl shift products **16** and **17** in the acetone-sensitized irradiations was unprecedented and unexpected. Since the ODPM products were capable of rearranging to **16** and **17**, a problem arose in deciding whether they were actually primary triplet products. The fact that **15** was isolable allowed us to demonstrate that it did not rearrange to **17** during work-up of the irradiation mixture or on analytical vpc. Next, the possibility that **15** rearranged to **17** during the photoreaction was ruled out by showing that **15** was inert to acetone sensitization; furthermore, both of these products formed at the same rate, even in the presence of a small amount of triethylamine. Direct light absorption by **5b** seemed unlikely since it was present at such a low concentration (0.04 *M*) that the ratio of its absorbance to that of acetone at 313 nm was only 0.048. **17** was not a product of **5b** sensitized by acetone singlet because addition of 0.052 *M* biphenyl, a good triplet quencher,[40] reduced the rate of formation of **15** and **17** by a factor of 3.5 but did not change their ratio. If singlet sensitization were important in **5b**, one would also expect it in **5c**, yet no cyclobutanol **23** was detected during irradiation of **5c** in acetone. Finally, the absence of **18** in sensitized irradiation of **5b** argues strongly that the singlet of **5b** is not produced. Having eliminated all of the trivial explanations which we could devise, we conclude that triplet acetone sensitizes the 1,3-acyl shift reaction of **5a** and **5b**.

Conversion of a β,γ-unsaturated ketone to its 1,3-acyl shift product may proceed by concerted shift at one mechanistic extreme to recombination of free radicals at the other.

One need not search very far to find precedent for α cleavage from ketone triplet states. Not only is this a common reaction of ordinary alkanones,[41] but a case of triplet sensitized photoepimerization of a β,γ-unsaturated ketone was recently reported.[35] However, the acyl shift reaction of triplet **5a** does not appear to involve free radicals because none of the expected dimers (**29–31**) are found. One might postulate that **16** is derived from acyl-allyl recombination within a solvent cage but it seems unlikely that the cage effect would exceed that found in the singlet pair. Perhaps the best rationalization is a concerted 1,3-acyl shift, with the inertness of the more flexible compounds **5c–5e** caused by rapid radiationless decay of the triplet. Although perusal of the literature[25,28] leads to some question about the generality of triplet sensitized 1,3-acyl shifts, a second example has very recently appeared.[42]

Ketone **19** differs from the others employed in this study by the absence of the α-methyl groups. As seen in Tables I and II, it is the only case in which direct irradiation leads to any ODPM product and it is the only one which sensitized dimerization of cyclohexadiene to a measureable extent. The experiments with added nitroxyl were particularly revealing because only the ODPM product was quenched. We conclude that reactions of the singlet state are slowed by removal of the α-methyl groups. Intersystem crossing to the triplet is then able to compete and the characteristic triplet product **14** is observed. This case exactly parallels one which we reported earlier[2] and the reader is referred to that work for a mechanistic discussion.

Direct Irradiation. Ketones **5a–e** do not intersystem cross to any measurable extent because no triplet products are detected under direct irradiation. Therefore, the decrease in Φ_{-k} seen on addition of nitroxyl (*cf.* Table II) must be due to quenching of the singlet state. Since the larger rings are more difficult to quench, either the singlet reaction rate or the decay rate must increase with ring size. However, the decreasing quantum yield in the series **5a–e** argues in favor of the latter hypothesis. In seeking an explanation for this correlation of radiationless decay rate with ring size, we noted an interesting trend in the ionization potentials (IP) of the π orbital, shown in the fifth column of Table II. These data, which were obtained from photoelectron spectra[16] of ketones **5a–e,** exactly parallel the IP's of the cycloalkenes themselves.[43] The decreasing IP with increasing ring size can be attributed to destabilization of the π orbital by the inductive effect of added alkyl groups. Alternately, one can view the IP as a measure of the electron-richness of the double bond. We suggest that increasing electron density in the olefin enhances singlet radiationless decay.

Aside from the variation in decay rate with ring size, which will be discussed below, there is an obvious change in the nature of the products. Only the four-membered ring undergoes α cleavage but the five-membered rings give 1,3-acyl shift products and cyclobutanols. The latter reach a maximum in the six-membered ring but oxetane formation gradually takes precedence as the ring size is further increased. Our rationalization of these results begins with the generally accepted mechanism for oxetane formation.[44,45]

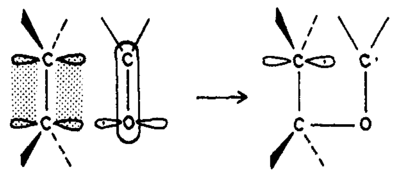


Figure 1. Pulsed ^{13}C FT nmr spectrum of chlorocyclohexane at −80°. Chemical shifts are given in parts per million in δ scale.

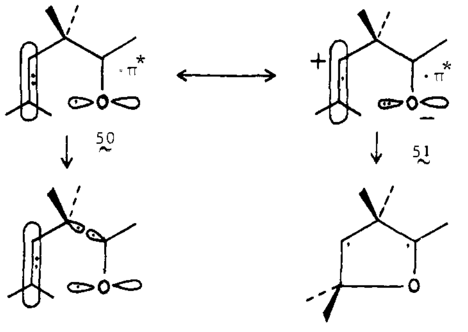
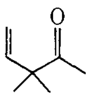


Figure 2. Pulsed ^{13}C FT nmr spectrum of fluorocyclohexane at −90° (in a mixture of methanol and acetone). Upper trace represents the high-field portion (20–35 ppm) in more detail.

Irradiation of a ketone produces its $^1(n,\pi^*)$ state in which one electron has been promoted from the oxygen nonbonding (n) orbital to the π* orbital. This excited ketone can react with an olefin in two distinct ways:[14,41] by direct addition of the olefin π orbital to that of the ketone or by initial attack of the electron deficient n orbital on the olefin π orbital (Figure 1). The first case, which is favored by electron-poor olefins, is inappropriate for our purposes because the one-carbon bridge between the π systems prevents them from attaining the required coplanar geometry; moreover, our oxetanes appear only in the more electron-rich olefins.

Consideration of the second case leads to a plausible explanation for our results. The $^1(n,\pi^*)$ excited state is represented in Figure 2 as a resonance hybrid of structure **50** and the charge-transfer (CT) structure **51,** in accord with recent MO calculations on β,γ-unsaturated ketones.[46] The importance of **51** increases with the polarizability of the olefin π electrons, which in turn is reflected by a lower π ionization potential. By analogy with previous studies,[41,45] this CT structure presumably lies on the reaction pathway to oxetane but ring closure requires rotation of the olefin p orbital into nearly the same plane as the oxygen n orbital. If one postulates that sufficient rotational motion in the excited state can be achieved only when the double bond is acyclic or in a ring of six members or larger, the steadily increasing yield of oxetane in the series **5c–e** becomes understandable. However, olefin flexibility cannot be the only requirement for production of oxetane because we have been unable to detect any such product from irradiation of **52.**[14] Aside from the obvious geometric requirement that the carbonyl and olefin moieties be situated so as to allow cycloaddition, we conclude that oxetane formation from β,γ-unsaturated ketones is favored when the olefin is both flexible and electron rich.



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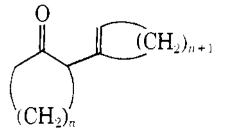


53a, $n = 3$
b, $n = 4$
c, $n = 5$

While this work was in progress, Cookson and Rogers[15] reported formation of a cyclobutanol from **53a** and oxetanes from the corresponding seven- and eight-membered compounds, **53b,c.** Although these ketones were a mixture of α,β- and β,γ-unsaturated isomers, their results are in accord with our own.

The picture just presented is also capable of explaining the faster rate of singlet decay in the larger rings. The re-

Table III. Identification of Vpc Columns

Letter	Column	Letter	Column
a	1/8 in. × 6 ft 10% SP-1000	g	1/8 in. × 20 ft 10% QF-1
b	1/8 in. × 18 ft 10% SP-1000	h	1/4 in. × 8 ft 10% QF-1
c	1/8 in. × 10 ft 10% XE-60	i	1/4 in. × 6 ft 10% OV-17
d	1/8 in. × 6 ft 20% DEGS	j	1/4 in. × 6 ft 10% FFAP
e	1/8 in. × 6 ft 5% OV-17	k	1/4 in. × 8 ft 20% DEGS
f	1/8 in. × 6 ft 10% FFAP	l	1/4 in. × 6 ft 10% DEGS

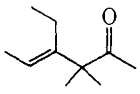
cent discovery[41,45,47] that electron-rich olefins are particularly good quenchers of alkanone singlet states immediately led to the suggestion that CT complexes were involved. Since the CT complexes were found to decay about an order of magnitude faster than they proceeded to oxetane,[44,45,48] it appears that charge transfer provides an efficient mechanism for radiationless decay. In the present system, a lower value for the olefin π IP leads to increased importance for CT structure **51**, which in turn leads to faster radiationless decay.

In light of the above explanation, the similarity of extinction coefficients (ϵ) for **5a–e** presents an interesting problem. It has been proposed[49] that increased olefin substitution raises ϵ when the geometry is constant and that no enhancement occurs when the olefin and carbonyl groups are coplanar. Since the observed values are about 100, there must be some interaction between the carbonyl n and olefin π orbitals. It follows that the compounds with the lower olefin π IP should exhibit a greater ϵ. The absence of such a trend suggests either that the effect of substitution on IP is far greater than it is on ϵ or that conformational differences compensate for the expected variations. No correlation of ϵ with photochemical behavior is apparent in this series of compounds.

Cyclobutanol formation has been reported previously in studies of β,γ-unsaturated ketones[14,15,50] and appears almost universally in the compounds reported here. Its only requirement seems to be geometric proximity of the allylic γ-hydrogen and the carbonyl oxygen. Ketone **5a** is the only one in which this distance is excessive, but in view of the instability of **18**, the cyclobutanol from **5a** could be so unstable as to preclude isolation. The data for the larger rings **5c–e** indicate that cyclobutanol and oxetane formation are competitive singlet state processes.

We were intrigued by the observation that only **5a** gave products of α cleavage, particularly since we had already noted[14] that **52** also showed this behavior. In fact, a pattern began to unfold that only β,γ-unsaturated ketones with high olefin π IP's would exhibit α cleavage. Based upon a perfect correlation in nine compounds, we devised the following explanation, again using Figure 2. α cleavage[51] depends upon stabilization of the incipient acyl radical by overlap with the half-filled oxygen n orbital lying in the same plane.[52] When the n orbital contains two electrons as in **51**, this overlap should be no more effective than it is in the ground state. α cleavage should therefore diminish when the importance of **51** as a description of the excited state increases. Since we already concluded that **51** is most favored in electron-rich olefins, it follows that α cleavage should be suppressed in such cases.

Unfortunately, this simple rationalization cannot be the entire answer because ketone **54** was found to produce more biacetyl than **5a**, although its olefin π IP (9.46 eV) was similar to that of **5c**. Conformational effects or stability of the incipient radicals may also influence α cleavage but further study will be required to evaluate these factors.



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Experimental Section

Materials and Equipment. Vpc was carried out using a Hewlett-Packard F & M Scientific Model 700 gas chromatograph and an Aerograph HY-Fl with columns described in Table III. Nmr spectra were obtained in CCl_4 using a Varian A-56/60-A or a Perkin-Elmer R-12 spectrometer while ir spectra were taken on a Beckman IR-8. Mass spectra were run on a CEC21-110B double focusing mass spectrometer and uv spectra were run on a Cary 17. All photochemical experiments employed a 450-W Hanovia lamp, with a K_2CrO_4 (0.2 g/l.) filter solution and a corex sleeve to isolate 313-nm light.

Synthesis of β,γ-Unsaturated Ketones 5a–e and 19. Methyl 2-Methyl-2-(1-hydroxycycloalkyl)propanoate (2a–e). Lithium *N*-isopropyl-*N*-cyclohexylamide[3,4] was prepared at −78° under N_2 by adding dropwise 55.5 ml of 2.1 *M* *n*-butyllithium (0.116 mol) in hexane to 18.6 g (0.116 mol) of isopropylcyclohexylamine in 100 ml of anhydrous THF. After addition was complete, the solution was stirred for 15 min; then 10 g of (0.116 mol) methyl isobutyrate was added dropwise to the mixture at −78°. Twenty minutes later, dropwise addition of 1 equiv of ketone was begun. After stirring at −78° for 1-2 hr, the reaction was worked up cold by acidifying with 20% hydrochloric acid and extracting three times with ether. The extracts were washed with saturated NaCl solution and dried over $MgSO_4$. **2b**, **2c**, and **2d** were obtained by rotary evaporation of the ether and used directly in the next step. **2a** and **2e** were distilled, bp 64-67° (1.4 mm) and 130° (1 mm), respectively.

β-Hydroxy Esters 2a–e *via* Reformatsky Procedure. Ethyl α-bromoisobutyrate and the cyclic ketones were reacted according to Frankenfeld and Werner,[53] giving the yields shown in Table IV.

Methyl 2-Methyl-2-(cycloalk-1-enyl)propanoate (3a–e). (a) Phosphorus Pentoxide Method. P_2O_5 (15 g) (0.108 mol, 20% excess) was placed in a three-neck flask containing 200 ml of benzene under N_2. β-Hydroxy ester (0.09 mol) was added dropwise at a moderate rate with mechanical stirring. The reaction mixture was then refluxed for about 3 hr until the hydroxy ester had disappeared (analysis by vpc). The P_2O_5 formed a dark, viscous deposit on the walls of the flask. The mixture was cooled to room temperature and filtered through alumina. After removal of benzene on the rotary evaporator, the residue was distilled through a packed column. **3a** was accompanied by two lactone by-products but **3c** was essentially pure without being distilled. **2e** underwent very rapid dehydration to give **3e**, bp 89-90° (1.5 mm).

(b) Thionyl Chloride–Pyridine Method. β-Hydroxy ester (0.11 mol) was dissolved in 200 ml of pyridine. The solution was cooled in an ice bath and stirred magnetically while 15 g (0.126 mol, 14% excess) of thionyl chloride was added dropwise at a slow rate. The

Table IV. Yields (%) of Intermediates and β,γ-Unsaturated Ketones (*Cf.* Scheme I)

	β-Hydroxy esters (**2a–e**)		Olefinic esters (**3a,e**)			
Ring size	Reformatsky	Rathke	P_2O_5	$SOCl_2$–C_5H_5N	Olefinic acids (**4a–e**)	Methyl ketones **5a–e**
a	33	97	38	65	100	90
b	55	100	64	85	99	96
c	96	98	85	86	97.4	94
d	96	98		86	97	95
e	29.8	80	87		97.5	96
19	22	96.5	51	74.6	81	91

Table V. Nmr and Ir Spectral Data

Compd	Nmr, δ, ppm				Ir, cm^{-1}
	CH_3	Vinyl	Ring	Other	
5a	1.16 (6 H, s) 2.03 (3 H, s)	5.82 (1 H, br s)	2.47 (m)		1711 s
5b	1.23 (6 H, s) 1.99 (3 H, s)	5.63 (1 H, m)	1.90–2.50 (m)		1714 s
5c	1.14 (6 H, s) 1.93 (3 H, s)	5.67 (1 H, m)	0.86–2.30 (m)		1708 s
5d	1.93 (3 H, s) 1.15 (6 H, s)	5.88 (1 H, br t)	0.90–2.50 (m)		1709 s
5e	1.14 (6 H, s) 1.92 (3 H, s)	5.54 (1 H, t)	1.32–2.33 (m)		1708 s
19	2.05 (3 H, s)	5.43 (1 H, m)	1.61–2.60 (m)	CH_2, 3.10 (2 H, br s)	1710 s
16	1.54 (6 H, m) 2.10 (3 H, s)		1.85–2.89 (m)	CH, 3.65 (1 H, m)	1705 s
10	1.10 (3 H, s) 1.31 (3 H, s) 2.02 (3 H, s)		0.84–2.68 (m)		1688 s
17	1.64 (6 H, br d) 2.00 (3 H, s)		1.70–2.40 (m)	CH, 3.37 (1 H, br m)	1709 s
15	1.00 (3 H, s) 1.08 (3 H, s) 2.08 (3 H, s)		1.50–2.10 (m)		1692 s
18	0.97 (3 H, s) 1.19 (6 H, s)	5.30 (1 H, m)	1.32–2.75 (m)		3620–3440 br OH
20	2.14 (3 H, s)	5.49 (2 H, br d)	1.55–2.95 (m)	CH, 2.23 (1 H, m)	1716 s
14	1.97 (3 H, s)		1.00–2.38 (m)	Cyclopropyl CH_2, 0.78 (2 H, m)	1688 s
21	1.17 (3 H, s)	5.32 (1 H, m)	1.50–3.31 (m)		3618–3400 br OH
23	0.97 (3 H, s) 1.15 (3 H, s) 1.17 (3 H, s)	5.28 (1 H, m)	1.20–2.87 (m)		3600–3500 br OH
24	0.87 (3 H, s) ~1.17 1.43 (3 H, s)			CH, 3.84 (1 H, t, $J = 7$ Hz)	
25	0.90 (3 H, s) 1.00 (3 H, s) 1.11 (3 H, s)	5.31 (1 H, s)	0.80–2.87 (m)		3612–3490 br OH
26	0.85 (3 H, s) 1.10 (3 H, s) 1.41 (3 H, s)		0.90–1.90 (m)	CH, 3.87 (1 H, br t)	
27	0.95 (3 H, s) 1.03 (3 H, s) 1.05 (3 H, s)	5.18 (1 H, m)	1.11–2.19 (m)		3630–3480 br OH
28	0.94 (3 H, s) 1.24 (3 H, s) 1.33 (3 H, s)		0.98–2.53 (m)	CH, 3.83 (1 H, br t)	
29	1.48 (12 H, m)		1.07–3.49 (m)		
30	1.52 (6 H, m) 1.01 (6 H, s)	5.62 (1 H, m)	1.63–2.60 (m)		

mixture was then stirred for 7.5 hr as it warmed to ambient temperature. The resulting brown suspension was poured onto cracked ice and the mixture was acidified with cold 20% hydrochloric acid. Products were isolated by ether extraction in the usual manner: **3a**, bp 49-50° (5 mm); **3b**, bp 66-68° (4 mm); **3c**, bp 82-83° (4.5 mm); **3d**, 98-99° (4 mm).

2-Methyl-2-(cycloalk-1-enyl)propanoic Acid (4a-e).[54] Olefinic ester (15 g) dissolved in 50 ml of EtOH was added to a solution of 10% molar excess KOH in 200 ml of EtOH. After refluxing for the times specified below, the solvent was removed by rotary evaporation and the residue was dissolved in H_2O. This mixture was extracted with ether to remove any unreacted ester. The aqueous layer was then acidified and the product isolated by ether extraction and rotary evaporation. **4a** was purified by distillation after 3 hr of reflux, bp 81-83° (1.5 mm). **4b** was distilled after 5 hr of reflux, bp 98-100° (1 mm). **4c** (mp 72-73.5°) and **4d** (mp 82-84°) were recrystallized from hexane after refluxing overnight. **4e** was purified by recrystallization from pentane after 5 hr of refluxing, mp 83-85°. **4a**, *Anal.* Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.02; H, 8.68. **4e**, *Anal.* Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.34; H, 10.27.

3-Methyl-3-(cycloalk-1-enyl)butan-2-one (5a-e). β,γ-Unsaturated acid **4a-e** (0.05 mol) was dissolved in 150 ml of anhydrous ether in a three-neck flask under N_2. The solution was cooled in an ice bath and 109 ml (0.12 mol) of 1.1 *M* methyllithium was added dropwise. After addition was complete, the mixture was allowed to stir at room temperature for 5-25 hr. The viscous, white suspension was slowly poured into 700 ml of water with very efficient stirring and this mixture was then subjected to the usual work-up procedure. **5a** after 12 hr of being stirred was distilled, bp 51-52° (5.5 mm). **5b** was isolated after 5 hr of reaction, bp 70-71° (6 mm). **5c-e** required 24 hr of reaction time: **5c**, bp 83-84° (6 mm); **5d**, bp 97-98° (6.5 mm); **5e**, bp 88-89° (1.5 mm). **5e**, *Anal.* Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.22; H, 11.59.

1-Cyclopentenylacetic Acid. Ethyl(1-hydroxycyclopentyl)acetate was prepared according to the procedure[3,4] described above, employing ethyl acetate and two equivalents of lithium isopropylcyclohexylamide, bp 75-77° (3.5 mm). The Reformatsky reaction, using methyl bromoacetate and cyclopentanone, gave the analogous methyl β-hydroxy ester, bp 71° (3.5 mm).

Dehydration of the β-hydroxy esters, using either P_2O_5 or $SOCl_2$-pyridine (*vide supra*), gave a mixture of β,γ- and α,β-unsaturated olefinic esters: ethyl esters, bp 90-96° (19 mm); methyl esters, bp 88-94° (19 mm). Refluxing these esters with KOH in ethanol for 4 hr converted both isomers into the β,γ-unsaturated acid. The solid residue was recrystallized from pentane to yield

Table VI. Exact Mass of Molecular Ions

Compd	Formula C	H	O	Calcd	Found
5a	9	14	1	138.1044	138.1013
5b	10	16	1	152.1200	152.1207
5c	11	18	1	166.1357	166.1364
5d	12	20	1	180.1514	180.1512
10	9	14	1	138.1044	138.1057
14	8	12	1	124.0887	124.0910
15	10	16	1	152.1200	152.1210
16	9	14	1	138.1044	138.1018
17	10	16	1	152.1200	152.1206
19	8	12	1	124.0887	124.0913
21	8	12	1	124.0887	124.0910
23	11	18	1	166.1357	166.1361
25	12	20	1	180.1514	180.1510
26	12	20	1	180.1514	180.1511
28	13	22	1	194.1670	194.1686

white crystals of 1-cyclopentenylacetic acid, mp 49-51°. *Anal.* Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.62; H, 8.02.

1-Cyclopent-1-enyl-2-propanone (19). The above olefinic acid was reacted for 12 hr with methyllithium according to the procedure described for **5a-e**. The product was distilled, bp 77-78° (19 mm). The yields for the above steps are summarized in Table IV.

Synthesis of Photochemical Products. 2-Chlorocyclobutanecarboxylic Acid (7). Ten grams (0.087 mol) of 2-chloro-1-cyanocyclobutane[55] were added to 100 ml of 18% HCl and heated at 105° for 5 hr. The chloronitrile was soluble in the hot acid solution. The cooled solution was extracted four times with methylene chloride. The carboxylic acid was extracted into K_2CO_3 solution and the aqueous layer was acidified. After the usual work-up procedure, the solid residue was recrystallized from ethyl acetate-hexane to yield 7.5 g (64.3%) of white solid: mp 96.5-98.5°; nmr (CCl_4) δ 2.15-2.84 (m, ring protons), 3.32-3.84 (m, proton adjacent to COOH), 4.19-4.85 (m, proton adjacent to Cl); ir (CCl_4) 1711 cm^{-1} (C=O), 2300-3400 cm^{-1} broad (OH). Concentration of the methylene chloride layer led to recovery of 30% unreacted chloronitrile; however, reaction times longer than 5 hr produced an excessive amount of a lactone by-product (ir 1787 cm^{-1}). *Anal.* Calcd for $C_5H_7O_2Cl$: C, 44.63; H, 5.24. Found: C, 44.68; H, 5.25.

1-Acetyl-5,5-dimethylbicyclo[2.1.0]pentane (10). In a three-neck flask under nitrogen was placed 2.5 g of 2-chlorocyclobutanecarboxylic acid in 25 ml of anhydrous ether. The flask was cooled in an ice bath while 3 equiv of 1.1 *M* methyllithium were added dropwise. The mixture was stirred at 0° for 4 hr and poured slowly into 300 ml of ice-water. The aqueous layer was then subjected to the usual work-up procedure. The ether solution was dried in the freezer over Na_2SO_4 and concentrated to yield 1 g (50%) of crude product. Bulb-to-bulb distillation afforded acetylcyclobutene contaminated with a small amount of 2-(1-cyclobutenyl)-2-propanol resulting from addition of methyllithium to the product: nmr (CCl_4) δ 2.12 (s, methyl), 2.33-2.74 (m, ring protons), 6.62 (m, olefin proton); ir (CCl_4) 1676 cm^{-1} (C=O), 1590 cm^{-1} (C=C).

In view of its tendency to polymerize, acetylcyclobutene was reacted immediately with 2-diazopropane. The procedure was identical with that used for 1-acetylcyclopentene (*vide infra*) and it afforded pyrazoline **9** in excellent yield. Purification was effected by filtering through fluorsil: nmr (CCl_4) δ 1.03 (s), 1.49 (s), 2.30 (s) (methyls), 2.00-2.70 (m, ring protons).

A 0.05 *M* solution of **9** was irradiated in acetone at 313 nm for 2 hr. Concentration of the acetone solution yielded 1-acetyl-5,5-dimethylbicyclo[2.1.0]pentane (**10**), which was purified by preparative tlc on silica gel. The spectral properties of **10** are listed in Tables V and VI. This compound was not stable to conventional distillation and had to be stored in the refrigerator.

1-Acetylcyclopentene. 1-Acetylcyclopentene was prepared in 41% yield from 1-cyanocyclopentene by reaction with methyllithium.[56] 1-Cyanocyclopentene was made by thionyl chloride dehydration[57] of cyclopentanonecyanohydrin.[58] 1-Acetylcyclohexene was prepared from cyclohexanone by the same series of reactions in low yield.

1-Acetylbicyclo[3.1.0]hexane (14) and 1-Acetyl-6,6-dimethylbicyclo[3.1.0]hexane (15). Diazomethane was prepared from 1 g of diazald and reacted with 200 mg of acetylcyclopentene in ether. After 8 hr, the yellow color had faded, and three drops of acetic acid were added to destroy any unreacted diazomethane. This solution was next washed with aqueous K_2CO_3 and the ether layer was dried over $MgSO_4$. Evaporation of the ether left a yellow liquid (**12**) which was not subjected to purification: nmr (CCl_4) δ 2.28 (s, methyl), 1.33-2.92 (m, ring protons), 4.00-4.99 (AB portion of ABX, J_{AB} = 19 Hz, CH_2 adjacent to N=N).

A 0.05 *M* solution of pyrazoline **12** was irradiated in acetone at 313 nm for 2 hr. After removal of the solvent, the residue containing **14** was purified by preparative vpc on column i at 120°.

For the synthesis of **15**, 2-diazopropane was prepared in ether according to the Organic Syntheses procedure[6] from 7 g of acetone hydrazone. Three grams of 1-acetylcyclopentene were added in one portion and the solution was stirred as it warmed to room temperature. After approximately 15 min, the initial red color of the solution had faded to a light pink. The ether solution was dried over $MgSO_4$ and concentrated to yield a mixture of the pyrazoline and acetone azine. Some of the acetone azine could be removed by dissolving the crude product in pentane and filtering through fluorsil, but small amounts of this by-product do not affect the next step. The yield of pyrazoline (**13**), based on 1-acetylcyclopentene, was 100%: nmr (CCl_4) δ 1.18 (s), 1.38 (s), 2.36 (s), (methyls), 1.30-2.55 (m, ring protons); uv (ether) λ_{max} 334 nm. The same procedure was tried with 1-acetylcyclohexene and 1-cyanocyclohexene, but these materials were recovered quantitatively, even in refluxing ether.

13 (0.2 g) was irradiated in 150 ml of pentane through an acetone filter. The reaction, which was monitored by disappearance of the uv band at 334 nm, was finished in 48 min. The pentane solution was concentrated, filtered through fluorisil, and bulb-to-bulb distilled at 0.18 mm to give compound **15**. The spectral properties of **14** and **15** are summarized in Tables V and VI.

Quantum Yields. The samples of β,γ-unsaturated ketones **5a-e** and **19** used in quantum yield measurements and for preparative scale irradiations were center distillation cuts which showed less than 0.1% impurity by vpc. Quantum yields were determined by irradiating 0.1-0.04 *M* solutions of the ketones with internal stan-

Table VII. Vpc Columns for Particular Compounds[a]

Compd	Column used for quantum yield determination	Temp, deg	Solvent and internal standard	Columns used for preparative vpc of products	Temp, deg
5a	a (T)	105	A, hexadecane	k (S)	120
	c (S)	115	B, anisole		
5b	d (T)	105	A, dodecane	h (S), l (T)	130, 110
	g (S)	110	B, anisole		
5c	e (S, T)	130	A, B, *o*-dichlorobenzene	i (S, T)	140
5d	f, e (S, T)	125, 130	A, B, *o*-dichlorobenzene	j (S)	130
5e	f (S, T)	130	*A*, *B*, *n*-butyl phenyl ether	j (S, T)	140
19	g (S, T)	110	A, B	i (T)	120
	b (T)	90	anisole	h (S)	100

[a] A = acetone, B = benzene, (S) for singlet products, (T) for triplet products.

dards in quartz tubes at 313 nm on a merry-go-round using 2,3-diazabicyclo[2.2.1]hept-2-ene as actinometer. The tubes were degassed three times to a pressure of 10^{-4} mm and sealed with a torch. Φ_{-k} and Φ_p were determined from vpc areas employing the columns listed in Table III. Response factors for isomeric products were assumed to be equal to those of the ketones and this was shown experimentally to be correct within 15% for **5c** and **23**.

Preparative Scale Irradiations. Typically, 1 g of ketone was dissolved in 150 ml of reagent grade acetone or benzene (0.034–0.047 *M*). The solution was poured into the outer chamber of a double-walled irradiation vessel (the inner chamber contained K_2CrO_4 solution) and was purged with N_2 for 20 min. Irradiations were run at room temperature except for **5a, 5b,** and **19,** which were cooled to 15–18°. Irradiations were continued until most of the ketone had disappeared (vpc analysis). After removal of solvent by rotary evaporation or distillation through a Vigreux column, the crude residue was analyzed by nmr. **10** was isolated by tlc on silica gel, eluting with 10% ethyl acetate-hexane. **17** was isolated by vpc on column 1 at 130°. **15** was purified by fluorsil chromatography, eluting with pentane. No products (except those arising from acetone itself) were observable on column i for **5c** irradiated in acetone. **25** and **26** were separated on a silica gel column with 20% ethyl acetate-hexane. All other products were isolated by preparative vpc, as summarized in Table VII.

Analytical vpc of the products from direct irradiation of **5a** showed three peaks at reasonable retention times for C_{14} hydrocarbons. The first peak to come out was very minor and was not resolved from the middle peak on preparative column i. After isolation, this mixture gave an nmr spectrum which was in accord with structure **30** except that the methyl singlet was slightly too large. This is consistent with the formulation of the minor component as dimer **31.** The longest retention time product was isolated and assigned structure **29** on the basis of its nmr spectrum. Strong support for the dimeric structures was derived from the mass spectrum of both major products, which showed a base peak at *m/e* 95 and a molecular ion at *m/e* 190. This behavior is as expected for cleavage of the weakest bond in the molecule and has also been observed for all three dimers of the 1,1-dimethylallyl radical.

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References and Notes

(1) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531, (1973); K. N. Houk, *Chem. Rev.*, in press.
(2) P. S. Engel, M. A. Schexnayder, H. Ziffer, and J. I. Seeman, *J. Amer. Chem. Soc.*, **96**, 924 (1974).
(3) M. W. Rathke, *J. Amer. Chem. Soc.*, **92**, 3222 (1970).
(4) M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.* **93**, 2318 (1971).
(5) M. Jorgensen, *Org. React.*, **18**, 1 (1970).
(6) A. C. Day, P. Raymond, and M. C. Whiting, *Org. Syn.*, **50**, 27 (1970).
(7) C. Berger, M. Franck-Neumann, and G. Ourisson, *Tetrahedron Lett.*, 3451 (1968).
(8) 1-Carbomethoxybicyclo[2.1.0]pentane[9] and a dimethyl analog[10] have been prepared by a similar route.
(9) W. G. Dauben and J. R. Wiseman, *J. Amer. Chem. Soc.*, **89**, 3545 (1967).
(10) T. H. Kinstle, R. L. Welch, and R. W. Exley, *J. Amer. Chem. Soc.*, **89**, 3660 (1967).
(11) The authors wish to thank Dr. S. C. Cherkovsky of E. I. du Pont de Nemours Company for a gift of this compound.
(12) J. W. Stankorb and K. Conrow, *Tetrahedron Lett.*, 2395 (1969).
(13) K. G. Hancock and R. O. Grider, *J. Amer. Chem. Soc.*, **96**, 1158 (1974).
(14) P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, **94**, 9252 (1972).
(15) R. C. Cookson and N. R. Rogers, *Chem. Commun.*, 809 (1972).
(16) K. N. Houk, private communication; P. S. Engel, *J. Amer. Chem. Soc.*, **92**, 6074 (1970); L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, **91**, 897 (1969).
(17) R. E. Schwerzel and R. A. Caldwell, *J. Amer. Chem. Soc.*, **95**, 1382 (1973).
(18) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N.Y., 1968.
(19) R. A. Moss and J. R. Whittle, *Chem. Commun.*, 341 (1969); W. R. Roth and K. Enderer, *Justus Liebigs Ann. Chem.*, **733**, 44 (1970).
(20) R. L. Cargill and A. B. Sears, *Tetrahedron Lett.*, 3555 (1972); N. P. Peet, R. L. Cargill, and J. W. Crawford, *J. Org. Chem.*, **38**, 1222 (1973); I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 2165 (1964).
(21) W. G. Dauben, G. W. Shaffer, and E. J. Deviny, *J. Amer. Chem. Soc.*, **92**, 6273 (1970).
(22) R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967).
(23) D. R. Paulson, F. Y. N. Tang, and R. B. Sloane, *J. Org. Chem.*, **38**, 3967 (1973); K. Takeda, I. Horibe, and H. Minato, *Chem. Commun.*, **87** (1971).
(24) J. Ipaktschi, *Tetrahedron Lett.*, 2153 (1969).
(25) E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969).
(26) J. Ipaktschi, *Chem. Ber.*, **105**, 1996 (1972).
(27) R. G. Carlson, R. L. Coffin, W. W. Cox, and R. S. Givens, *Chem. Commun.*, 501 (1973).
(28) R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, **93**, 3957 (1971).
(29) J. R. Williams and G. M. Sarkisian, *Chem. Commun.*, 1564 (1971); J. R. Williams, private communication.
(30) L. A. Paquette, R. F. Eizember, and O. Cox, *J. Amer. Chem. Soc.*, **90**, 5153 (1968).
(31) A. C. Pratt, *J. Chem. Soc., Perkin Trans.*, 2496 (1973).
(32) H. Sato, K. Nakanishi, J. Hayashi, and Y. Nakadaira, *Tetrahedron*, **29**, 275 (1973).
(33) J. R. Williams and H. Ziffer, *Tetrahedron*, **24**, 6725 (1968).
(34) K. Kojima, K. Sakai, and K. Tanabe, *Tetrahedron Lett.*, 1925 (1969).
(35) R. J. Chambers and B. A. Marples, *Tetrahedron Lett.*, 3747 (1971).
(36) J. I. Seeman and H. Ziffer, *Tetrahedron Lett.*, 4413 (1973).
(37) W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 1786 (1970).
(38) L. P. Tenny, D. W. Boykin, and R. E. Lutz, *J. Amer. Chem. Soc.*, **88**, 1835 (1966).
(39) D. I. Schuster and D. H. Sussman, *Tetrahedron Lett.*, 1661 (1970).
(40) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2820 (1967).
(41) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, P. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, **5**, 92 (1972).
(42) R. K. Murray and K. A. Babiak, *Tetrahedron Lett.*, 319 (1974).
(43) P. Bischof and E. Heilbronner, *Helv. Chem. Acta*, **53**, 1677 (1970).
(44) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970).
(45) J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, **94**, 8761 (1972), and references cited therein; see also W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972).
(46) K. N. Houk, D. J. Northington, and R. E. Duke, *J. Amer. Chem. Soc.*, **94**, 6233 (1972).
(47) N. C. Yang, M. H. Hui, and S. A. Bellard, *J. Amer. Chem. Soc.*, **93**, 4056 (1971).
(48) K. Shima, Y. Sakai, and H. Sakurai, *Bull. Chem. Soc. Jap.*, **44**, 215 (1971).
(49) D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc. B*, 215 (1967), and references cited therein.
(50) J. C. Dalton and H. F. Chan, *J. Amer. Chem. Soc.*, **95**, 4085 (1973).
(51) For recent discussions of α cleavage, see W. D. Stohrer, G. Wiech, and G. Quinkert, *Angew. Chem., Int. Ed. Engl.*, **13**, 199 (1974); L. Salem, *J. Amer. Chem. Soc.*, **96**, 3486 (1974).
(52) H. E. Zimmerman, *Advan. Photochem.*, 1, 183 (1963); D. I. Schuster, R. G. Underwood, and T. P. Knudsen, *J. Amer. Chem. Soc.*, **93**, 4304 (1971).
(53) J. W. Frankenfeld and J. J. Werner, *J. Org. Chem.* **34**, 3689 (1969).
(54) Carboxylic acids **4b–d** have been synthesized previously. See D. B. Bigley and R. W. May, *J. Chem. Soc. B*, 557 (1967).
(55) D. M. Gale and S. C. Cherkofsky, *J. Org. Chem.*, **38**, 475 (1973).
(56) G. Sumrell, *J. Org. Chem.*, **19**, 817 (1954).
(57) W. S. Rapson and R. Robinson, *J. Chem. Soc.*, 1533 (1935).
(58) L. Ruzicka and W. Brugger, *Helv. Chem. Acta*, **9**, 399 (1926).